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The Equilibrium Melting of Polymers

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For the last few years it has been possible to grow polymer crystals which have their molecular chain fully or at least largely extended¹. These crystals are, in contrast to the metastable folded chain crystals, often close to equilibrium. At present extended chain crystals of polyethylene, polyoxymethylene, polycaprolactam, and polytetrafluoroethylene have been made². New techniques for growing extended chain crystals are being studied³. With this development it becomes possible to discuss the question of equilibrium melting of polymers on the basis of *experimental results*.

As a starting point the equations described by Flory and Huggins⁴ for a pure equilibrium polymer crystal, *melting into a solution* will be used. Somewhat reorganized this equation is:

$$\frac{1}{T_m^0} - \frac{1}{T_m^0} = \frac{R}{\Delta H} \{- \ln v_p + (x-1)v_i - xv_i^2 \chi\} \quad [1]$$

Where T_m is the observed equilibrium melting point of the polymer dissolving into a melt of volume fraction v_p . T_m^0 is the equilibrium melting point of the same polymer into its pure melt. ΔH is the heat of fusion of one mole of polymer. x is the ratio of molar volume of polymer to that of the second component i , and χ is an appropriate interaction parameter defined per mole of the second component, which may also be polymeric. On decreasing the molecular size of the noncrystallizable component the $(x-1)v_i$ term becomes more and more significant leading finally, for $x > 10$, and for a system with negligible interaction, to a limiting equation for melting point lowering:

$$\Delta T = \frac{RT^2}{\Delta H} xv_i \quad [2]$$

Figure 1 represents an eutectic phase diagram calculated using equation 1 for different values of x . The other parameters were chosen to fit the case of polyethylene of molecular weight 24 500. T_m^0 is 413.1°K, $R/\Delta H = 1.23 \cdot 10^{-6}$, and χ is 0.4. x equal 4, 20, 45, and 85 corresponds approximately to molecular weights of 6 000, 1 300, 450, and 250, respectively. The melting points of these lower molecular weights⁵ are in order 408.5°K, 387.4°K, 341.8°K and 297.4°K. Such low

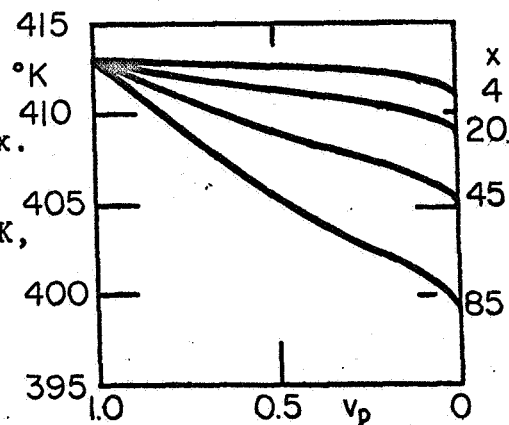


Figure 1

melting points cause the eutectic point to be very close to the zero polymer volume fraction ordinate. Figure 1 represents thus the full phase diagram.

To describe the melting of a broad molecular weight homopolymer it is necessary to derive a multicomponent eutectic melting equation. At ultimate equilibrium it must be assumed that all different molecular weights crystallize in separate crystals. The equilibrium melting equation 1 has to be modified to accommodate the multicomponent melt.

v_i is replaced by Σv_i [3]

x is replaced by \bar{x}

$$\bar{x} = \frac{\Sigma n_i}{\Sigma n_i \left(\frac{1}{x} \right)} = \frac{\Sigma x_i v_i}{\Sigma v_i}$$

The interaction parameter is assumed to be also an appropriate average. (A similar treatment was developed previously by Kilian for copolymers without interaction⁶.) Figure 2 represents the melting curve of a polyethylene calculated using equation 1 and 3 assuming the lowest molecular weight melts into its own pure melt, the next fraction melts into a two component melt etc. The last trace melting would then be the highest molecular weight equilibrium crystal melting into a solution of all species given by the molecular weight distribution. The marked experimental points are described below.

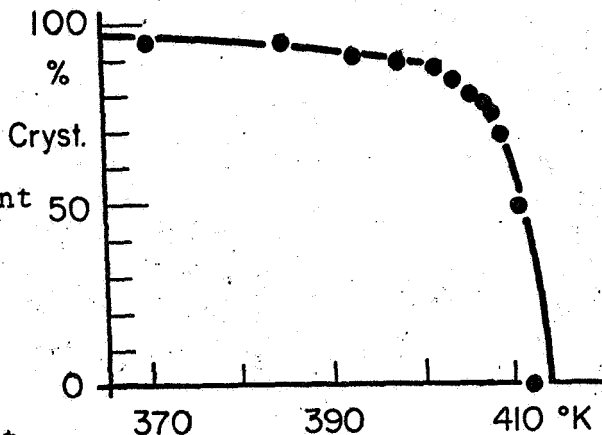


Figure 2

To investigate the validity of the above equations two sets of experiments were performed. A linear polyethylene was crystallized under elevated pressure so that its morphology showed only extended chain lamellae by electron microscopy. Slices of 6-8 μ thickness of this polymer cut with a microtome were immersed in molten paraffins and sharply fractionated samples of polyethylene so that the volume ratio was about 10 parts melt to 1 part crystals. The specific heat of this composite sample was then measured in a Perkin Elmer Scanning Calorimeter using previously established techniques.⁷ At the suspected melting point a halt of 5 hours was scheduled. After this time heating was resumed to detect any heat of fusion. About 1% of residual crystals could be detected. By repeated trials on fresh samples at slightly different temperatures the dissolution temperature of extended chain polymer crystals in paraffins and well characterized fractions could be established to an accuracy of $\pm 0.5^\circ\text{K}$ or better. This procedure avoids superheating, a difficulty in fast measuring techniques, but still allows to work with milligram sized samples.

The second set of experiments dealt with a linear polyethylene

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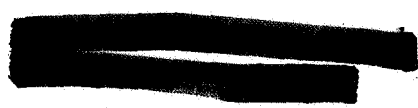
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of known molecular weight distribution. It was crystallized at 500°K and 4800 atm. hydrostatic pressure. Its density at atmospheric pressure at 298°K was 0.995 g/ml. Electron microscopy showed again only extended chain crystals. About 1 g of this material was sealed in a dilatometer and its *melting characteristics* was determined by standard dilatometry. The measured specific volume was converted to crystallinity using known X-ray and melt specific volumes as a function of temperature.

The results of the dissolution experiments are shown in Fig. 3, while those of the dilatometry are indicated by the filled circles in Fig. 2.

The drawn out curve in Fig. 3 represents the experimental data well. It has been calculated using equation 1, inserting the following independently

determined experimental parameters. T_m^0 for infinite

molecular weight is 414.6°K as found on up to 10^4 extended chain single crystals melting into a $1.4 \cdot 10^7$ M.W. melt⁸. For lower molecular weights the interpolation formula derived by Broadhurst⁵ was modified with this experimental value to:

$$T_m^0 = 414.6 (n-1.5) / (n+5.0) \quad [4]$$

where n is the number of carbon atoms. Equation 4 has been shown⁵ to work well for paraffins above 44 carbon atoms with a value of 414.3. The change to 414.6 makes it also fit the polymer experiments cited here. ΔH as a function of temperature was calculated using a value of 929 cal/mole CH_2 at 414.6°K as determined by calorimetry.⁹ The variation with temperature was calculated using the thermodynamic relationship.

$$d\Delta H/dT = \Delta C_p \quad [5]$$

Experimental values for the heat capacity of completely amorphous and completely crystalline polymer were taken from references 7,9, and 10. Molar volumes and densities of paraffins are also available¹¹. χ and T_m^0 for the extended chain crystals used in the measurements can be calculated for the best fit of equation 1. A constant value of 0.4 for χ and 412.1°K for T_m^0 was obtained. 412.1°K corresponds according to equation 4 to a molecular weight of 15 000. The experimental number average molecular weight in the crystals used was 8 200, about 40% by weight of the sample has a molecular weight above 15 000. Electron microscopy can

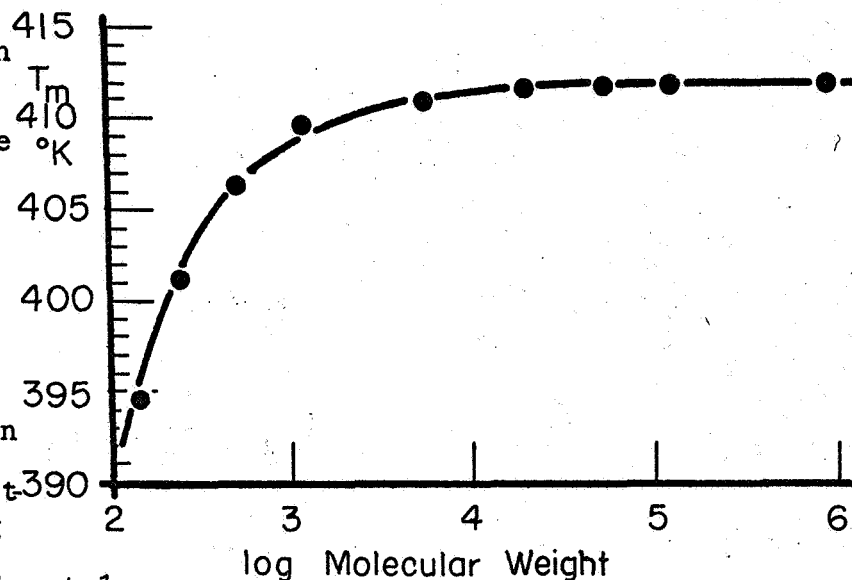


Figure 3

detect lamellar thicknesses up to 20 000 Å. Most lamellae were in the 1-3 000 Å range. This agrees reasonable well with T_m of 412.1°K. A constant value of χ seems contradictory to similar experiments carried out with paraffins and folded chain crystals.¹²

The analysis of the *dilatometer data* Fig. 2 shows agreement of the calculated curve and experimental data for the first 50% melting. At higher temperatures the experimental melting curve is *sharper* than the calculated one. The maximum melting point finally is about 2.5°K lower than the calculated one. This means the last 40% by weight of the extended chain crystals behave as if their chain length corresponds to about 15 000 molecular weight. The only change being the increase of molecular weight of the melt. This experimental observation parallels the dissolution experiments described above. It could be interpreted such that about 15 000 molecular weight little separation into different molecular weights on crystallization took place under the chosen crystallization conditions.

Summarizing it can be said that if crystals which are close to equilibrium are molten, keeping equilibrium throughout the experiments, previously derived equilibrium melting equations can be used for the description. A self consistent set of homopolymers crystallized with a largely extended chain conformation seems to be caused by a diluent effect of the lower molecular weight. The chosen pressure crystallization conditions seemed to be able to achieve separation into different molecular weight crystals up to about 15 000 molecular.

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