

bide ions as such were present, although the rate of exchange of methane over nickel in the presence of excess hydrogen is quite low. It is, further, not surprising that no very large difference in catalytic activity was found for the carbided *versus* the fresh catalyst. Nickel-silica is notoriously difficult to poison for the H₂-D₂ exchange even with hydrogen sulfide as poison. The poisoning effect of pre-adsorbed ethylene, even for the hydrogenation of ethylene, is so well established as to require no further verification.¹²

The widely different conclusion reached by various investigators concerning the mode of adsorption of ethylene on nickel is seen to be due to the peculiar sensitivity of the ethylene molecule to

(12) L. A. Wanninger and J. M. Smith, *Chem. Weekblad*, **56**, 273 (1960).

temperature, to the specific nature of the catalyst surface and to the presence of ethane formed by self-hydrogenation. The poisoning effect of ethylene on films is more than likely due to the carbiding reaction rather than to polymer formation. The only major area of disagreement seems to be with the infrared absorption spectra which demands extensive dissociation at room temperature. Further elucidation of this difficulty must wait for measurements under identical conditions which are now possible through development of the ferromagnetic resonance method for studying chemisorption.¹³

Acknowledgment.—It is a pleasure to acknowledge support from the National Science Foundation and the Office of Ordnance Research, U. S. Army, in connection with this work.

(13) D. P. Hollis and P. W. Selwood, forthcoming publication.

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PA.]

Equilibrium between Crystalline and Amorphous Phases in Polyethylene¹

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Crystallization and melting of fractionated linear polyethylenes (Marlex-50 and a specially prepared low pressure polyethylene) have been investigated by dilatometric methods. Crystallization was carried out at the highest feasible temperature (131.3° in most instances) in order to promote growth of a crystalline phase of maximum perfection. Melting of fractions thus crystallized is extraordinarily sharp; for $\bar{M}_v = 490,000$ the degree of crystallinity decreases from *ca.* 50 to 0% from 136.5 to 138.5°; for $\bar{M}_v = 32,000$ from *ca.* 70 to 0% from 134° to 136°. The melting point 138.5° established for the former fraction is the highest yet recorded for polyethylene; it is 1.5° greater than for the unfractionated polymer crystallized under comparable conditions. Melting of binary mixtures of a polyethylene fraction with α -chloronaphthalene has been investigated over the temperature range immediately preceding final disappearance of crystallinity. Results are compared with the relationship of the degree of crystallinity to temperature calculated assuming equilibrium between a pure crystalline phase and a binary phase comprising amorphous polymer and diluent. Agreement with the thermodynamic expression relating temperature to liquid composition (the latter depending directly on the fraction of polymer melted) is excellent up to degrees of crystallinity as high as 50%. Thus, attainment of phase equilibrium in polymer systems is not restricted to very low degrees of crystallinity.

Introduction

Crystallization of a polymer from its melt or concentrated solution invariably yields a composite of crystalline and amorphous regions. The retention of a considerable fraction of residual amorphous material distinguishes the crystalline state in polymers from other polycrystalline materials. Despite exhaustive investigations employing the techniques of X-ray diffraction and electron microscopy, the textural description of the interspersed crystalline and amorphous regions remains incomplete. Results of these investigations, evaluated in light of implications of mechanical properties of semi-crystalline polymers, nevertheless assure that crystalline and amorphous portions exist in intimate association. The two regions doubtless are joined by molecular chains, some of which pass from one of them through the other, and so on.

Whether or not it is warranted to regard the crystalline and the amorphous zones as discrete phases poses a question of long-standing controversy. From a strictly morphological point of view, the answer is to be sought in the sharpness of the boundaries between crystalline and amorphous

zones. Evidence bearing directly on this issue is elusive, however. The low degree of order usually indicated by X-ray diffraction patterns for indiscriminately crystallized samples, the repugnance of sharp boundaries penetrated by continuous molecular chains and the undeniable capability of the macromolecule to assume intermediate states of order have conspired to engender a body of opinion in support of a negative answer to the question raised above. Thus, on the basis of morphological information alone, a continuous gradation of degrees of order ranging from chaos to something approaching the regularity in molecular crystals of organic compounds has been offered as an adequate representation in preference to description in terms of two coexisting phases.³

Phase transformations are characterized by features other than alteration of structure, namely, by discontinuous changes in thermodynamic functions. Description of the zone in question as a phase is legitimate if, and only if, its properties may be uniquely defined by an appropriate set of thermodynamic variables such as temperature, pressure and composition. To the extent that this stipulation is fulfilled for each of two coexisting phases, the transformation from one phase to the other *at*

(1) Presented before the Division of Polymer Chemistry at the 138th meeting of the American Chemical Society, New York, Sept. 12, 1960.

(2) Visiting Fellow from the Chemstrand Corporation, Chemstrand Research Center, Inc., Durham, N. C.

(3) See for example V. A. Kargin, *J. Polymer Sci.*, **30**, 247 (1958) and H. A. Stuart, *Ann. N. Y. Acad. Sci.*, **93**, 3 (1959).

equilibrium must be discontinuous. The appearance, or disappearance, of one phase in the presence of the other must occur abruptly with change in one of the thermodynamic variables, such as the temperature. The extensive thermodynamic variables such as volume and enthalpy undergo finite (latent) changes at the transition. The issue in question should therefore be amenable to resolution through investigation of the characteristics of the transformation from one form to the other.⁴

Crystalline polymers melt over fairly narrow ranges, with latent changes in volume and enthalpy which are commensurate with those for single molecular crystals.^{5,6} The fact that the transition generally takes place over a range of several degrees is often cited in opposition to the concept of a phase transition. The transition is sharpened by measures which promote approach to equilibrium; further evidence on this point is presented in this paper. There are good grounds therefore for asserting that the residual breadth of the transition (*ca.* 2°), after effecting all reasonable measures to suppress time effects and to eliminate the adverse influences of foreign constituents, is an insurmountable experimental artifact.

Additional experimental substantiation of the coexistence of discrete phases is afforded by the successful application of thermodynamic relationships to the depression of the melting point brought about by incorporation of a second component, *e.g.*, a diluent. Compliance with these relationships has been demonstrated for many polymer systems.⁵⁻⁷ Moreover, the heat of fusion calculated from the depression of the melting point of polyethylene by diluents has been confirmed by calorimetric measurements⁸ and by extrapolation of the heat of fusion of the *n*-paraffin hydrocarbons.⁹

Inasmuch as the melting point is customarily identified with the temperature at which the last vestiges of crystallinity disappear, adherence to the dictates of thermodynamics is assured by the experiments cited only when the degree of crystallinity is vanishingly small. At higher levels of crystallinity, representation of the system as comprising two discrete phases, each fully characterized by its composition, temperature and pressure, has not heretofore been validated by experiments. We present results which demonstrate adherence to a state of equilibrium up to fairly high degrees of crystallinity under favorable conditions. Specifically, the degree of crystallinity in polyethylene-diluent systems has been observed as a function of temperature. By assuming the diluent to be confined to the amorphous phase and distributed uniformly throughout that phase, the temperature for equilibrium between the phases may be related, on the basis of elementary thermodynamic considerations, to the degree of crystallinity. Comparison of this relationship with that observed provides a

rigorous test of the validity of the postulated equilibrium between two phases.

Experimental

Preparation of Samples.—Two linear polyethylenes, Marlex-50 and a specially prepared sample furnished by the Union Carbide Plastics Company,¹⁰ and designated here as "Polymer-B," were fractionated by elution through a chromatographic column packed with sand or with Celite according to the method of Desreux¹¹ as further developed by Francis, Cook and Elliott¹² and by Henry.¹³ *m*-Xylene and hydroxyethyl butyl ether were used as solvent and non-solvent, respectively. Special measures were adopted to assure uniform packing of the column and to avoid bubbling and channeling of liquid through the column during its use.¹⁴ According to results of Francis, *et al.*,¹² and of Henry,¹³ it may be assumed that \bar{M}_w/\bar{M}_n did not exceed 1.2 for our fractions. Narrow fractions were not required, however, for the experiments to be described.

Samples used in this investigation are listed in Table I. Viscosity average molecular weights were calculated from intrinsic viscosities determined in decalin at 135° using the relationship $[\eta] = 6.2 \times 10^{-4} M^{0.70}$ given by Chiang.^{15,16}

The sample, in the form of the finely divided flakes which precipitated from the solvent-non solvent mixture, was melted at 160° under vacuum in order to remove traces of volatile matter. It was subsequently pressed into the form of a sheet by compression molding, then cut into strips suitable for insertion in the dilatometer.

Polymer-diluent mixtures were prepared by combining a weighed sample of polymer with α -chloronaphthalene in a glass tube of slightly smaller diameter than the dilatometer bulb. Mixing was accomplished by passing a slow stream of nitrogen through the liquid mixture at 190° for several hours. The composition was ascertained by weighing tube and contents after completion of the mixing and deducting the weight of the former as previously determined. The tube and contents were then transferred to the dilatometer, which was sealed, evacuated and filled with mercury, in the usual manner. The dilatometer and contents were maintained at 120° overnight to assure uniform distribution of diluent. The crystallization cycle was commenced at once. Cooling to room temperature was avoided at this stage in order to prevent segregation of crystallized polymer from the diluent, and consequent development of inhomogeneity within the sample.

Dilatometry.—The dilatometers used for following changes in the degree of crystallinity were similar to those previously described.¹⁷ A weighed sample of 0.7 to 1.2 g. was placed in the dilatometer bulb having a capacity of about four cc. The confining liquid was mercury. Silicone oil thermostat baths, capable of regulation within a range of $\pm 0.01^\circ$, served to maintain the desired temperature without interruption throughout the several months required for an experiment.

The basis for converting dilatometer capillary readings to specific volumes of the sample was established from observations immediately above the melting point. The volumes of the mercury and of the polymer sample at the relevant temperature were computed from their weights, the specific volume \bar{v}_1 of the liquid polymer being provided by

(10) We are indebted to Dr. J. J. Smith of the Union Carbide Plastics Company for placing this sample at our disposal.

(11) V. Desreux, *Rec. trav. chim.*, **68**, 789 (1949); V. Desreux and M. C. Speigels, *Bull. soc. chim. Belges*, **59**, 476 (1950).

(12) P. S. Francis, R. C. Cook, Jr., and J. H. Elliott, *J. Polymer Sci.*, **31**, 453 (1958).

(13) P. M. Henry, *ibid.*, **36**, 3 (1959).

(14) The column was packed according to the procedure recommended by A. J. P. Martin; see "Practical Chromatography," ed. by R. C. Brimley and F. C. Barrett, Reinhold Publishing Corp., New York, N. Y., 1953, p. 66.

(15) R. Chiang, *J. Polymer Sci.*, **36**, 91 (1959).

(16) The intrinsic viscosity-molecular weight relationships for linear polyethylene given by Henry¹³ and by L. H. Tung, *ibid.*, **36**, 287 (1959), are in close accord with the one given above over the range of intermediate molecular weights with which we shall be concerned here. The relationship cited above is believed to be more reliable in the range of higher molecular weights, owing to correction of the light scattering results for back reflection.¹⁵

(17) P. J. Flory, L. Mandelkern and H. K. Hall, *J. Am. Chem. Soc.*, **73**, 2532 (1951); L. Mandelkern and P. J. Flory, *ibid.*, **73**, 3206 (1951).

(4) P. J. Flory, *Ricerca sci. (Suppl. A)*, **25**, 636 (1955).

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

(6) L. Mandelkern, *Rubber Chem. Tech.*, **32**, 1392 (1959).

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

(8) M. Dole and B. Wunderlich, *Makromol. Chem.*, **34**, 29 (1959). M. Dole, *Fortschr. Hochpolym.-Forsch.*, **2**, 221 (1960).

(9) F. A. Quinn, Jr., and L. Mandelkern, *J. Am. Chem. Soc.*, **80**, 3178 (1958).

TABLE I
CRYSTALLIZATION AND MELTING OF POLYETHYLENES
(Samples crystallized 40 days at 131.3°, etc., as described in text.)

Sample	[η] (g./100 ml.) ⁻¹	\bar{M}_v $\times 10^{-4}$	Days at 131.3° for onset of crystalliza- tion	Specific volumes, cc. g. ⁻¹		% crystallinity		Melting point T_m^* , °C
				$\bar{v}_{131.3^\circ}$	\bar{v}_{30°	At 131.3°	At 30°	
Marlex-50, unfractionated	1.71	80	20	1.2550	1.0310	5.3	83.3	137.0
Marlex-50, fraction ^a	0.89	32			1.0344		81.4	136.2
Marlex-50, fraction	2.25	126	1	1.1168	1.0377	64.0	79.5	137.7
Marlex-50, fraction	5.98	490	4	1.1280	1.0425	59.2	76.8	138.5
Polymer-B, fraction	4.4	309	1.5	1.1490	1.0447	50.3	75.6	138.2
Polymer-B, fraction	5.6	458	2	1.2155	1.0639	22.1	64.7	137.7

^a This fraction did not crystallize at 131.3°; crystallization commenced at 130° in the course of the standard cooling cycle described in the text.

the relationship (M. J. Richardson, unpublished)

$$\bar{v}_1 = 1.152 + 8.8 \times 10^{-4} t \quad (1)$$

where \bar{v}_1 is expressed in cc. g.⁻¹ at the temperature t in Centigrade degrees. This relationship is in virtual accord with that given earlier by Gubler and Kovacs,¹⁸ and the thermal expansion coefficient in eq. 1 agrees with Quinn and Mandelkern's result.⁹ The thermal expansion coefficient of the sample was observed at the outset over a range of about 25° above its melting point. Values for undiluted polyethylenes within limits 8.7 – 8.9×10^{-4} cc. g.⁻¹ deg.⁻¹ assured that the dilatometer had been filled properly.

In the case of mixtures of polyethylene with the diluent, α -chloronaphthalene, the conversion of dilatometer readings to specific volumes was similarly established from measurements on the homogeneous liquid system just above its melting point. Additivity of volumes was assumed, the specific volume of α -chloronaphthalene being given by

$$\bar{v}_{\text{CIN}} = 0.8257 + 6.0 \times 10^{-4} t \quad (2)^{19}$$

Crystallization of Samples.—After determination of the thermal expansion of the molten sample, the temperature was adjusted to the highest level at which crystallization would proceed within a reasonable period of time. In the case of undiluted polymers of high molecular weight, a temperature of 131.3° proved satisfactory. Crystallization, as evidenced by decrease in volume, became apparent after the intervals of time given in the fourth column of Table I. The volume reached a fairly steady value after 40 days in most instances. The temperature subsequently was decreased 2° each day from 131 to 121°; after reaching 120° it was allowed to fall to room temperature over a period of about 24 hr. Specific volumes at 131.3° and at 30° are recorded in Table I. The degrees of crystallinity included in Table I have been calculated from the observed specific volumes using the relationship²⁰

$$\% \text{ crystallinity} = 100(\bar{v}_1 - \bar{v})(\bar{v}_1 - \bar{v}_c) \quad (3)$$

the specific volume \bar{v}_1 for the liquid state being provided by eq. 1, and the crystal specific volume \bar{v}_c by^{18,21,22}

$$\bar{v}_c = 0.993 + 3.0 \times 10^{-4} t \quad (4)$$

This relationship approximates the quadratic expression proposed by Swan²¹ on the basis of unpublished X-ray diffraction spacings. The specific volume calculated for 25° approximates Bunn's²² result, 1.000 cc. g.⁻¹. The thermal expansion coefficient in eq. 4 has been selected on the basis of the work of Gubler and Kovacs.¹⁸

Crystallization of polymer-diluent mixtures was carried out similarly, although on a somewhat accelerated schedule. It was initiated at a temperature approximately eight degrees below the melting point T_m , the temperature being decreased one degree each day over an interval of ten degrees. The sample was then cooled somewhat more

(18) M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **34**, 551 (1959).

(19) This equation was calculated from the densities at 25 and 100° kindly supplied by Dr. Leo Mandelkern.

(20) Equation 3 is predicated on the usual assumption that the specific volume of the amorphous phase depends only on the temperature and pressure; possible influences of the co-existing crystalline phase are assumed negligible. The accuracy of this assumption is a detail with which we need not be concerned.

(21) See also P. R. Swan, *J. Polymer Sci.*, **42**, 525 (1960).

(22) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

rapidly to a temperature of about 100°; in order to prevent segregation of diluent from the polymer, the melting cycle was commenced at once without exposing the sample to lower temperatures.

Melting Curves.—The specific volume-temperature curves for melting of undiluted samples were determined by raising the temperature according to the temperature schedule of Quinn and Mandelkern,⁹ namely, 15° per day from 25 to 100°, 5° per day from 100 to 125°, 1° per day from 125 to 137° and 0.5° per day above 137° until melting was complete. In a few instances the sample was held for periods of several days at temperatures just below the melting point where a definite, though very small, fraction of crystalline polymer persisted.

The sample volume increased rapidly to a constant value after each successive elevation of the temperature, except for temperatures within 2 or 3° of the melting point. The increase in volume due to melting became both larger and more prolonged at temperatures very near the melting point. In one instance, the volume increase continued for 24 hr. at a temperature approximately one degree below T_m ; it approached constancy thereafter at a value substantially lower than that of the liquidus.

Samples crystallized by comparatively rapid, uncontrolled cooling behave otherwise when melted by incremental elevation of the temperature. As the melting point is approached, the initial volume increase at a given temperature is followed by a subsequent decrease in volume. This reversal of the direction of volume change obviously denotes recrystallization. Samples crystallized at elevated temperatures according to the procedure adopted for the present investigation gave no similar indication of recrystallization at any stage of the melting cycle. It is possible, of course, that recrystallization may have occurred to a limited degree simultaneously with partial melting, the volume change due to recrystallization being obscured by that due to melting.

The course of the melting of polymer-diluent mixtures, crystallized as described above, was similarly determined, the sample being held at each temperature for a period of one day.

Results

Crystallization of Polyethylene.—The higher molecular weight fractions of Marlex underwent substantial crystallization in the course of 40 days at 131.3°, as is shown by results summarized in Table I. The lowest fraction ($\bar{M}_v = 32,000$) failed to crystallize within the allotted period at this temperature. Crystallization proceeded readily at 130°, however. The lower temperature required for crystallization of this fraction appears to be a consequence of its slightly lower melting point. The rate of crystallization is an extremely sensitive function of temperature^{6,23}; for polyethylene in the vicinity of 130° it decreases about seven-fold per degree. The rate is determined primarily by the

(23) L. Mandelkern, in "Growth and Perfection of Crystals," ed. by H. Doremus, B. W. Roberts and D. Turnbull, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 467.

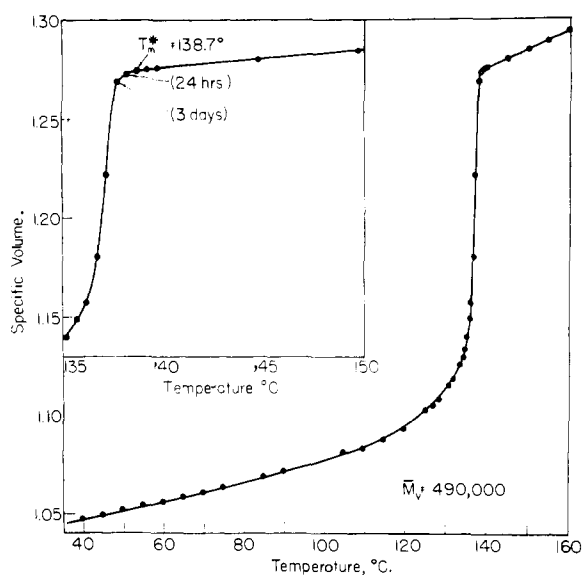


Fig. 1.—Melting curve for a polyethylene fraction of high molecular weight.

degree of supercooling $\Delta T = T_m - T$. Hence, the slightly lower melting point T_m of the fraction in question necessitated a corresponding reduction of temperature for attainment of a comparable crystallization rate.

The figures given in the fourth column of Table I afford rough inverse measures of the relative rates of crystallization at 131.3° . A decrease in rate with molecular weight at equivalent supercoolings is indicated. Thus, the highest Marlex fraction crystallized at approximately one-fourth the rate of the intermediate fraction, notwithstanding the difference of 0.8° in their melting points. This difference in rate is corroborated by measured half times of 280 and 80 hr., respectively, for crystallization of the two samples. Comparison at equal supercoolings ΔT would increase the discrepancy.

Fractions of intermediate molecular weight reached higher levels of crystallinity at 131.3° than higher fractions (Table I). Degrees of crystallinity, similarly calculated from specific volumes according to eq. 3, increased further in the course of the cooling cycle. Degrees of crystallinity of the fractions at 30° vary in the reverse order of their molecular weights. These results are in accord with those of Tung and Buckser²⁴ on the crystallization of polyethylenes of various molecular weights under conditions of *rapid cooling*. Although the unfractionated Marlex crystallized to only a limited degree during the interval at 131.3° , its extent of crystallization at room temperature exceeded that of any of the fractions. Evidently, the low molecular weight components, present in substantial quantity in this polymer, contribute materially to the total crystallinity developed at temperatures well below the melting point.

The increase in degree of crystallinity with decrease in molecular weight is attributable to the enhanced facility of rearrangement of polymer chains conferred by proximity to chain ends on adjoining portions of the polymer chains. During

(24) L. H. Tung and S. Buckser, *J. Phys. Chem.*, **62**, 1530 (1958).

the process of crystallization these chain segments may thus achieve a more expeditious arrangement with respect to the growing crystalline region. The same factor may account for the somewhat greater rates of crystallization in fractions of low molecular weight at equivalent supercoolings.

It will be observed that fractions of Polymer-B crystallized to a lesser extent at 131.3° than did those prepared from Marlex. This difference doubtless is related to the slightly lower melting points of the Polymer-B fractions. Both observations are indicative of the presence of a small proportion of structural irregularity in this polymer. Branch points, or other abnormal constituents, in the amount of approximately 0.2% of the methylene groups, would suffice to account for the differences noted.

Melting of Polyethylene.—Figure 1 presents the specific volume-temperature relationship, established by incremental elevation of the temperature, for the Marlex fraction of highest molecular weight after it had been allowed to crystallize at 131.3° , etc., as set forth in the Experimental section. Interpolated values of the percentage crystallinity calculated according to eqs. 1, 3 and 4 are:

Temp., °C.	30	50	70	90	110
% Crystallinity	76.9	76.9	76.6	75.7	74.2
Temp., °C.	120	125	130	135	
% Crystallinity	71.9	68.9	65.5	56.0	

The degree of crystallinity calculated in this manner remains precisely constant up to 70° ,²⁵ diminishes slightly in the vicinity of 90° and more rapidly above 125° . The degree of crystallinity at 131.3° , namely 64%, is somewhat greater than the value, 59% (Table I), attained during crystallization at this temperature.

Results in the vicinity of the melting point are re-plotted in the inset of Fig. 1 using an expanded temperature scale. At 137.7° the specific volume reached a constant value of 1.268 cc. g.⁻¹ after three days; upon raising the temperature to 138.2° , it increased to 1.273 cc. g.⁻¹ and remained constant for 24 hr. When the temperature was raised to 138.7° , the specific volume increased at once to the value 1.275 for the liquidus line. The melting point of this sample is therefore taken to be 138.5° . Within an interval of only 2° , the crystallinity decreases approximately from 50 to 0%.

Persistence of a small degree of crystallinity above 138° appears to be real. The results suggest a continuity of the melting line with that for the liquidus, the former rounding over to the latter within a range of about 1° . Theory, on the other hand, is explicit in requiring a discontinuity at the conclusion of a process of melting carried out *at equilibrium*. We are inclined to discount the significance of the evidence for diffuse disappearance of the last vestiges of crystallinity. The observation may be indicative of the presence of a small proportion of crystalline material of excep-

(25) These results are at variance with those of Swan,²¹ who computed degrees of crystallinity for linear polyethylene which varied with temperature over this range and, moreover, passed through a maximum in the vicinity of 40° . Swan's expression for the specific volume for the liquid differs numerically from our eq. 1. This may account for the anomaly which he cited.

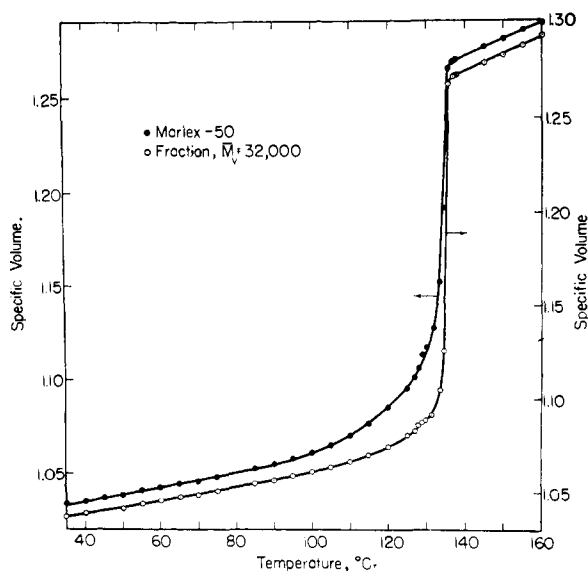


Fig. 2.—Melting curves for Marlex-50 and a fraction of low molecular weight.

tionally high degree of order, the melting point of which more closely approximates that for the hypothetical perfect crystal. It would follow from this suggestion that the true melting point is higher than that reported, perhaps by as much as 1 or 2°.

Melting curves similarly determined for whole Marlex-50 and for the lowest fraction recorded in Table I are presented in Fig. 2. The melting range for the former is substantially broader than for the high molecular weight fraction, owing no doubt to the presence of an appreciable fraction of polymer of very low molecular weight. The fraction for which $\bar{M}_v = 32,000$ displays even sharper melting than the high molecular weight fraction; the degree of crystallinity falls from 70 to 0% within an interval of 2°. Melting points for all samples are recorded in Table I.

The melting point, 137.0°, found for unfractionated Marlex-50 agrees with previous results of Quinn and Mandelkern⁹ and of Marker, Early and Aggarwal.²⁶ It is higher than the values reported by Gubler and Kovacs¹³ and by Tung and Buckser.²⁴ These latter investigators used more rapid heating schedules.

The melting points for the fractions of high molecular weight are the highest yet reported for linear polyethylene. Moreover, the use of fractionated samples crystallized according to the procedure employed here results in melting ranges which are narrower than any previously achieved for this polymer and probably for any other crystalline polymer as well. The effects of low molecular components on the melting range of the unfractionated polymer are apparent.

The Marlex fractions display a consistent increase in melting point with molecular weight (Table I). The reverse is true for the two Polymer-B fractions. According to theory, the effect of molecular weight should scarcely be perceptible throughout the range investigated. Thus, the de-

(26) L. Marker, R. Early and S. L. Aggarwal, *J. Polymer Sci.*, **38**, 369 (1959).

pression of the melting point due to the foreign constituent or structural imperfection, should be given by²⁷

$$\Delta T \cong (RT_m^2/\Delta H_u)X_B \quad (5)$$

where ΔH_u is the heat of fusion of the polymer per unit and X_B is the mole fraction of foreign constituent relative to repeating unit of the chain. If the foreign constituents are end groups, *i.e.*, if the melting point is depressed by the finite molecular weight, X_B may be replaced approximately²⁷ by $2x^{-1}$, where x is the degree of polymerization. Then

$$\Delta T \cong 2RT_m^2/x \Delta H_u \quad (6)$$

which in the present instance ($T_m \cong 410^\circ \text{K}$; $\Delta H_u = 1940$ cal. per mole of C_2H_4) reduces to

$$\Delta T \cong 345/x = 9600/M \quad (6')$$

The changes in melting point with molecular weight of the Marlex fractions, exceeding 2° according to the last column in Table I, are almost an order of magnitude greater than would be calculated from eq. 6'. Differences in degrees of branching in the various fractions offer a possible explanation, the proportion of the postulated branches decreasing with molecular weight in the Marlex series and increasing for Polymer-B.

Polymer-Diluent Mixtures.—In Fig. 3 the specific volume is plotted against the temperature

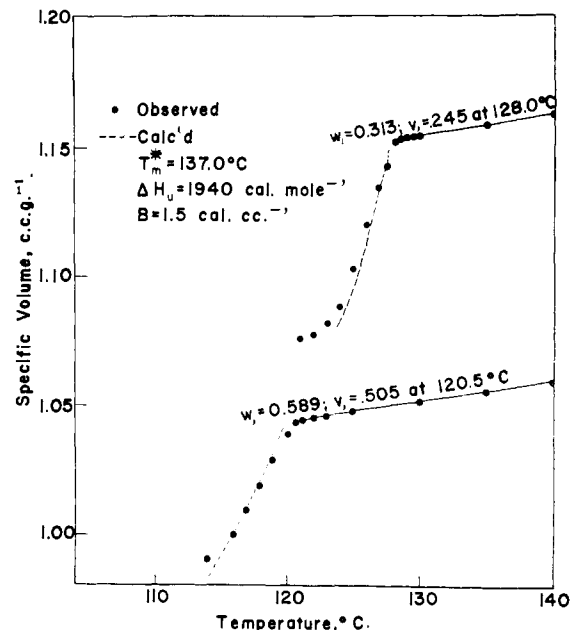


Fig. 3.—Relationship of specific volume to temperature for mixtures of polyethylene ($M = 50,000$) with α -chloronaphthalene of the indicated weight (w_1) and volume (v_1) fractions. Dashed lines represent calculations assuming equilibrium between crystalline and liquid phases.

for two mixtures of a Marlex polyethylene fraction ($\bar{M}_v = 50,000$) with α -chloronaphthalene. A solid line is drawn through the points representing the homogeneous liquid region for each mixture. The experimental points in the melting ranges are to be compared with the broken lines calculated on the assumption that equilibrium prevails between the

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

discrete crystalline and amorphous phases, all of the diluent being confined to the amorphous phase. These lines represent the change in temperature required for maintenance of equilibrium as the composition of the amorphous phase is altered by transfer of polymer from one phase to the other in the course of melting.

This calculation has been performed on the basis of the familiar relationship^{7,27}

$$1/T - 1/T_m^* = (R/\Delta H_u)(V_u/V_1)[v_1 - (BV_1/RT)v_1^2] \quad (7)$$

where T_m^* is the melting point of the undiluted polymer,²⁸ 410.2°K. in this instance; V_u/V_1 denotes the ratio of molar volumes of the structural unit (C_2H_4) and the diluent, its value being 0.2415, with negligible dependence on temperature; $\Delta H_u = 1940$ cal. mole⁻¹ is the heat of fusion per unit, $B = 1.5$ cal. cc.⁻¹ represents the polymer-diluent interaction²⁹ and v_1 is the volume fraction of diluent in the amorphous phase coexisting in equilibrium with crystalline polymer. In compliance with the assumption introduced above, we take

$$v_1 = v_1^0/[v_1^0 + (1 - v_1^0)\lambda] \quad (8)$$

λ being that fraction of the polymer which occurs in the amorphous phase; v_1^0 is the nominal volume fraction of diluent calculated from the weights and specific volumes of the two components. Substitution of eq. 8 in 7 provides a relationship between T and the degree of crystallinity $1 - \lambda$. The thus calculated (theoretical) degrees of crystallinity are readily translated to specific volumes using eq. 3 and assuming additivity of volumes with respect to the diluent. The dashed lines in Fig. 3 have been deduced in this manner.

It is to be noted that T_m^* and ΔH_u are independently known. The value of B rests on application

(28) Inasmuch as the melting points for the polymer samples vary somewhat, being generally slightly less than T_m^0 for the precisely linear polymer of infinite chain length, we introduce the symbol T_m^* to represent the melting point of a given pure polymer sample in absence of diluent.

(29) The values of ΔH_u and B originally reported by Quinn and Mandelkern⁹ were subject to a numerical error. We are indebted to Quinn and Mandelkern for communicating the corrected values which are quoted here. See also ref. 6.

of eq. 7 to the melting points T_m of the mixtures, *i.e.*, to the temperatures for completion of melting where $v_1 = v_1^0$. Thus, given T_m for one mixture (as required for evaluation of B), the broken lines are prescribed by the dictates of phase equilibrium as embodied in eq. 7. Excellent agreement up to degrees of crystallinity $1 - \lambda$ in excess of 0.5 is evident. It is thus established that phase equilibrium is by no means confined to very low degrees of crystallinity. Deviations from equilibrium at temperatures far below T_m nevertheless are to be expected.

Conclusions.—An interspersed of crystalline and amorphous regions which fails to meet the criteria for representation as two discrete phases may indeed be of common occurrence in polymers rapidly crystallized by uncontrolled cooling from the melt. In addition to being imperfectly ordered, the crystalline regions in such systems may be separated from adjoining amorphous material by ill-defined boundaries. Whether or not this is the case is largely a matter of conjecture. Marked departures from equilibrium, however, are demonstrated unequivocally in polymers thus crystallized by their susceptibility to recrystallization upon raising the temperature and by their broad melting ranges.

As the results of the present investigation demonstrate, stringent measures may be required to achieve close approach to conditions of equilibrium in semi-crystalline polymer systems. Requirements in this regard are much more severe than in substances consisting of small molecules. This is a consequence of the long relaxation times for diffusive processes involving long polymer chains. Yet, it is noteworthy that even in monomeric substances the characteristic discontinuity at the first order transition may be obscured by rapid cooling to frozen-in states of non-equilibrium, by imperfect mixing, or by adventitious retention of impurities. The difference in comparison with polymers is one of degree. Departures from the precise requirements for phase equilibrium in semi-crystalline polymers are more plausibly attributable to inadequacies of experimental procedure than to any inhomogeneity of substances consisting of macromolecular chains.

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Free Diffusion in a Two-component System in which There Is a Volume Change on Mixing

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For one-dimensional free diffusion in two-component systems in which volume changes occur on mixing, a formal series solution to the diffusion equation is obtained correct up to terms of order $(\Delta c)^2$, where Δc is the difference in concentration across the initial sharp boundary. Equations are derived by which observed data for the reduced height-area ratio and reduced second moment of the refractive index gradient curves can be used to evaluate the correct dependence on concentration of the diffusion coefficient. For this calculation separate data are required for the partial specific volume of the solute and the refractive index of the solution, both as functions of solute concentration.

Introduction

Assuming that the Fick first law is valid, Gosting and Fujita² and Creeth and Gosting³ have recently

discussed the effects of concentration dependence of the diffusion coefficient and of non-linear concentration dependence of the refractive index of

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(2) L. J. Gosting and H. Fujita, *J. Am. Chem. Soc.*, **79**, 1359 (1957).
(3) J. M. Creeth and L. J. Gosting, *J. Phys. Chem.*, **62**, 58 (1958).