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Thermodynamics of Crystallization in High Polymers: Poly-(ethylene)[1]

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The melting points of linear poly-(ethylene) and its mixtures with various diluents have been determined employing dilatometric methods. The melting point of the linear poly-(ethylene) was found to be 137.5 ± 0.5°. The data were analyzed by the application of thermodynamic equations appropriate to a first-order phase transition. The heat of fusion per mole of methylene units, ΔH_u, deduced from these experiments was 940 ± 30 cal. This value is in excellent agreement with the corresponding quantity deduced from the analysis of thermodynamic data for the low molecular weight *n*-alkanes. It is estimated that the contribution to the total entropy of fusion of the configurational change that occurs in the polymer on melting is 1.84 cal./deg./mole of CH_2.

Introduction

It has been demonstrated that the melting of a semi-crystalline polymer, when carried out under appropriate conditions, can be treated as a first-order phase transition.[2-4] Consequently, the laws of phase equilibria apply, and the equilibrium melting temperature $T_m{}^0$ of a homopolymer is systematically depressed when a low molecular weight diluent is added. From a consideration of the thermodynamic properties of concentrated and moderately concentrated polymer solutions, it has been deduced that the relation

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

expresses the dependence of the melting temperature T_m of the polymer–diluent mixture on the type and concentration of diluent. In this equation ΔH_u is the heat of fusion per mole of chemical repeating units, V_u and V_1 are the molar volumes of the repeating unit and diluent, respectively, v_1 is the volume fraction of the diluent and χ_1 is the thermodynamic interaction parameter.[5] Equation 1 is very similar to the usual expression obtained for the melting of a binary system, where only one component is crystalline. This equation has received ample experimental verification for many polymer–diluent mixtures[2-4] and offers the means of determining ΔH_u for a given polymer repeating unit. Thus from appropriate experiments, the thermodynamic quantities $T_m{}^0$, ΔH_u and ΔS_u, the entropy of fusion per repeating unit, can be determined for a given semi-crystalline polymer without the necessity of specifying the fraction of the material that is in the crystalline state. Though this method has been used to determine values of ΔH_u and ΔS_u for many polymers representing a wide variety of repeating units, these quantities have not as yet been determined for the linear homopolymer composed entirely of methylene repeating units. The simplicity of the chemical formula of this polymer as well as the vast amount of thermodynamic data available on the fusion of the low molecular weight aliphatic hydrocarbons make the determination of the heat and entropy of fusion of the linear poly-(ethylene) a matter of interest.

A sample of a linear poly-(ethylene) was prepared by us several years ago by the catalytic decomposition of diazomethane and the nature of its fusion as well as its equilibrium melting temperature were reported.[6] However, because of the very high molecular weight of this polymer no method could be devised to mix it quantitatively with diluents so the above-mentioned procedures could not be used. With the recent development of various processes for the synthesis of linear poly-(ethylene) of lower molecular weight, this problem was re-examined and a suitable polymer was found with which the necessary polymer–diluent mixtures could be prepared.

The polymer selected for study was a poly-(ethylene) manufactured by the Philips Petroleum Company under the name Marlex-50. The published infrared data[7] for this polymer indicate that it consists mainly of unbranched polymethylene chains, terminated at one end by a vinyl group and at the other end by a methyl group. This structural analysis is supported by the high degree of crystallinity that the polymer possesses at room temperature[8,9] and also by the fact that the nature of its fusion as well as its equilibrium melting temperature are very similar to those for the polymer prepared by the decomposition of diazomethane. Since this polymer could be quantitatively mixed with a variety of diluent types by methods to be described, it was chosen for further study.

Experimental

Materials.—A sample of the polymer was furnished by the Phillips Petroleum Company and was used without any further purification. The diluents employed in this study, tetralin, α-chloronaphthalene, *n*-butyl phthalate, ethyl benzoate and *o*-nitrotoluene were of reagent grade and were used as received.

Sample Preparation.—A specimen of the pure polymer suitable for use in the dilatometer was prepared by compression molding at 150 to 160°. This procedure yielded bubble-free specimens which easily could be cut into rectangular strips and inserted in the dilatometer bulb. The polymer–diluent mixtures were prepared by methods similar to those previously described.[10] Several grams of accurately weighed polymer and the desired amount of diluent were placed in a glass tube, which was inserted in a vapor bath maintained at a predetermined temperature. The sample tube was so constructed that it either could be evacuated or oxygen-free nitrogen could be introduced. By maintaining the sample at temperatures well above its

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(1) Presented in part at the 131st Meeting of the American Chemical Society, Miami, Florida, April 8, 1957.

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 568.

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

(4) L. Mandelkern, *Chem. Revs.*, **56**, 903 (1956).

(5) See ref. 2, p. 509.

(6) L. Mandelkern, M. Hellmann, D. W. Brown, D. E. Roberts and F. A. Quinn, Jr., THIS JOURNAL, **75**, 4093 (1953).

(7) D. C. Smith, *Ind. Eng. Chem.*, **48**, 1161 (1956).

(8) R. L. Collins, *Bull. Am. Phys. Soc.*, Series II, **1**, 216 (1956).

(9) R. C. Rempel, H. E. Weaver, R. H. Sands and R. L. Miller, *J. Applied Phys.*, **28**, 1082 (1957).

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melting temperature, a homogeneous bubble-free molten mixture could be obtained. Temperatures ranging from 190 to 240° were used to prepare the mixtures, the appropriate temperature being determined by the diluent concentration. The time of heating and mixing in the molten state ranged from 2 to 6 hr. The glass tube and its contents were allowed to cool slowly to room temperature and then reweighed. A slight loss of weight of the contents invariably occurred, which was attributed to the loss of diluent due to volatilization. When this correction is made to the original weight of diluent, the composition of the mixture on a weight fraction basis is deduced easily. The mixture was removed from the tube and a weighed sample was transferred to the dilatometer bulb.

The composition, on a volume fraction basis, was computed at the respective melting temperatures of the mixtures from the interpolated densities of the diluents and the density of the polymer in the liquid state at the appropriate temperature, assuming the additivities of volume of each component on mixing. The densities of the diluents were obtained from the literature where available; otherwise they were measured at two temperatures about 100° apart and assumed to vary linearly between these temperatures. The density of the molded specimen of the homopolymer was determined at 25° by the method of hydrostatic weighings using water as a flotation fluid.[11] The value obtained was 0.9607 cm.^{3}/g. The specific volume at any temperature was then calculated from the dilatometer scale readings.[12] The appropriate value of the specific volume in the supercooled liquid state was obtained by an extrapolation of the linear volume–temperature relation observed above T^0_m.

Melting Point Determinations.—The dilatometric method was used to determine the melting temperatures of the homopolymer and of the polymer–diluent mixtures containing up to 80% diluent. At higher diluent concentrations the polymer–diluent mixtures were prepared in nitrogen-filled sealed glass tubes and the melting point taken as the temperature at which the turbidity due to the white crystalline polymer disappeared. This temperature could be determined to within ±0.5°. The type of dilatometers used and the method of sealing and filling the dilatometers with mercury has been described previously in detail.[10] For measurements at room temperature and above, the dilatometers were immersed in a thermostat filled with silicone oil that could be maintained constant to within ±0.1° at any desired temperature.

In order to determine reliably the equilibrium melting temperature of a polymer and describe adequately the nature of the fusion process, conditions as close as possible to those for equilibrium must be established. For polymeric systems it has been shown[4,13] that, in order to obtain these conditions, extremely slow heating rates must be employed, particularly in the vicinity of the melting temperature. Though this requirement makes the carrying out of the experiments extremely tedious, it appears to be mandatory. It is for this reason that the dilatometric method offers great advantage for the reliable determination of the melting temperature of polymers. For the poly-(ethylene) studied in this work a heating rate of 15° per 24 hr. was used from 25 to 100°; between 100 and 125° the heating rate was reduced to 5° per 24 hr. and above 125° the rate was further reduced to 1° per 24 hr. Very few of the experimental techniques commonly used to determine the changes of crystallinity in a polymer can be utilized at such slow and carefully controlled heating rates.

Low Temperature Measurements.—Length–temperature measurements were made on a sample of the pure homopolymer using an automaticrec ording interferometer originally developed by Work.[14] The experimental procedure involving this technique already has been described[14,15] and the experiments covered the temperature range from 25 to −180°. The volume at any temperature could be computed from the observed change in length ΔL, by means of the relation

$$\bar{v} = \bar{v}_0 (1 + \Delta L/L_0)^3$$

where $\bar{v}_0$ and L_0 are the specific volume and length at a reference temperature.

Results

Pure Polymer.—The specific volume–temperature data for the linear poly-(ethylene), encompassing a temperature range from −180 to 160°, are plotted in Fig. 1. This plot, curve A in the figure, is a composite of the dilatometric data obtained above room temperature and the data determined interferometrically below room temperature. The values of the specific volume plotted for temperatures above 25° represent the equilibrium values obtained by use of the heating rates previously described. The course of the fusion above this temperature is marked by partial melting and recrystallization manifested by the fact that at any given temperature in the range 85 to 132° the specific volume first increases with time then decreases and finally levels off. As in the case of the polymer prepared by the decomposition of diazomethane the melting of the polymer studied herein is relatively sharp, about 60 to 70% of the melting occurring in about a 5° temperature range, with the last traces of crystallinity disappearing between 137 to 138°. $T_m{}^0$ is then taken to be 137.5 ± 0.5° which is about 1° higher than that for the corresponding polymer prepared from diazomethane.[6] A 16% change in volume occurs on melting, and the volume–temperature coefficient in the liquid state is 8.8×10^{-4} cm.^{3}/g./deg. The latter value is similar to the values previously reported by Charlesby[16] and Hunter and Oakes[17] for poly-(ethylene) polymers known to contain many side chain branches.

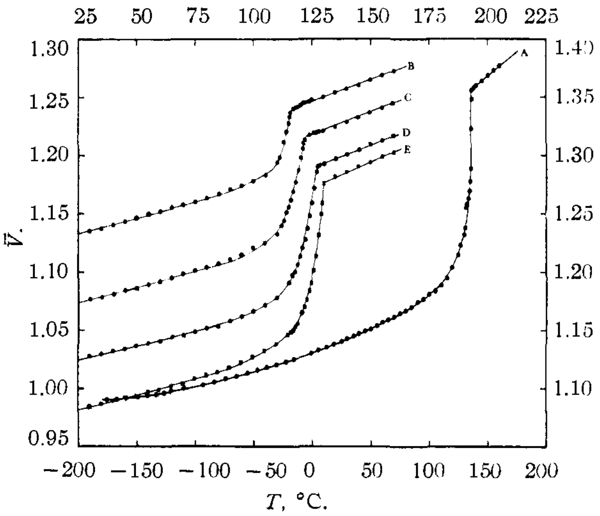

Fig. 1.—Plot of specific volume as a function of temperature for poly-(ethylene) and its mixtures with diluents: curve A, pure poly-(ethylene) (lower abscissa and left hand ordinate); curves B, C, D and E, poly-(ethylene)-α-chloronaphthalene mixtures of composition v_1 equal to 0.699, 0.504, 0.311 and 0.205, respectively (upper abscissa and right hand ordinate).

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[11] L. A. Wood, N. Bekkedahl and F. L. Roth, *J. Research Natl. Bur. Standards*, **29**, 391 (1942).

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[13] D. E. Roberts and L. Mandelkern, THIS JOURNAL, **77**, 781 (1955).

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The specific volume–temperature data below room temperature are best represented by a curve of gradually decreasing slope which appears to be tending toward zero at the lowest temperatures of measurement. However, over any limited temperature range in this region the data could be represented by a pair of intersecting straight lines. In particular, if the experimental observations were limited to the range −75 to +25°, the data could be represented by two straight lines intersecting at −20° with slopes of 3.95×10^{-4} and 2.80×10^{-4} cm.^{3}/g./deg., respectively. This observation is in agreement with the recent results reported by Danusso, Moraglio and Talimini.[18] Since it is customary in many instances to determine the glass temperature of a polymer by the point of intersection of two straight lines in a volume–temperature plot, these investigators have assigned a value of −20° to the glass temperature of poly-(ethylene). However, the plot of Fig. 1 indicates that this is not a valid procedure to follow for this polymer. For example, if only the data between −180 and −50° were considered, they could also be represented by two straight lines which intersect at −100°, the change in slope in this instance being much greater than in the case just cited. As already has been pointed out,[19] to determine reliably the glass temperature of a polymer from dilatometric experiments the measurements must encompass a very wide temperature range.

It would appear that for highly crystalline polymers of this type, other methods, such as dynamical mechanical experiments,[20–24] are preferable for the determination of the glass temperature. Experiments of this latter type[20–22] indicate a transition in the vicinity of −20° for poly-(ethylene) polymers that are branched. This transition can be attributed to the motion of the side groups that are attached to branch points. Furthermore, dynamic mechanical experiments[20–22] as well as nuclear magnetic resonance experiments[9] indicate a transition in the vicinity of −100° attributable to the motion of segments along the main chain and hence corresponding to glass formation.

Polymer–Diluent Mixtures.—Also plotted in Fig. 1 are volume–temperature curves for some typical polymer–diluent mixtures. The addition of diluent causes a broadening of the melting range and a decrease in the volume change on melting, though the melting temperature is still easily discernible. The melting temperature of a mixture is usually systematically depressed, from that of the homopolymer. The amount of the depression will depend on the type and concentration of diluent added. However, when a diluent is added which is either a very poor solvent, characterized by a large positive value of χ_1, or possesses an abnormally large molar volume, it is found that at a critical polymer concentration the melt consists of two immiscible liquid phases rather than one homogeneous phase. Equation 1 will no longer be appropriate under these conditions, and according to the phase rule the melting temperature will become invariant with composition upon further dilution. This situation was observed when *n*-butyl phthalate was mixed with the polymer; at a value of v_2 (volume fraction of the polymer) equal to 0.75, the melting temperature remained invariant at 133 ± 0.5° even in very dilute solutions. A similar phenomenon was observed with *o*-nitrotoluene as a diluent. However, the invariance of T_m did not occur until a v_2 of 0.40 was reached. When ethyl benzoate, tetralin and α-chloronaphthalene were used as diluents, a systematic depression of the melting temperature occurred over the whole composition range, and these data together with a portion of the data with *o*-nitrotoluene as diluent could be analyzed by means of equation 1.

To use this equation most conveniently the assumption is made that $\chi_1 = BV_1/RT$, where B represents the interaction energy density characteristic of the solvent–solute pair,[5] so that at the melting temperature equation 1 can be written as

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

Thus a plot of the quantity $(1/T_m - 1/T_m^0)/v_1$ against v_1/T_m should yield a straight line whose intercept is related to ΔH_u and whose slope is related to the quantity B. In making the assumption that χ_1 is inversely proportional to the absolute temperature, any entropy contribution to the thermodynamic interaction parameter has been neglected. The exclusion of this term should give rise to negligible error in the determination of ΔH_u by this method because of the small temperature range covered by the experiments and the consequent limited accuracy of the quantity $1/T_m - 1/T_m^0$. However, the value deduced for the quantity B could be in error by several calories per cm.^{3}.

In Fig. 2 the experimental data are plotted with the coördinates suggested by equation 2 for each of the four diluents. In each case the data are well represented by straight lines. From the intercept of these straight lines and the molar volumes of the polymer and diluent (at the melting temperature of the pure polymer), the values of ΔH_u can be deduced and are listed in the second column of Table I. The values obtained with each of the diluents are in good agreement with each other, the average value being 940 ± 30 cal. per mole of methylene units which corresponds to a value of 67 ± 2 cal. per gram of polymer. The values of B determined from the slopes of these plots are also given in Table I. Though the values of B deduced by these methods are not deemed too reliable, the classification of solvent according to the magnitude and sign of the slopes of the plots in Fig. 2 should not be in serious error.

Discussion

Thermodynamic Quantities.—The equilibrium melting temperature of the polymer studied in this

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TABLE I

THERMODYNAMIC QUANTITIES FOR POLY-(ETHYLENE)-DILUENT MIXTURES

Diluent	ΔH_u (cal./mole)[a]	B (cal./cm.^{3})
Ethyl benzoate	930 ± 30	3.8
o-Nitrotoluene	920 ± 65	5.0
Tetralin	990 ± 70	1.0
α-Chloronaphthalene	920 ± 50	0
Mean value:	940 ± 30	

[a] The uncertainty given for ΔH_u is estimated from the intercepts of the slightly different straight lines to which the data in Fig. 2 can be fitted. The results are expressed in terms of a calorie equal to 4.185 joules.

work is about 2.5° higher than that reported by Wunderlich and Dole[25] for the same polymer using the specific heat method to determine the melting point and is one degree higher than that previously reported by us[6] for the polymer prepared by the catalytic decomposition of diazomethane. The difference in melting temperature for the same polymer studied by the two different techniques can be attributed to the different heating rates employed. In contrast to the calorimetric method, the dilatometric experiments were carried out using extremely slow heating rates. Thus the latter experiment should yield more perfectly annealed crystallites and consequently a higher melting temperature. It is therefore unnecessary to invoke copolymer melting theory to explain the low melting point observed by the calorimetric method.[25] The slight difference in melting temperature observed by the same technique between the two different types of linear poly-(ethylene) is not as easily understood since infrared studies indicate that neither is detectably branched. The reality of this difference could be clarified by careful studies of the crystallization rate of the two polymers in the region near their melting temperatures.[4,26]

Since the fusion behavior of the lower molecular weight *n*-alkanes has been subject to a great deal of study many predictions have been made as to the expected melting temperature and thermodynamic parameters of a linear poly-(ethylene) polymer of very high molecular weight. These predictions and calculations are either completely empirical in nature, based solely on analyses of the melting temperatures of the lower molecular weight homologs, or are based on analyses of the heats and entropies of fusion of these materials. The latter analysis is complicated by the fact that a transition, accompanied by a latent enthalpy and entropy, usually occurs a few degrees below the melting point[27] and also by the fact that the form stable at low temperature has a different crystal structure, depending on whether the *n*-alkane contains an odd or an even number of carbon atoms.[28] The usual crystal form occurring in poly-(ethylene) is orthorhombic, which corresponds to the low temperature form of *n*-paraffins containing an odd number of carbon atoms.

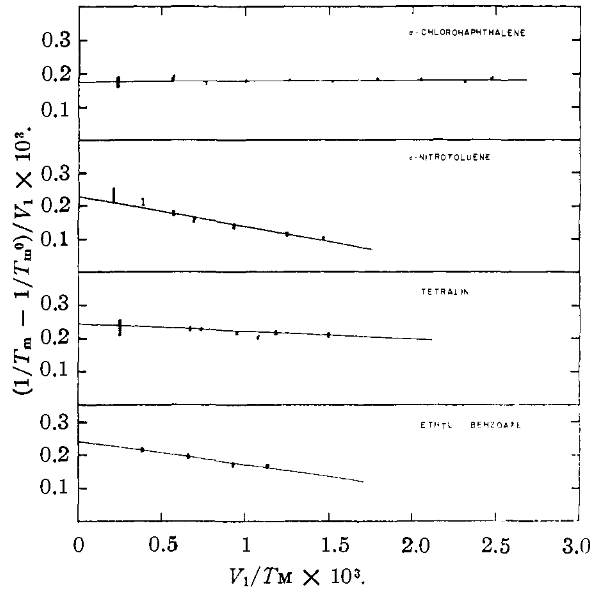

Fig. 2.—Plot of $(1/T_m - 1/T_m^0)/v_1$ *vs.* v_1/T_m for poly-(ethylene) mixed with the indicated diluents.

Empirical relations between the melting temperature and the number of carbon atoms in the molecule have been given by Etessam and Sawyer[29] and Van Nes and Van Westen[30] who predict melting temperatures for the infinite molecular weight polymers of 141.5 and 138°, respectively. Both of these empirical relations predict within 1° the melting temperature of *n*-hectane ($C_{100}H_{202}$), recently reported by Dawson[31] to be 115°. An analysis of the thermodynamic data for the normal paraffins containing 22, 26, 30 and 34 carbon atoms led Garner, van Bibber and King[32] to predict an asymptotic melting temperature of 135°, while the deductions of Meyer and van der Wyk[33] led to a corresponding melting temperature of 141°. Thus the various predicted values for T_m^0 for a linear, high molecular weight poly-(ethylene) are in very good accord with the value actually observed.

In addition to the interest in the asymptotic melting temperature various predictions and calculations have been made for the value of the heat of fusion per methylene unit to be expected for a high molecular weight poly-(ethylene) polymer. The inherent difficulty in performing this type of analysis due to the differences in crystalline modification and the transition occurring below the melting point has already been indicated. The often quoted value of 56.5 cal./g. for the heat of fusion[34] undoubtedly suffers from this deficiency.

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More recently Schaerer, Bayle and Mazee[35] have analyzed the thermodynamic data for highly purified n-paraffins in the series C_{21} to C_{30}. They calculated the heats of fusion of the crystalline form stable at low temperatures at their respective melting points and included, in an appropriate manner, the contribution due to the transition that occurs below the melting temperature. If it is assumed that the contributions of the methyl and methylene groups are additive, then a plot of their data indicates that the heat of fusion per methylene group is 910 cal./mole. This is in good accord with a similar estimate made by Dole, Hettinger, Larson and Wethington[36] and a more recent estimate made by Billmeyer.[37] Thus the estimates of the heat of fusion per methylene group, based on an analysis of the thermodynamic data for the low molecular weight n-alkanes, are in excellent agreement with the value deduced from the present study. The agreement obtained between these quantities for the linear high molecular weight poly-(ethylene) and the low molecular weight n-alkanes lends additional support to the treatment of the fusion of polymers as a first-order phase transition.

It has been observed[4] that the melting temperature of a polymer is governed to a large extent by its entropy of fusion. This behavior is characteristic of polymers because of the increased configurational freedom gained by the chain segments on melting. The entropy of fusion must therefore reflect in some measure the relative stiffness of the polymer chain. Consequently, it is of interest to compare the entropy of fusion of poly-(ethylene) with that of other polymers. However, to make this comparison consideration must be given to the portion of the entropy of fusion arising from the volume change that occurs on melting. This quantity already has been calculated for natural rubber and gutta percha[38] and found to be a significant portion of the total entropy of fusion. To calculate the change in entropy due to the volume change that occurs on melting, it is required that the volume–temperature coefficient, the volume–pressure coefficient and the latent volume change per repeating unit be known at the melting temperature.[39,40] The latter two quantities have not as yet been determined for linear poly-(ethylene), but an estimate of their magnitudes can be made from the previously reported work on branched poly-(ethylene). From the work of Parks and Richards[41] the volume–pressure coefficient can be estimated to be 13.2×10^{-5} cm.^{3}/g./atm. at 140°. If the specific volume of the crystal is taken to be 1.000[42] at 25° and a volume–temperature coefficient of the crystal is taken as 4.8×10^{-4} cm.^{3}/g./deg.,[16] then at the melting temperature the volume change on melting is 2.87 cm.^{3}/mole of methylene units. The substitution of these quantities together with the experimentally observed volume–temperature coefficient in the liquid state of 8.8×10^{-4} cm.^{3}/g./deg. into the standard relations for the change in entropy with volume leads to a contribution of 0.46 cal./mole/deg. from this effect. The total entropy of fusion ΔS_u at the melting point is 2.30 cal./deg./mole. If it is assumed that ΔS_u consists of the additive contribution of the volume change and configurational change on melting, a value of 1.84 cal./deg./mole of CH_2 is deduced for the latter quantity. This value of the gain of configurational entropy on fusion, at constant volume, subject to the uncertainty in the aforementioned quantities, is very similar in magnitude to the value 1.7 cal./deg./mole deduced for natural rubber.[38] It affords no basis for assigning any undue rigidity to the poly-(ethylene) chain in the liquid state.

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