



## Understanding crystal nucleation in solution-segregated polymers

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### ARTICLE INFO

#### Article history:

Received 30 January 2009

Received in revised form

11 April 2009

Accepted 4 June 2009

Available online 10 June 2009

#### Keywords:

Solution

Phase diagram

Crystal nucleation

### ABSTRACT

We report dynamic Monte Carlo simulations of crystal nucleation in polymer bulk phase segregated from solutions. We found that poorer solvent enhances crystal nucleation in the concentrated phase of polymers. In addition, when the solvent becomes poor enough, crystal nucleation prefers to occur at the diffuse interfaces. The results are consistent with the predictions from theoretical phase diagrams, but something different from immiscible polymer blends. The surface-enhanced crystallization may explain the bowl-shaped crystal aggregates observed experimentally in poor solvent.

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### 1. Introduction

Liquid–liquid demixing and polymer crystallization are two basic phase transitions in multi-component polymer materials. Current investigations, however, often targeted one of these phase transitions and overlooked their interplay. As a matter of fact, the interplay of polymer phase transitions reveals the diversity of practical paths toward the multi-stage and hierarchical self-assembly of multi-component polymeric systems.

In polymer solutions, the first experimental measurement for phase diagrams exhibiting both liquid–liquid demixing and polymer crystallization was reported by Richards dating back to 1946 [1]. Flory made an introduction to this issue in his classic textbook [2]. In his recent book, Cheng made a summary on the experimental progress of this issue [3]. The interplay of phase transitions makes one major kind of thermoreversible sol–gel transitions in polymer solutions, as reviewed by Keller in 1995 [4]. In this case, polymer crystallization will freeze the evolution of the gel structure made by prior spinodal decomposition, so the interplay of these thermally induced processes dominates structure formation of microcellular foams as well as microporous membranes [5]. Recently, by means of dynamic Monte Carlo simulations of polymer solutions, we studied polymer crystal nucleation enhanced by prior metastable liquid–liquid demixing [6], as well as the morphologies of polymer crystallites modulated by prior spinodal decomposition [7]. Even in the extremely diluted polymer solutions like in a single

homopolymer chain, the intramolecular crystal nucleation can be greatly accelerated by the prior hydrophobic-like collapse transition, which sheds light on the fast pathway of protein folding [8].

In polymer blends, the experimental measurement of phase diagrams of polyolefin blends in which only one component appears crystallizable was reported by Wang et al. in 2002 [9]. Molecular theory and simulations have demonstrated that, liquid–liquid demixing can be driven solely by the component-selective crystallizability of polymers in polymer blends [10], and the demixing will be further enhanced by thermal fluctuations toward crystalline order in the vicinity of the melting point [11].

Recently, Zhang et al. observed that crystal nucleation in immiscible polymer blends can be enhanced by the decrease of annealing time at a slightly higher temperature for prior spinodal decomposition [12]. Such an observation could be attributed to the interface-enhanced crystal nucleation. Theoretical phase diagrams and molecular simulations have verified that those polymers diluted at diffuse interfaces of immiscible polymer blends contain higher melting points and thus stronger thermodynamic driving force for crystal nucleation [13]. Similar experimental observations also exist in polyethylene solutions, where Schaaf et al. have investigated the bowl-shaped abnormal crystal aggregates grown in poor solvent and have proposed the idea of interface-enhanced crystal nucleation [14]. Such an idea has not yet been verified by the theoretical and simulation studies of polymer solutions, and thus constitutes the main issue addressed in our present report.

In this report, we performed theoretical calculations of phase diagrams and dynamic Monte Carlo simulations of crystal nucleation in solution-segregated polymers. The results will show that poorer solvent enhances polymer crystal nucleation in the

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concentrated bulk phase; in addition, a preference of crystal nucleation occurs at the interfaces only when the solvent becomes poor enough. These results are in accord with the predictions of theoretical phase diagrams, but be something different from immiscible polymer blends. The differences can be explained by a comparison of theoretical phase diagrams between polymer solutions and polymer blends. Our observation may provide evidence to the interpretation of the bowl-shaped abnormal crystal aggregates observed in experiments.

The content of this paper is organized as follows. After **Introduction**, we make theoretical calculations of phase diagrams in polymer solutions, followed with a brief description of simulation techniques and a report of simulation results. The paper ends up with a summary of our conclusions.

## 2. Theoretical phase diagrams

Polymer solutions have been well understood since the lattice model of polymers was successfully applied to calculate the mixing entropy, in addition to the mean-field treatment of mixing interactions (represented as  $B$  for each mixing pair of monomer and solvent) [15]. The well-known Flory–Huggins theory has become a paradigm in the study of statistical thermodynamics of multi-component polymer systems such as polymer solutions [15], polymer blends [16], semiflexible polymer solutions [17], diblock copolymers [18], and polymer networks [19]. The mixing interactions will drive liquid–liquid demixing in polymer solutions. Recently, we employed local anisotropic interactions of polymers (represented as  $E_p$  for each pair of bonds packing parallel in the lattice model) as the molecular driving force for polymer crystallization [20]. Both phase diagrams for liquid–liquid demixing and polymer crystallization can thus be calculated by the developed mean-field lattice statistical theory [21]. This allows us to study the interplay between two kinds of phase transitions.

For homogeneous polymer solutions containing  $n_2$  polymer chains, each having  $r$  monomers, and being mixed with  $n_1$  solvent sites in a regular lattice (the total volume  $n = n_2 + n_1$ ), the partition function is thus given by [21]

$$Z = \binom{n}{n_1}^{n_1} \binom{n}{n_2}^{n_2} \left(\frac{q}{2}\right)^{n_2} e^{-(r-1)n_2 z_c^{(r-2)n_2} z_m^{n_2} z_p^{(r-1)n_2}}, \quad (1)$$

where

$$z_c \equiv 1 + (q-2) \exp\left(-\frac{E_c}{kT}\right),$$

$$z_m \equiv \exp\left[-(q-2) \cdot \frac{n_1}{n} \cdot \frac{B}{kT}\right],$$

$$z_p \equiv \exp\left\{-\frac{q-2}{2} \cdot \left[1 - \frac{2(r-1)n_2}{qn}\right] \cdot \frac{E_p}{kT}\right\};$$

$q$  is the coordination number of the lattice,  $E_c$  is the conformational energy for each collinear connection of two consecutive bonds along the backbone chain,  $E_p$  is the parallel-packing interaction for two non-bound bonds,  $B$  is the net mixing interactions for each pair of monomer and solvent;  $k$  is the Boltzmann's constant and  $T$  the temperature. The mixing free energy change is thus obtained as

$$\frac{\Delta F_{\text{mix}}}{nkT} = \phi_1 \ln \phi_1 + \frac{\phi_2}{r} \ln \phi_2 + \phi_1 \phi_2 \left[ (q-2) \frac{B}{kT} + \left(1 - \frac{2}{q}\right) \left(1 - \frac{1}{r}\right)^2 \frac{E_p}{kT} \right], \quad (2)$$

where  $\phi_1$  and  $\phi_2$  are the volume fractions of solvent and polymers, respectively. According to the equivalence of chemical potentials (denoted as  $\mu$ ) between two coexisting phases (denoted by ' and ', respectively), as given by

$$\begin{cases} \mu'_1 = \mu''_1 \\ \mu'_2 = \mu''_2 \end{cases}, \quad (3)$$

the liquid–liquid binodal can be calculated. When we calculate each kind of phase diagrams in the homogeneous phase, we disregard another kind of phase transitions potentially coexisting in reality. This means that we disregard all the practical instability and metastability in the present theoretical calculation.

At the liquid–solid coexistence curves, there also exists the equivalence of chemical potentials between liquid and crystalline states, as given by

$$\mu^S - \mu^0 = \mu^L - \mu^0, \quad (4)$$

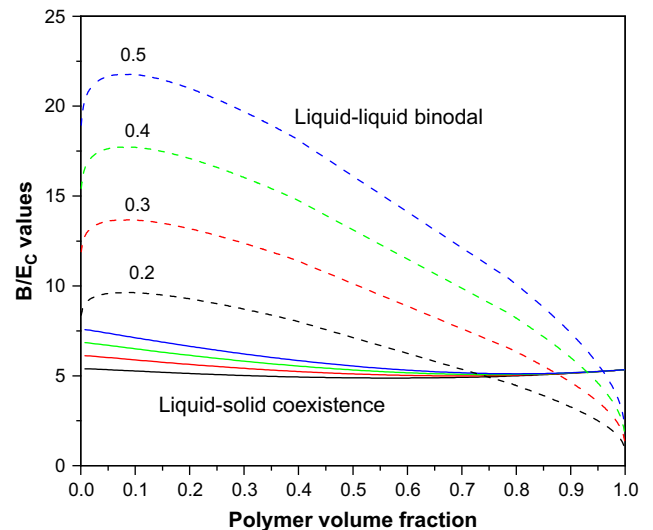
where  $\mu^0$  is the chemical potential of polymers at the fully ordered ground state. Since the free energy  $\Delta F$  of crystalline polymers is close to their ground state, we assume the approximation result

$$\mu^S - \mu^0 = \frac{\partial \Delta F^S}{\partial n_2} = \frac{\Delta F^S}{n_2} \approx 0. \quad (5)$$

The chemical potential of the liquid phase can be derived from the partition function shown in Eq. (1), so one can obtain the equilibrium melting point for variable solution compositions of polymers according to Eq. (4).

The results for equilibrium phase diagrams are shown in Fig. 1, with both the energy parameters and  $kT$  normalized by  $E_c$ . In practice, we preset  $E_p/E_c$  fixed at one to maintain the molecular driving force for crystallization under a good flexibility of chains,  $B/E_c$  variable to reflect the solvent quality, and  $kT/E_c$  specified for the reduced temperature. One can see that the larger the  $B/E_c$  values, the higher the liquid–liquid binodals, and hence the larger the intercepted polymer concentrations on the liquid–solid coexistence curves.

If we compared the liquid–solid phase diagrams of segregated polymer solutions with immiscible polymer blends demonstrated



**Fig. 1.** Phase diagrams of polymer solutions for 128-mers with variable  $B/E_c$  values as denoted and  $E_p/E_c = 1$ . The curves are calculated from the developed lattice statistical theory [21]. The dashed curves are for liquid–liquid binodal, and the solid curves are for liquid–solid coexistence in the same sequence of temperatures as denoted for the dashed curves.

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