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Interphases and Mesophases in Polymer Crystallization III

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Interphases and Mesophases in Polymer Crystallization III

Volume Editor: Giuseppe Allegra

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Preface

In polymer crystallization the challenge is to identify and clarify the transformations by which chain molecules pass from a disordered, molten state to the ordered supra-molecular organization known as the semi-crystalline state. The subject is highly relevant in terms of both basic science and technology; it is indeed clear that many modern applications require complete control of the structure and the morphology of polymers from macroscopic dimensions down to below the nanoscale. As a simple example, making the crystallites in a polymer fiber equally oriented and reducing the number of chain folds (or hairpins) therein, usually turn out to be very favorable requisites for mechanical performance.

Is the onset of polymer crystallization, at least in some instances, preceded or accompanied by partial ordering of the system, possibly with influence on the kinetics and the equilibrium at both the molecular and the supra-molecular level? We may look at this issue, addressed in the present collection of contributions to *Advances in Polymer Science*, from very different sides. Modern microscopic techniques enable us to explore localized morphological aspects down to the observation of individual molecules, whereas X-ray, neutron and electron scattering provide molecular structure information down to the atomistic level. Experimental techniques allow us to explore kinetic aspects and are paralleled nowadays by fast-expanding molecular simulation approaches, increasingly able to give clues to the many open problems relating to structure development and morphology. Besides, the statistical-mechanical viewpoint may help to make sense out of the many experimental results and related simulations.

While in volumes 180 and 181 of this series several basic aspects of morphology, inter-phase structure and disorder were addressed, in the present volume, molecular interactions, modeling, phase transformation and crystallization kinetics are considered (see the subject index including keywords from volumes 180 and 181 at the end of the book). Needless to say, in spite of substantial success over 60 years or more we are still far from having a complete and unambiguous picture of polymer crystallization. We firmly believe that a fruitful approach to such a complex problem requires one to give way to many different and sometimes conflicting viewpoints, as we have attempted to do in these volumes. We do hope that they are not only a time-capsule left for

future scientists, but that they also contain the seeds of a coherent view that will eventually develop.

I would like to renew my gratitude to Valdo Meille for his very creative, intelligent and active co-operation.

Milan, October 2005 *Giuseppe Allegra*

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Polymer Crystallization Driven by Anisotropic Interactions

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Abstract In this review, we consider a variety of aspects of polymer crystallization using a very simple lattice model. This model has three ingredients that give it the necessary flexibility to account for many features of polymer crystallization that have been observed experimentally. These ingredients are (1) a difference in attraction between neighboring (nonbonded) components, (2) attraction between parallel bonds, and (3) temperature-dependent flexibility due to the energy cost associated with kinks in the

polymer chain. We consider this model using both dynamic Monte Carlo simulations and a simple mean-field theory. In particular, we focus on the interplay of polymer crystallization and liquid–liquid demixing in polymer solutions. In addition, we study the factors that are responsible for the characteristic crystal morphologies observed in a variety of homopolymer and statistical-copolymer crystals. Finally, we consider how the freezing of polymers in the bulk can be related to the crystallization of a single polymer chain.

Keywords Crystallization · Lattice statistics · Melting · Monte Carlo simulations · Phase diagram

1 Introduction

The building blocks of liquid-crystalline polymers are anisometric, and many of them form liquid-crystalline mesophases, even in monomeric form. Monomers that have this property are called mesogens. The molecular driving force to form a nematic phase can be due to anisotropic steric repulsions between the anisometric hard cores of the mesogens. This mechanism was proposed by Onsager [1]. It provides a successful description of many lyotropic disorder–order phase transitions. Alternatively, nematic ordering can be induced by the anisotropy of the polarizability of the mesogens, making the parallel orientation of mesogens energetically favorable. This mechanism for the isotropic–nematic transition was proposed by Maier and Saupe [2, 3]. It provides a useful description of thermotropic disorder–order phase transitions. In many cases of practical interest, both interactions play a role and should be taken into account in a description of the isotropic–nematic transition [4–11].

The building blocks of nonmesogenic polymers are also nonspherical; however, their degree of nonsphericity may be insufficient to induce nematic ordering. As already pointed out by Flory [12], the rigidity of a polymer chain – and thereby the anisometry of the Kuhn segments—tends to increase with decreasing temperature. Flory argued (on basis of the Onsager model) that, at sufficiently low temperatures, the anisometry of the Kuhn segments becomes so large that the isotropic (disordered) state is no longer stable and spontaneous ordering—in this case crystallization—must occur [12]. Note that this freezing mechanism is rather different from the one considered in simple liquids: there it is assumed that freezing occurs simply because the molecules can pack more densely in the solid state than in the liquid. The density change on freezing of simple liquids is typically much less than that observed in the orientational ordering of hard rods. Moreover, most lattice models cannot be used to describe a freezing transition driven by packing alone. However, this does not imply that a lattice model cannot properly describe polymer crystallization other than as an isotropic–nematic transition driven by anisotropic excluded-volume effects. In fact, it is possible to describe polymer freezing by taking into account the enhanced attraction between bonds with parallel orientation.

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A lattice model that takes such attractions between parallel bonds into account provides a reasonable prediction of polymer melting points [13] and of their interplay with liquid–liquid demixing in polymer solutions [14]. The same factors that favor freezing do affect to a greater or lesser extent the formation of mesophases; hence, there is a close relation between polymer crystallization and the formation of mesophases, which are frequently observed before polymer crystallization (see other papers in this issue).

In this review, we focus on the effect of anisotropic interactions, in particular parallel attractions, and demonstrate that the inclusion of such interactions in a model leads to a great richness in possible polymer phase behavior. From a practical point of view, the model that we describe has the advantage that it is computationally very cheap—although this advantage comes at the price of sacrificing the greater realism of an off-lattice model.

In what follows, we use simple mean-field theories to predict polymer phase diagrams and then use numerical simulations to study the kinetics of polymer crystallization behaviors and the morphologies of the resulting polymer crystals. More specifically, in the molecular driving forces for the crystallization of statistical copolymers, the distinction of comonomer sequences from monomer sequences can be represented by the absence (presence) of parallel attractions. We also devote considerable attention to the study of the free-energy landscape of single-chain homopolymer crystallites. For readers interested in the computational techniques that we used, we provide a detailed description in the "Appendix."

2
Lattice Model for Polymer Crystallization

2.1
Flory's Treatment for Semiflexible Polymers

The structure of a simple mixture is dominated by the repulsive forces between the molecules [15]. Any model of a liquid mixture and, *a fortiori* of a polymer solution, should therefore take proper account of the configurational entropy of the mixture [16–18]. In the standard lattice model of a polymer solution, it is assumed that polymers "live" on a regular lattice of n sites with coordination number q. If there are n_2 polymer chains, each occupying r consecutive sites, then the remaining n_1 single sites are occupied by the solvent. The total volume of the incompressible solution is $n = n_1 + rn_2$. In the case $r = 1$, the combinatorial contribution of two kinds of molecules to the partition function is

$$Z_{\text{comb}} = \frac{n!}{n_1!n_2!} \approx \left(\frac{n}{n_1}\right)^{n_1} \left(\frac{n}{n_2}\right)^{n_2}. \tag{1}$$

This expression accounts for the configurational entropy of an ideal binary mixture with identical molecular sizes, but not for that of a polymer solution, since polymer chains are large and flexible. For that case, more contributions arise from the chain conformational entropy, first considered by Meyer [19] and then derived by Huggins [20] and Flory [21]. In analogy with a nonreversing random walk on a lattice, the conformational contribution of polymer chains to the partition function is given by

$$Z_{\text{conf}} = \frac{\left(\frac{q}{2}\right)^{n_2} z_c^{(r-2)n_2}}{a^{(r-1)n_2}}, \tag{2}$$

where the first factor 1/2 is the symmetry factor of chain ends. This factor accounts for the fact that the calculation can start from either of two chain ends. In Eq. 2, q is the number of possible ways to put the second chain unit along the chain, z_c $(= q - 1)$ is the number of possible ways to place each subsequent chain unit of the rest, and a is a correction term for each step of random walk due to the presence of other chains. Flory showed that if one assumes random mixing (i.e., ignores all local structural correlations), $a = e$. Huggins used a somewhat more sophisticated procedure to estimate the probability of finding two consecutive vacant sites and obtained the estimate $a = (1 - 2/q)^{-(q/2-1)}$ [22]. To account for semiflexibility, Flory introduced a potential energy penalty E_c for every "kink" in the lattice polymer. The presence of this kink energy changes z_c, the intramolecular part of the partition function, to $z_c = 1 + (q - 2)\exp[-E_c/(k_B T)]$, where k_B is Boltzmann's constant and T the temperature [12]. For the fully disordered state at very high temperatures, the so-called "disorder parameter" d, defined as the mean fraction of consecutive bonds that are not collinear, should be

$$d = \frac{(q-2)\exp\left(-\frac{E_c}{k_B T}\right)}{1 + (q-2)\exp\left(-\frac{E_c}{k_B T}\right)}. \tag{3}$$

As the temperature is decreased, the chains become increasingly rigid: z_c then approaches 1 if we assume that there is only one fully ordered crystalline structure and Z_{conf} for the liquid becomes smaller than 1. This means that, at this level of approximation, the disordered state becomes less favorable than the crystalline ground state. A first-order disorder–order phase transition is expected to occur under these conditions. Flory interpreted this phase transition as the spontaneous crystallization of bulk semiflexible polymers [12]. However, since the intermolecular anisotropic repulsion essential in the Onsager model is not considered in the calculation, only the short-range intramolecular interaction is responsible for this phase transition.

The calculation of Z_{conf} makes use of the random mixing approximation for the fully disordered state. Several authors [23–27] have reported improved estimates of Z_{conf} that take into account the effect of local ordering at low temperatures; however, the resulting improvement in the prediction of the

melting point is not very large [22]. Another approach in the calculation of configurational entropy of semiflexible lattice chains was suggested by DiMarzio [28] and was expanded by Ronca [29], and this has been found useful in the study of orientational relaxation of stretched polymer liquids [30–32].

A number of Monte Carlo simulations have verified the spontaneous disorder–order phase transition of semiflexible polymers in 3D lattice models [33–36]. In molecular dynamics simulations, even the metastable chain-folding in the supercooled melt has been observed [37]. However, the ordering transition studied in these simulations was the one from the isotropic to the nematic phase, rather than the actual crystallization transition [38]. At high densities, cooling results in the formation of a glassy disordered state rather than a crystal [39].

2.2 Implications of Parallel Attractions in Polymer Systems

In Monte Carlo simulations, it has been found that introducing a parallel attraction between the polymer bonds, in addition to the bending-energy penalty, could significantly enhance the first-order nature of the isotropic–nematic phase transition at high concentrations [40, 41]. In fact, the inclusion of attraction between parallel bonds has been found to be useful in many studies of nonmesogenic polymers. Such attractions between parallel bonds can mimic the short-ranged orientational order in polyethylene melts that was observed in molecular dynamics simulations [42], in agreement with experimental observations on *n*-alkane liquids [43]. The anisotropic interactions have been considered in the study of orientational relaxation of stretched polymer melts [30–32] and of local order in polymer networks [44, 45].

An early study on the role of parallel attraction in polymer crystallization was made by Bleha [46], who considered the enthalpic effect of parallel packing on the melting point of polymers. In addition, Mansfield [47] took parallel interactions into account in his Monte Carlo calculation of the chain-folding probability at the interphase zone between lamellar crystals and amorphous liquid. Monte Carlo simulations by Yoon [48] showed that parallel attraction can lead to the formation of ordered domains and a density-functional theory study of melt crystallization by McCoy et al. [49] revealed the existence of an effective "chain straightening force" originating from attractive potentials [50]. In Monte Carlo simulations of AB-copolymer crystallization, parallel attractions were used to distinguish the crystallizable sequences from the noncrystallizable sequences [50–52]. Parallel attractions were also applied in the Monte Carlo study of polymer crystallization from dilute solutions on 2D [53] and 3D lattices [54], as well as from the homopolymer melt in 2D [55] and 3D [56] lattices. In earlier work, we showed that the incorporation of attraction between adjacent, unconnected bonds allows us to reproduce the sectorization of chain-folding in a single lamellar crystal-

lite [57] and the shish-kebab morphology of polymer crystallites induced by a single pre-aligned chain [58]. More details of some simulation results are discussed in Sects. 3 and 4.

2.3 Mean-Field Treatment of Parallel Attractions

We now consider a lattice model for a polymer solution that has both isotropic and anisotropic interactions. A mean-field expression for the free energy of the system can be obtained by approximating the local concentration of polymer chain units by its average value. We consider a solution of polymers consisting of r units on a cubic lattice. The volume fraction occupied by the polymers is denoted by ϕ. Two energetic interaction parameters play a role. One is the "mixing energy" B. It is a measure for the energetic cost (relative to the unmixed situation) for having a solvent particle and a polymer chain unit on adjacent lattice sites: $B = E_{us} - (E_{ss} + E_{uu})/2$, where E_{ab} represents pair interactions of the chain units (u) and the solvent particle (s). The second interaction energy E_p denotes the energy cost to break up a pair of adjacent, parallel polymer bonds. The mixing interactions act between sites and are isotropic, while the parallel attractions act between bonds and are anisotropic.

In the fully disordered state, the probability to find a bond at a given bond site is simply given by the ratio of the total number of bonds $[n_2(r-1)]$ to the total number of bond positions $(nq/2)$. The probability that a given bond has a specific parallel neighbor is therefore given by $2n_2(r-1)/(nq)$. Every bond has $q-2$ neighbors, since two consecutive neighbors along the chain should be subtracted from the coordination number. Unless a neighboring site is occupied by a parallel bond, its energy cost equals E_p. The average potential energy cost due to nonparallel packing is therefore $\ln(z_p) = -1/2(q-2)[1-2n_2(r-1)/(nq)]E_p/(k_BT)$, where the factor $1/2$ eliminates double counting of pair interactions. At the mean-field level, the potential energy due to nonparallel packing reduces the partition function by a factor of $z_p^{n_2(r-1)}$. Similarly, most chain units can have $q-2$ neighbors occupied by solvent. The probability of finding a solvent molecule on a specific neighboring site is n_1/n. It then follows that the total mixing potential energy per chain unit is $\ln(z_m) = -(q-2)n_1B/(nk_BT)$. The corresponding contribution to the partition function is $z_m^{n_2r}$.

Combining all contributions to the partition function of the disordered state of a lattice polymer solution, we obtain

$$
\begin{aligned}
Z &= Z_{\text{comb}} Z_{\text{conf}} z_p^{n_2(r-1)} z_m^{n_2 r} \qquad (4)\\
&= \left(\frac{n}{n_1}\right)^{n_1} \left(\frac{n}{n_2}\right)^{n_2} \left(\frac{q}{2}\right)^{n_2} z_c^{n_2(r-2)} e^{-n_2(r-1)} z_p^{n_2(r-1)} z_m^{n_2 r},
\end{aligned}
$$

where $z_c = 1 + (q-2)\exp\left(-\frac{E_c}{k_B T}\right)$, $z_p = \exp\left\{-\frac{q-2}{2}\left[1 - \frac{2n_2(r-1)}{qn}\right]\frac{E_p}{k_B T}\right\}$, and $z_m = \exp\left[-\frac{(q-2)n_1}{n}\frac{B}{k_B T}\right]$.

The mean-field expression for the free-energy density of the polymer solution is therefore [13, 14]

$$f(\phi) = (1-\phi)\ln(1-\phi) + \frac{\phi}{r}\ln\phi - \phi\ln\left(\frac{qr}{2}\right) - \phi\left[-\left(1-\frac{2}{r}\right)\ln z_c + 1 - \frac{1}{r} + (q-2)B + \frac{q-2}{2}\left(1-\frac{1}{r}\right)E_p\right] - \phi^2\left[(q-2)B + \frac{q-2}{q}\left(1-\frac{1}{r}\right)^2 E_p\right]. \quad (5)$$

In the perfectly ordered crystalline ground state, all polymer bonds are parallel and no solvent–polymer contacts are present. If we ignore disorder (vacancies, kinks) in the polymer crystal at finite temperatures, the free-energy density of the crystalline state is zero.

2.4 Predictions of the Polymer Melting Point

Inspection of the mean-field free-energy density given in the previous paragraph allows us to see the relationship between the (microscopic) molecular parameters of the lattice-polymer model and its (macroscopic) phase diagram. Let us first focus on the equilibrium melting point, i.e., the temperature at which the crystalline phase and the isotropic liquid phase are in thermodynamic equilibrium. We first consider the effect of the energy parameters in the model and of the polymer chain length on the melting point of bulk homopolymers. Polymer solutions and mixtures will be discussed in the next section.

At coexistence, the chemical potentials of given species must be equal. In a plot of $f(\phi)$ versus the polymer concentration ϕ, this equality leads to the familiar common-tangent condition: at coexistence, the tangents to the free-energy densities of the solid and liquid phases must coincide. In the lattice model that we use, the partition function for the fully ordered ground state is given by $Z = 1$ and hence its free-energy density is zero. At finite temperatures, the presence of defects will change the free-energy density of the solid. We ignore this effect. In addition, the lattice model ignores the effect of the vibrational degrees of freedom of the polymers.

In a pure homopolymer system, the free-energy density only depends on E_c (the quantity that determines the chain rigidity) and E_p (the quantity that determines the tendency of backbone chains to form parallel, close-packed structures). Let us first consider the relative stability of the pure polymer melt and the polymer solid in the limit of infinitely long chains. In that case, we

find that the free energies of the liquid and solid are equal when

$$1 + (q-2)\exp\left(-\frac{E_c}{k_B T_m}\right) = \exp\left[1 + \frac{(q-2)^2}{2q}\frac{E_p}{k_B T_m}\right]. \quad (6)$$

If $E_c < k_B T$ at melting, we can ignore the first term on the left-hand side and we obtain

$$T_m = \frac{E_c + \frac{(q-2)^2}{2q}E_p}{k_B[\ln(q-2) - 1]}. \quad (7)$$

Equation 7 shows that both an increase in chain rigidity and an increase in the interaction between parallel chains will lead to an increase in the melting point, in agreement with experiments [59–62]. For example, semirigid chains that contain aromatic groups in the chain backbone usually have high melting points. Similarly, aliphatic polyamides that have strong interchain interactions, due to hydrogen bonding, tend to have higher melting points than aliphatic polyesters. In addition, strong interchain interactions are only possible in the absence of steric obstructions. For example, polypropylene has smaller side branches than poly(1-butene) and, *a fortiori*, than poly(1-pentene). And indeed, polypropylene has a higher melting point (460.7 K) compared with poly(1-butene) (411.2 K) and poly(1-pentene) (403.2 K) [63]. Bunn [64] has observed a linear dependence of T_m on the cohesive energy density of the same series of homologues [64]. This observation is understandable because both E_c and E_p contribute to the cohesive energy density of solid polymers in a linear way, and in addition the compounds in the same homologous series should have similar E_c and E_p values.

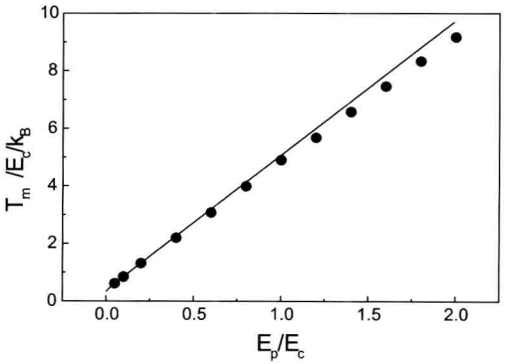

Fig. 1 Melting temperatures of polymers ($k_B T_m/E_c$) with variable E_p/E_c values. The *line* is calculated from Eq. 10 and the *circles* are the simulation results obtained from the onset of crystallization on the cooling curves of disorder parameters, in a short-chain ($r = 32$) system (occupation density is 0.9375 in a 32-sized cubic box) with a template substrate (Hu and Frenkel, unpublished results)

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