

Thermodynamics of Crystallization in High Polymers II. Simplified Derivation of Melting Point Relationships

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Thermodynamics of Crystallization in High Polymers

II. Simplified Derivation of Melting-Point Relationships^{1,2}

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July 24, 1947

RECENT attempts to treat crystallization in polymers by statistical thermodynamical methods, have yielded several relationships between the melting temperature and polymer constitution. The melting-point-composition relationship derived for copolymers, for example, is analogous to the freezing-point composition relationship for ideal mixtures of simple molecules (see Eq. (4) below). As is also shown by x-ray studies, the structural units of polymers occupy a role corresponding to the molecules of simple substances. While a comprehensive treatment covering various complicating circumstances which may be anticipated in crystalline polymers is somewhat cumbersome, the essentials devoid of these complications can be presented briefly as follows.

A chain polymer containing identical units A will be considered, these units are capable of forming a crystal lattice. Other units B , unable to enter the crystal lattice characteristic for A , also may be present. It will be assumed that the structure of the liquid can be described in terms of a pseudo-lattice, each cell of which is occupied by a polymer segment. (The configurational segment is assumed to be identical with the structural unit in the present treatment.) The formation of a crystallite composed of σ -chains in its cross section and ζ -units in length, requires first of all the location of a planar array of σ -cells each occupied by type- A units. Each of these A units must be succeeded by an uninterrupted sequence of $\zeta-1$ additional A units if the array is to be acceptable as a nucleus for the formation of a crystallite of the prescribed length. The probability of such a constellation will be W_ζ^σ , where W_ζ is the probability of a sequence of ζ A segments in a given chain, starting with an arbitrarily selected unit. The corresponding entropy term will be $k\sigma \ln W_\zeta$.

It is further required that the segments (units) involved become aligned in perfect array, packed in the more dense arrangement of the crystal lattice. The entropy associated with this step will be assumed, as an approximation, to be proportional to the number of units, i.e., the entropy change

will be expressed as $-\sigma\zeta s_u$, where s_u is the entropy of fusion per unit when $W_\zeta=1$. Actually, the configurational entropy contribution, which may account for the major part of the entropy of fusion, should be taken proportional to $\zeta-1$ (see Eq. (8) of reference 3).

The total entropy change involved in the formation of the crystallite will be

$$-\Delta S_f = \sigma(R \ln W_\zeta - \zeta s_u), \quad (1)$$

where ΔS_f represents the total entropy of fusion expressed in molar units. The free energy of fusion is correspondingly

$$\Delta F_f = \sigma\zeta[h_u - Ts_u + (RT/\zeta) \ln W_\zeta]. \quad (2)$$

In the case of a random copolymer containing a "mole" fraction X_A of A units, $W_\zeta = X_A^\zeta$. Hence,

$$\Delta F_f = \sigma\zeta(h_u - Ts_u + RT \ln X_A). \quad (3)$$

The equilibrium condition at which $T = T_m$, the temperature ("melting point") for complete disappearance of crystallinity, may be applied by differentiating with respect to either σ or ζ and equating to zero, giving

$$1/T_m = s_u/h_u - (R/h_u) \ln X_A.$$

Setting $s_u/h_u = 1/T_m^0$ where T_m^0 refers to the melting point for the polymer composed exclusively of A units,

$$1/T_m - 1/T_m^0 = -(R/h_u) \ln X_A. \quad (4)$$

Corresponding expressions may be derived similarly for the melting points of non-random copolymers as functions of their compositions and the kinetic factors governing order along the chain.

If the polymer chains are composed exclusively of A units, but are limited in length, $W_\zeta = (x-\zeta+1)/x$, where x is the number of repeating units per molecule. Substituting in Eq. (2) and proceeding as above, there is obtained in the limit of vanishing ζ

$$1/T_m - 1/T_m^0 = R/xh_u.$$

However, the more detailed treatment leads to an additional term arising from the increased concentration of ends of molecules in the liquid phase. Thus,

$$1/T_m - 1/T_m^0 = (R/xh_u)(1+1/z), \quad (5)$$

where z is the number of configurational segments per structural unit. If the molecules are of random length such that the probability of continuation of the chain from one unit to the next is p ,

$$1/T_m - 1/T_m^0 = (R/h_u)[- \ln p + (1-p)/z], \quad (6)$$

which is approximately equivalent to Eq. (5) if x is replaced by its number average \bar{x}_n .

A direct measurement of the heat of fusion of a high polymer invariably yields a value dependent on the degree of crystallinity, the latter being difficult to determine. By means of the above relationships the latent heat (and the entropy) for the transformation from totally crystalline to amorphous polymer may be deduced readily from mere melting-point measurements on polymers of known constitution.

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² Contribution No. 142 from the Goodyear Tire and Rubber Company Research Laboratory.

³ P. J. Flory, J. Chem. Phys. 10, 51 (1942).