I. INTRODUCTION

The behaviors of melting and crystallization are of fundamental importance for polymer materials. However, the relation between equilibrium melting temperature and the molecular structure is not well understood. Early in 1955, Bunn wrote a paper on this topic and considered the stiffness and the interchain attractive interactions of the chain molecules as the controlling factors to the melting points. This idea was widely accepted. Almost at the same time, Flory considered the stiffness in his lattice statistics, but assumed the interchain attraction to be small and neglected its contribution. This neglect was subsequently criticized.

On the experimental side, the exact measurement of the equilibrium melting point of homopolymers is also complex. Kinetic factors such as the small size of the crystallites and their metastability in chain folding, and structural factors such as the defects of the crystallizable chains and the impure environment of crystallites contribute to variations in the melting point. Although many relationships about the melting point depression with structural factors may be found in the literature, they were based upon semiempirical assumptions. It is desirable to explain these relationships from the more fundamental consideration of the molecular nature of the materials. Therefore, interpretation of the driving forces of polymer crystallization needs to be explored in more detail.

In this paper, we regard the anisotropic aspect of polymer interactions to be the dominant factor in the molecular nature of polymer crystallization and then develop the classical lattice statistics to predict the melting point. The results are compared with the current semiempirical relationships and are also verified by dynamic Monte Carlo simulations of the lattice model, with respect to a change of value in driving force, chain length, content of random comonomers, and content of diluentlike small molecules or noncrystalline polymers.

II. DRIVING FORCES OF POLYMER CRYSTALLIZATION

The most fundamental characteristic of polymers is the chainlike structure, which is formed by anisotropic connection of the monomers. This causes local interchain interactions to appear anisotropic. This anisotropy will be enhanced by chain stiffness, nevertheless, it originates from the characteristic of the molecular shapes. From this point of view, the nature of polymer crystallization will be similar to that of mesophase formation and especially so in the case of the isotropic–nematic liquid crystal (LC) phase transition of the molecules containing anisotropic shapes.

The interchain interactions can be divided into repulsion and attraction. Following the van der Waals approach, the interactions between the local chains can be simplified into a hard-core volume exclusion and a short-range attraction. Flory has considered that, on cooling, chain stiffness will strengthen gradually and generate local extended rigid rods with stable helical conformations, which enhances the anisotropic volume exclusion between local chains. This kind of steric repulsion makes the random packing of those rods in high density become impossible, unless they pack themselves in parallel. This idea is similar to the Onsager theory for lyotropic LC phase transition. In addition, the short-range attraction between local chains will also appear anisotropic, especially when they pack themselves densely. The packing for the minimum potential energy (most of the cases are compact packing) will be in a regular arrangement of the local chains and in parallel. So the compact packing energy change of the local chains will appear as orientation dependent. If the contribution of this kind of energy change...
is enhanced on cooling, a disorder–order phase transition also becomes inevitable. The similar case for thermotropic LC phase transition has been well described in the Maier–Saupe theory.

These two driving forces are rather independent of each other, because the anisotropic volume exclusion mainly contributes to the entropic change of phase transition, whereas the anisotropic attraction (sometimes called the “nematic interaction”) mainly contributes to the enthalpic change of phase transition. Both of them have been considered as the molecular nature of the LC phase transition of polymers. In the case of polymer crystalization, we can also say that both chain stiffness and compact packing tendency are the driving forces, and their contributions are independent of each other.

In fact, local anisotropic interaction of the nonmesogenic polymer chains is not a new concept. It has been observed in a molecular dynamic simulation of polyethylene. It was also found to contribute to the molecular motions and the local ordered domains in cross-linked polymers. Bleha has discussed the effect of orientation-dependent packing of chains upon the melting point. For polyethylene and polytetrafluoroethylene, the molecular density-functional theory of melt crystallization gave an effective “chain straightening force” originating from a background attractive potential.

According to Ostwald’s stage law, a transformation from one stable state phase to another will progress through metastable states whenever such states exist. The dependence of mesophases of crystalline polymers upon temperature and pressure has been considered previously. Chain stiffness favors nematic LC mesophases, while the condics (conformational disorder) crystals are usually found as a result of the flexible portion of polymer chains. The latter contains a hexagonal column structure like columnar LCs, which is stabilized by partially compact packing of the chains, such as the condensed polyethylene chains under higher pressure. This implies that the driving force for condics crystal formation is the anisotropic aspect of the attraction between local chains. The similarity in the nature of polymer crystallization to the mesophase formation is thus tenable. In both cases, a disorder–order phase transition occurs, and the compact packing during crystallization gives preference to the nucleus-growth mechanism and the positional order like the solid state.

The energy change in compact packing of the crystallizable chains should be distinguished from the cohesive energy of the melt. While both contribute to the cohesive energy of the final crystalline state, they are independent in sequence. Thus, for a mixture system containing polymers, three independent molecular parameters for the minimum potential energy, i.e., chain extending energy change, compact packing energy change, and the unmixing energy change, can be adjusted. Their contribution to the disorder–order phase transition as well as phase separation is predictable. Here, we focus our attention on the former behavior for a mixture with high concentration of lattice chain molecules.

III. CLASSICAL LATTICE STATISTICS

The lattice model is appropriate to describe a molecular system with volume exclusion. In a lattice space, a polymer molecule is represented as a group of sites (monomers) sequentially connected by the bonds. A mixture system is thus defined with \( n_2 \) chains, each containing \( r \) monomers, and \( n_1 \) void sites. Here, we consider the void sites as solvent molecules or free volume. The overall volume is \( n = n_1 + n_2 \) and the concentration is \( v_2 = r n_2 / n \). We can adjust three parameters to minimize the potential energy of the lattice chains. The first is the collinear energy change, \( E_c \), of two consecutive bonds along the chain to represent the stiffness of the chains. The second is the parallel energy change, \( E_p \), of the neighboring packing between two nonbonded bonds to represent the compact packing energy change of the chains. And the third is the mixing energy change, \( B \), for each monomer–solvent pair, \( B = E_{mm} - (E_{nn} + E_{ss})/2 \) according to the quasichemical approximation, here, \( E \) represents the two-bead cohesive energy in the liquid state and its subscripts \( m, s \) represent monomers and solvent molecules, respectively.

The phase-separated and fully ordered state of the chain system can be regarded as the ground state, in which all the chains are extended and packed in parallel. The partition function of the mixing and disordered states can then be calculated through sequentially putting the monomers onto the lattice with the assumption of random distribution of occupations. For the probability of the next unoccupied site, the volume fraction proposed by Flory works quite well, the surface fraction proposed by Huggins is more elegant but at the expense of complexity.

The disorder parameter \( f \), which is defined by the mean fraction of noncollinear bond connections along the chains, provides an indication of the degree of system order. For the fully ordered state, \( f = 0 \); for the stable disordered state, the disorder parameter depends only on the chain stiffness,

\[
f = \frac{(q-2)\exp \left( -\frac{E_c}{kT} \right)}{1 + (q-2)\exp \left( -\frac{E_c}{kT} \right)},
\]

in which \( q \) is the coordination number of the regular lattice, \( k \) is Boltzmann constant, and \( T \) is the system temperature.

Flory has calculated the partition function with the contributions of noncollinear bond connections of the bonds and the mixing interactions between monomer and solvent. The previously neglected contribution of nonparallel packing (i.e., noncompact packing) of the bonds can be approximately calculated in the following way.

For an arbitrary bond, the greatest number of lateral packed bonds in parallel will be \( q - 2 \), here two consecutive bonds along the chain have been subtracted. Concerning one of these lateral bond positions, if one of the sites is occupied by a monomer with the probability \( v_2 \), the probability of its two adjacent monomers along both directions of the chain occupying another site involving this bond position will be \( 2/q \). Double occupation of these two sites has the probability...
\[ v_2^2 \text{, in which the probability of this bond position really occupied by a bond is } 2v_2^2/2q, \text{ so the probability of non-parallel but double occupation of these two sites is the difference } v_2^2 - 4v_2^2/q. \text{ The probability of single occupation on these two sites is } 2v_2(1-v_2), \text{ thus the overall probability of the non-parallel occupation on this bond position is the sum } v_2^2 - 4v_2^2/q + 2v_2(1-v_2). \text{ The potential energy of the compact packing contribution for the arbitrary bond will be } (q-2) \times (2v_2^2 - 4q) \times v_2^2 \times E_p. \]

The partition function of the disordered state for the mixture system is obtained as

\[ Z = (n/n_1)^{n_1}(n/n_2)^{n_2}(q/2)^{n_2}e^{(1-r)n_2}v_2^{n_2} (r-1)^{n_2}v_2^{n_2} (r-2)^{n_2}v_2^{n_2}, \]

in which

\[ z_l = \exp \left( -\frac{n_1}{n} \times \frac{q_{\text{eff}} B}{kT} \right), \]

\[ z_p = \exp \left( \frac{1}{2} (q-2) \left( \frac{2 - \frac{r n_2}{n} - \frac{4}{q} + \frac{r n_2}{n} \times \frac{E_p}{kT} }{n} \right) \right), \]

\[ z_c = 1 + (q-2) \exp \left( -\frac{E_c}{kT} \right). \]

Here, \( q_{\text{eff}} \) is the effective coordination number for mixing interaction. If the partition function of the crystalline state is assumed to be approximately one, the equilibrium melting-crystallization temperature \( T_m \) can be calculated from \( Z = 1 \) through the iteration method, as will be shown in the following.

When the system temperature is much lower than \( T_m \), the conformation entropy of the condensed chains may be less than 0. This is the so-called “entropy catastrophe” like the well-known Kauzmann’s paradox, and seems to be an inevitable result of the calculation from the disordered state. Fortunately, a disorder–order phase transition will always take place at \( T_m \), as we shall demonstrate by the following computer simulations in a lattice polymer system, unless it is blocked by a glass transition in actual polymer systems. So here, this “catastrophe” has no physical meaning.\(^{28}\)

\[ \text{IV. MONTE CARLO SIMULATION} \]

The dynamic Monte Carlo simulations of the lattice model can directly verify the calculation of lattice statistics. This simulation method moves the local chain on a cubic lattice with periodic boundary condition according to a microrelaxation model, in which single-site jumping along either the lattice grid or the diagonal lines is permitted and the sliding diffusion is terminated by extending the nearest kink along the chain.\(^{29}\) This model is highly efficient in relaxing local chain conformation, and especially facilitates chain extension when ordering. The coordination number is high up to 26.

The typical sample system was generated in the following way. We put 240 chains, each containing 16 monomers, onto a \( 16 \times 16 \times 16 \) cubic lattice in a fully ordered state, so the occupation density is 0.9375. The chains are allowed to relax to their stable disordered state under athermal solvent conditions. At this density with larger chain length (up to 128 monomers) and larger cubic box (\( 32 \times 32 \times 32 \)), the scaling laws for the “unperturbed” coil size\(^{29}\) and the Rouse-type chain motions\(^{30}\) have been verified by the simulations, which indicate a reasonable representation of the melt state of short-chain polymers.

The athermal state of this sample system can be regarded as the liquid state with infinitely high temperature. Through a cooling process from this state, the expected disorder–order phase transition or phase separation will occur depending upon the assumption of three energy parameters. The well-known METROPOLIS importance sampling method\(^{31}\) was employed for each step of microrelaxation and the energy barrier was defined as

\[ \Delta E/(kT) = (c \times E_c + p \times E_p + m \times B)/(kT) \]

\[ = (c + p \times E_p/E_c + m \times B/E_c \times E_c)/(kT), \]

in which \( c, p, \) and \( m \) are counted for change in the number of noncollinear connections between the consecutive bonds, the number of non-parallel packings of the neighboring bonds, and the number of monomer–solvent pairs, respectively. By changing the form of Eq. (3), we can adjust three reduced parameters—\( E_p/E_c \), which represents the driving forces of crystallization, \( B/E_c \), which represents the quality of the solvent, and \( E_c/(kT) \), which represents the system temperature.

For the typical sample system with fixed setting \( E_p/E_c = 1 \) and \( B/E_c = 0 \), \( E_c l/(kT) \) was increased step by step from zero with the step length 0.02, and the system was allowed to relax for 300 Monte Carlo steps (MCS) in each temperature step, to correspond to a cooling process. One Monte Carlo step is defined as the average one attempt of each monomer to perform microrelaxation. During the cooling process, the disorder parameter \( f \) shows a sharp disorder-to-order phase transition in Fig. 1. Before that transition, it follows the prediction of Eq. (1) quite well. This transition should correspond to the melt crystallization due to the high occupation density of the system. Doubling the size of the cubic box does not change the transition temperature, which implies that the finite size effect is not significant at this time. The reverse heating curve shows an apparent thermal hysteresis,
can be neglected here.

compared to the melting point of short-chain polymers, and for the supercooling of crystallization will be very small.

In Fig. 2, (a) The disorder parameter $f$ vs annealing time in the simulation of an isothermal process for a $32 \times 32 \times 32$ cubic lattice system with occupation density 0.9375, chain length 16, and the assumption of $E_c/E_r = 1$, $B/E_r = 0$, $E_c/(kT) = 0.22$ after jumping from the athermal state. (b) A snapshot of thin section film with thickness 5 at the time 15 000 MCS for the above system, 32-sized cubic boundary is periodic.

nevertheless their onset points are almost the same. So in the following simulations, we approximately define the onset point of crystallization as the melting point, and the reported data are averaged over at least five individual cooling processes with step length 0.002. The typical values of $E_c/(kT)$ for the supercooling of crystallization will be very small compared to the melting point of short-chain polymers, and can be neglected here.

The isothermal process at $E_c/(kT) = 0.22$ was performed on a $32 \times 32 \times 32$ cubic lattice after jumping from the athermal state. In Fig. 2(a), one can observe the delay before phase transition. The final ordered state, as shown in Fig. 2(b) appears rather semicrystalline and lamellae like. The delay for phase transition implies an incubation period of nucleation, which is a typical indication for first-order phase transition. The chain folding in the lamellae in relation to their in situ movability has been investigated with large chain length, the result will be reported in another paper.

In fact, many Monte Carlo simulations have been performed to test Flory’s lattice statistics, and the first-order phase transition has been observed in a three-dimensional model. Even simulations with both chain stiffness and parallel packing energy change have been investigated but at that time, the interest was focused on LC phase transition.

V. RESULTS AND DISCUSSION

A. Driving forces

For the typical sample system undergoing melt crystallization, the driving force parameter $E_p/E_c$, was varied while holding $B/E_r = 0$, the corresponding melting points are compared with the calculations from Eq. (2) and $Z=1$. The results show good agreement in Fig. 3.

With the limits of infinite chain length ($r \rightarrow \infty$) and high density ($v_2 \rightarrow 1$), Eq. (2) and $Z=1$ can be simplified as

$$1 + (q-2) \exp\left(-\frac{E_c}{kT_m}\right) = \exp\left[1 + \frac{1}{2}(q-2)(1 - \frac{4}{q}) \times \frac{E_p}{E_c} \frac{kT_m}{E_c}\right].$$

The value on the right-hand side is usually much larger than one, so the first term (one) on the left-hand side can be omitted, we further obtain

$$T_m = -\frac{E_c + \frac{1}{2}(q-2)\left(1 - \frac{4}{q}\right)E_p}{k \ln(q-2) - k}.$$  

Equation (5) shows that the melting point has an almost linear relation with $E_c$, as well as with $E_p$. This agrees with current experience on actual polymers. All the elements favoring chain extension, such as the stable helical conformations due to difficulty of internal rotation in most of the polymers or due to local hydrogen bonding in DNA and most of the proteins, will contribute to the high melting point. All the elements favoring close packing of the chains, such as the sequential regularity (chemical, geometrical, or spatial) and small side substituent, will contribute to the high melting point too. In fact, the linear relation between the melting point and the cohesive energy has been reported for some series of polymers in Bunn’s paper.\[1\]
B. Chain length

The semiempirical expressions about the chain length dependence of the melting point have been well compared with the measurement of paraffin and polyethylene.\(^{39,40}\) The typical expression used for paraffin is the Flory–Vrij equation,\(^{41}\) which assumes two sequential steps in melting: first, melting of chains but maintaining the connection between the pairs of chain ends, followed by cutting the pairs. If the chain end is regarded as diluent, a linear relation between the reciprocal melting point and the reciprocal chain length fits well for polyethylene with low molecular weight. Here, for comparison, the Flory–Vrij equation is expressed as

\[
\Delta G = r \Delta g_u + \Delta g_c - RT_m \ln r = 0,
\]

with the bulk free energy of fusion for each monomer, \(\Delta g_u = E_u - (q - 2)(1 - 4q) E_u^f / 2 - kT_m \ln (q-2)^{1.5}\), obtained from the condition \(T_m = \Delta h_u / \Delta s_u\) in Eq. (5), and the bulk free energy of fusion for each chain end, \(\Delta g_c = (q - 2)(1 - 4q) E_u^f / 2 - kT_m \ln (q - 1)^{1.5}\), calculated similarly for \(Z = 1\) with \(r = 2\) and the high density approximation. The results obtained from the calculations with \(Z = 1\) and the Monte Carlo simulations are shown in Fig. 4. One can find that the Flory–Vrij equation agrees perfectly with the calculation from \(Z = 1\). A good linear relation between the reciprocal melting temperature and the reciprocal chain length is also found for \(r > 100\). The small deviation of the simulation results from the prediction of lattice theory may be due to a number of reasons, however for very short chains, the failure of the mean-field assumption may be dominant.

C. Content of random comonomers

In practical polymers, there are many kinds of sequence irregularities along the chains. There can be different chemical species, different geometrical connections, or different stereo optical isomers of the crystallizable monomer. Usually the irregular sequences contain different shapes or shapes or sizes and cannot match the close packing of the crystallizable monomers. So they can be represented as comonomer \(B\) in the lattice model without distinction, and the bonds containing the comonomers are assumed to have no potential energy change in nonparallel packing \((E_p = 0)\). Randomly denoting a definite number of monomers along the chains as the comonomers, we can perform the same cooling process as mentioned previously and compare the melting points with the calculations from \(Z = 1\) by using existing semiempirical relationships.

Flory\(^{42}\) gave the first expression of the melting point depression due to random comonomers, in analogy to the ideal solution of small molecules and with the assumption of comonomer exclusion from the crystals. For comparison, this semiempirical relation can be shown as

\[
\frac{E_c}{kT_m} - \frac{E_c}{kT_m^0} = \frac{E_c}{\Delta h_u} \ln X_A,
\]

in which \(T_m^0\) is the equilibrium melting point of homopolymers, \(\Delta h_u\) is the heat of fusion for each crystallizable monomer, and \(X_A\) is the molar fraction of the monomers. Coleman\(^{43}\) gave the same expression for stereo irregularity on the sequence of polymers. Sanchez and Eby\(^{44}\) gave the general expression with the assumption of the comonomers existing in the crystallites with an arbitrary concentration. Here, for comparison, we consider the typical case with a homogeneous distribution of comonomers in the system, as given by Kolson and Eby,\(^{45}\)

\[
\frac{kT_m}{E_c} = \frac{kT_m^0}{E_c} \left(1 - \frac{\Delta h_B}{\Delta h_u} X_B\right),
\]

in which \(\Delta h_B\) is the heat of fusion for each comonomer as a defect in the crystal and \(X_B\) is the mole fraction of the comonomers.

The results of calculations and simulations with the assumptions \(E_p / E_c = 1\) and \(B / E_c = 0\) are shown in Figs. 5(a) and 5(b) corresponding to the above-mentioned expressions. They still agree with each other quite well, but Fig. 5(b) shows a better linear relation than Fig. 5(a). This is because the comonomers have not been obliged to move out of the crystals either in the calculation or in the simulation.

D. Content of small molecules as diluent

Adding some small molecules as a solvent to improve the performance of polymers in processing and applications has become a conventional procedure in the preparation of polymer products. These additives surrounding the crystallites will cause melting point depression. Flory\(^{46}\) gave the first semiempirical expression,

\[
\frac{E_c}{kT_m} - \frac{E_c}{kT_m^0} = \frac{E_c}{\Delta h_u} \left[ n_1 - \frac{q \rho B}{kT_m} \left( \frac{n_1}{n} \right)^2 \right].
\]

The linear relationship predicted in this equation has been well verified by the measurement of some actual polymer systems,\(^{47}\) and the heat of fusion seems really independent of the solvent quality.

Here in our simulations, we change the occupation density to study the diluent effect from small molecules. On a \(16 \times 16 \times 16\) cubic lattice, 240, 224, 192, 160, and 128 chains with the length \(r = 16\) are preset corresponding to the volume concentration \(v_2 = 0.9375, 0.875, 0.75, 0.625,\) and 0.5, re-
respectively. Again setting $E_p/E_c = 1$ and $B/E_c = 0$ in the above-mentioned cooling process, the resulting melting points obtained from the simulations are compared with the calculations as shown in Fig. 6. In the high concentration region, they agree with each other quite well and follow the linear relation of Eq. (9), while in the semidilute region, the predictions of lattice theory deviate from a linear relation on account of the failure of mean-field assumption. After linear regression of the simulation data with the correlation coefficient 0.99976, the slope gave $\Delta h_u \approx 4.23E_c$.

Next, $B/E_c$ was set to 0.1, 0.3, $-0.1$, $-0.3$ respectively, and the simulation results are shown in Fig. 7(a). Except for the case of $B/E_c = 0.3$, where the disorder–order phase transition may be disturbed by the phase separation behavior, all the data points agree with the linear relationship of Eq. (9). Linear regressions gave their intercept $E_c/\Delta h_u$ values and their slope $q_{\text{eff}}B/\Delta h_u$ values, and we find that the $(q_{\text{eff}}B/\Delta h_u)$ vs $(E_c/\Delta h_u)\times (B/E_c)$ curve also shows a good linear relationship with the correlation coefficient 0.99927 and the slope $q_{\text{eff}} = 17.54$. The results of substituting this $q_{\text{eff}}$ value into the melting point calculation with $Z=1$ corresponding to various $B/E_c$ values are shown in Fig. 7(b). In a comparison with the simulation results, the agreement for $B<0$ is not good. The reason may be the inexact expression of the mixing heat in the classical lattice statistics and further correction is needed. 48

Except for $B/E_c = 0.3$, the other four points on the $\Delta h_u/E_c$ vs $B/E_c$ curve also show a good linear relationship with the correlation coefficient 0.99807. However, the curve is not a horizontal line. From the intercept and the slope, $\Delta h_u \approx 4.282E_c - 4.509B$ can be obtained with the assumption $E_p = E_c$. This relation implies that the macroscopic

FIG. 5. (a) The reduced melting point $E_c/(kT_m)$ vs the logarithmic mole fraction of the crystallizable monomers $X_A$ for a $16 \times 16 \times 16$ cubic lattice system with occupation density 0.9375, coordination number 26, chain length 16, and $E_p/E_c = 1$, $B/E_c = 0$. The solid line is calculated from Eq. (2) and $Z = 1$; the closed circles are the simulation results with the error bar less than their size. (b) The reduced melting point $kT_m/E_c$ vs the mole fraction of comonomers $X_B$ for the same condition as in (a).

FIG. 6. The reduced melting point $E_c/(kT_m)$ vs the diluent concentration $n_1/n$ for a $16 \times 16 \times 16$ cubic lattice system with coordination number 26, chain length 16, and $E_p/E_c = 1$, $B/E_c = 0$. The solid line is calculated from Eq. (2) and $Z = 1$; the closed circles are the simulation results with the error bar less than their size; the dashed line is the linear regression result of the data points.

FIG. 7. (a) $(E_c/(kT_m) - E_c/(kT_m^{B=0}))/v_1$ vs $v_1E_c/(kT_m)$ for a $16 \times 16 \times 16$ cubic lattice system with coordination number 26, chain length 16, $E_p/E_c = 1$, and different $B/E_c$ values as indicated. The error bar is less than the size of the reported data points. (b) The reduced melting point $E_c/(kT_m)$ vs the diluent concentration $n_1/n$ for a $16 \times 16 \times 16$ cubic lattice system with coordination number 26, chain length 16, $E_p/E_c = 1$, and different $B/E_c$ values as indicated. The solid lines are calculated from Eq. (2) and $Z = 1$, and sequentially correspond to the data points of simulation results. The error bar is less than the size of data points.
The melting point of chain polymers

The partition function of the disordered mixture system \( n = n_1 + n_2 + n_v \) with polymer B \( (n_1 \text{ chains with the length } r) \), polymer A \( (n_2 \text{ chains with the length } r) \), and the voids \( (n_v) \) will become

\[
Z_B = \left( \frac{n}{n_v} \right)^{n_0} \left( \frac{n}{n_1} \right)^{n_1} \left( \frac{n}{n_2} \right)^{n_2} \times 
\left( \frac{q}{2} \right)^{n_1 + n_2} e^{(1-r)(n_1 + n_2)} z_c^{(r-1)n_2} z_p^{(r-2)n_2}.
\]

in which \( Z_i = \exp(-m_i/ln\times q_{eff}Bk/T) \) and \( Z_p, Z_c \) are the same as in Eq. (2). After the crystallization of polymer A, the final liquid phase is a disordered mixture of polymer B with the voids, and the partition function of final state is

\[
Z_{ca} = \left( \frac{rn_1 + n_v}{n_v} \right)^{n_0} \left( \frac{rn_1 + n_v}{n_1} \right)^{n_1} \left( \frac{q}{2} \right)^{n_1} e^{(1-r)n_1}.
\]

So the equilibrium melting point can be calculated from \( Z_B = Z_{ca} \) with \( q_{eff} = 17.54 \) (see Sec. V D). The results are shown in Fig. 8 for a comparison with Eq. (10).

In Fig. 8, the results of simulations and calculations show good agreement and a linear relationship for the case of \( B/E_c = -0.2 \). Similar to the diluent effect of small molecules, these agreements are not unexpected since both Eqs. (9) and (10) were derived from the classical lattice statistics of the mixing behavior (the well-known Flory–Huggins theory). But an apparent deviation between the simulation and the calculation occurs for the case of \( B/E_c = 0 \). This deviation is unexpected and needs further study. Under this athermal mixing condition, Eq. (10) does not predict any change of melting point with the concentrations. This change is caused by the contribution of the compact packing. Nevertheless, for actual polymer blend, the independence of the melting point with the concentration may still be feasible due to the small contribution of the packing energy and the uncertainty in the conventional measurement of the melting point.

VI. SUMMARY

The lattice model can be employed to elucidate a disorder–order phase transition of a mixture containing polymers, because this kind of structural transformation is not only a local departure from the fully ordered arrangement of atom positions, but also a huge change in the chain isomerization, as in the so-called “anticrystalline” case. With the view of statistical thermodynamics, large-scale transformation is driven by local interactions. The similarity in the molecular driving forces of polymer crystallization with the mesophase formation of the anisotropic-shaped molecules sheds light on the dependence of the melting point upon the details of molecular structure and the impure environment of crystallites. Calculation of the classical lattice statistics accompanying verifications of Monte Carlo simulations and our experience continues to be a powerful tool for studying polymer systems. Three locally molecular parameters of polymers, i.e., chain extending energy change, compact packing energy change (appears orientation dependent), and unmixing energy change, were found to control disorder–order phase transition as well as phase separation of the mult...
ticomponent systems containing polymers. New insights about the details of these behaviors and their competition are expected in further simulation research.

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39. See Ref. 7, p. 25.