Polymer 49 (2008) 2368–2372

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Nucleation induced by phase separation in the interface of polyolefin blend

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ARTICLE INFO

Article history:
Received 19 December 2007
Received in revised form 14 March 2008
Accepted 26 March 2008
Available online 28 March 2008

Keywords:
Crystallization
Spinodal decomposition
Interfacial evolution

ABSTRACT

The two-step quenching experiments, which were performed to investigate the interplay between phase separation and crystallization in polyolefin blend system (Zhang XH, Wang ZG, Muthukumar M, Han CC. Macromol Rapid Commun 2005 26:1285 and the following papers.), showed that almost all the nuclei appear in the interfacial regions of phase separation. The nucleation rates in the second step quenching decay with the time of phase separation with simple power law. These novel phenomena are attributed to that the interdiffusion in the spinodal decomposition process makes the polymer chains oriented in the interfacial regions. The orientation of polymer chains decreases the nucleation barriers of crystallization. A reasonable assumption is that the nucleation rate is proportional to the interfacial volume. In the early stage of phase separation, the interface thinning process is faster than the phases coarsening process, and hence the interfacial area is approximately kept the same; the nucleation rate is then proportional to the interfacial thickness. In present work, we explore the interfacial forming of spinodal decomposition in an asymmetric polymer blend through numerical integral of the Cahn–Hilliard equation with Flory–Huggins–de Gennes free energy functional. The numerical results demonstrate that the time-dependent evolutions of the nucleation rate satisfy the power law with the index of -0.47, which is well consistent with the experiments.

1. Introduction

Because the conformational entropy plays an important role in the polymer thermodynamics and kinetics, the crystallization of polymers becomes complicated. Practically, the polymer crystals are metastable and their morphologies depend on the thermodynamic history. Usually, many paths, such as isotropy–liquid crystal transition, order–order transition and vitrification, may take place simultaneously during the crystallization process and interplay with each other. Numbers of experiments have been performed in some special systems to investigate this interesting competitive process, for example, crystallization in confined systems, in the oriented field, in the blends and so on. These experiments provide the opportunities to understand the mechanism of polymer crystallization profoundly, because in these processes some probable kinetic paths are restrained, while others are enhanced.

For the crystallization in polymer blends, there are many additional kinetic and thermodynamic degrees of freedom. What happens in a particular system, among others, mainly depends on the miscibility of the blend components, i.e., whether they exhibit a miscibility gap or demix at all conditions. Jungnickel has reviewed the kinetic peculiarities of these systems in detail [1]. Recently more and more investigators concentrated on the interplay between phase separation and crystallization [2–4]. However, these works mostly referred to the traditional epitaxy and kinetic competition of two components. None of them was related to the conformational statistics of polymer chains. Unlike the crystallization of simple liquids, in polymer crystal the oriented chains are packed together and nearly lose all of their conformational entropy, which contributes to the nucleation barrier additionally [5]. One evidence of the crystallization of polymer blends involving the conformation-assistant nucleation was found in the system formed by poly(ethylene-*co*-hexene) (PEH)/poly(ethylene-*co*-butene) (PEB) blends [6–10] during a liquid–liquid phase separation (LLPS) process. Since PEH and PEB are quite similar, the Flory–Huggins parameter χ is very small but positive. There is a weak phase separation between PEH and PEB and their interface is relatively wide. Thus there will be plenty of phenomena attributed to the interface. In this system only the PEH can crystallize with melting point of 127 °C in the blend. The experiments of one-step quenching showed an overwhelming change in crystallization kinetics of PEH. The PEH chains in the blends are nucleated much faster than those in the neat PEH. In the two-step quenching experiments, the system firstly underwent a LLPS for different periods of time above the melting point of PEH, then the system was quenched below the melting point. In the phase separated systems,

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0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.03.039

the crystallizable positions were selected by the kinetics processes, nearly all of the nuclei appeared in the interfacial regions of phase separation (see Fig. 4 in Ref. [7]). A similar phenomenon has been observed in the PP/EPR blend system [11], however, the mechanism relating conformational entropy was not discussed clearly. Furthermore, the experiments [7,8] showed that the nucleation rate in the second step quenching decayed with the phase separation time in a simple power law $R(t) \sim t^{-\alpha}$ with $\alpha = 0.42$. These phenomena are attributed to that the interdiffusion in the spinodal decomposition process makes the chains oriented in the interfacial regions, and hence decreases the nucleation barrier.

In present work, to explain how the nucleation rate varies with the LLPS time, a reasonable assumption is put forward that the nucleation rate is proportional to the interfacial volume. This is because the nucleation is based on the orientation of polymer chains, and in the interfacial region the polymer chains are oriented. Actually, the experimental results show that almost all the nucleations occur on the interfacial region [7]. In the early stage of the phase separation, the interface thinning process is much faster than the phases coarsening process. Thus the interfacial area approximately keeps the same, and the nucleation rate is then proportional to the interfacial thickness. Based on this assumption, the time-dependent interface thinning down has been investigated theoretically with the Cahn–Hilliard (C–H) equation. A single planar interface model is chosen to describe the local properties of the interface regions. Our calculations focus on the specific system of the experiments [7–10]. The PEH and PEB mixtures are modeled as asymmetric binary blends by means of the mean field theory fitting of phase diagram from the light scattering experiments [12]. The interfacial profile evolution is investigated at the LLPS temperature (135 °C). In the following sections, we first briefly review the experiments and then give the calculation model. The theoretical results of interfacial thickness evolution are compared with the nucleation rate decay law from the experiments [8] in the third section.

2. Model and numerical method

In the two-step quenching experiments, at first PEH/PEB = 40/60 samples underwent the LLPS at 135 °C during different periods of time. According to the phase diagram of PEH/PEB blends shown in Fig. 1, from the Flory–Huggins theory, the blends are nearly critical compositions $\phi_c = 0.44$ and the LLPS temperature was in the region of spinodal [12]. During the whole time range of LLPS, the equilibrium state was not reached. With the help of LLPS, the system was divided into the PEH rich domains with composition of ϕ_α, PEB rich domains with composition of ϕ_β, and the interfacial regions with composition ϕ_i varying gradually from ϕ_α to ϕ_β, where ϕ_i is the volume fraction of PEH in different phases. When the blend stayed at 135 °C for enough time, the LLPS became more complete and the interface gradually became sharp. At the second step quenching temperature (117 °C), which is below the melting temperature of PEH (127 °C), spinodal decomposition can only take place in the interfacial regions, and the two bulk phases ϕ_α and ϕ_β are metastable. In these three kinds of regions, different kinetic processes were involved in the competitions between LLPS and crystallization.

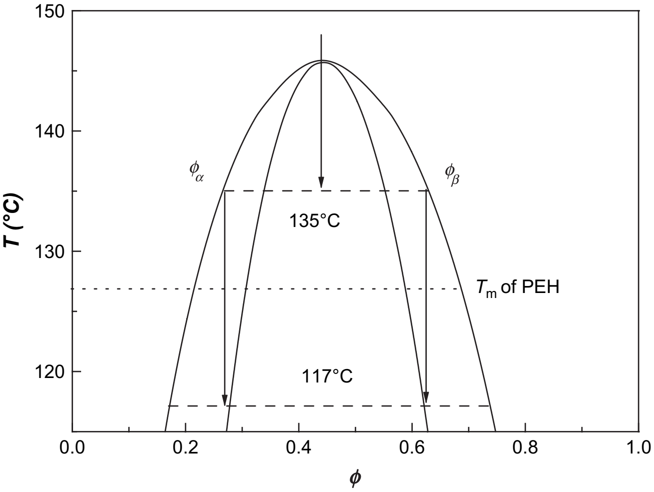

Fig. 1. Phase diagram of PEH and PEB blends calculated from Flory–Huggins theory. A two-step quench process with temperature at 135 °C and 117 °C is shown.

In the spinodal decomposition process, the interdiffusion of PEH chains and PEB chains takes place spontaneously, leading to an enhancement of the fluctuations both on density and orientation of polymer chains. In the dense polymeric system like the melts, the density fluctuations are coupled with the conformation of the chains [13,14]. Namely, in the interfacial regions of LLPS the chains are oriented by their interdiffusion. In the work of the kinetics of induction period of nucleation [14], the coupling of fluctuations both in the conformational order and density order has been considered in the free energy functional of the polymer melts. This work showed that the conformation-assistant fluctuation contribution to the nucleation barrier is coincided with the early stage nucleation. Based on this model, if the polymer chains are oriented, the barrier will be lowered and then the nucleation rate will be enhanced. The blend system is patterned with the help of the first step LLPS. The nucleation barrier of PEH in the interfacial regions is decreased with the orientation of polymer chains, while the barrier of the bulk phases is the same with the neat system. Therefore, the nucleation rate in the interface is much higher than that in the bulk phases and almost all of the nuclei appear in the interfacial regions.

With the LLPS time elongating the volumes of the interfacial regions shrink, and the orientation of the chains in these regions relax. Then the nucleation rate will decrease with chain orientation relaxing, namely, the regions where PEH chains can nucleate in the investigated time range decrease. It can be assumed that the nucleation rate is proportional to the interfacial volume. In the LLPS time range, the total interfacial area approximately does not change and the interfacial evolution is only attributed to the interfacial thickness thinning down, i.e., $V_{\text{int}}(t) = S \times l(t) \sim l(t)$, where V_{int} is the interfacial volume, S is the interfacial area and l is the interfacial thickness. Therefore, the evolution of thickness $l(t)$ will follow the same law with nucleation rate versus phase separation time. The experiments showed that nucleation rate depends on the phase separated time t with a simple power law $R(t) \sim t^{-\alpha}$ with $\alpha = 0.42$, which reminds us that the phase separation time-dependent interfacial thickness $l(t)$ may satisfy the same law of $l(t) \sim t^{-\alpha}$.

Now, the problem is to investigate the evolution of interface in the process of spinodal decomposition. Unfortunately, the direct experimental data of this topic are scarce. One effort was taken by Chan to study the dynamics of phase separations of a non-equilibrium single interface by laser scattering [15]. However, there is little information about the dynamics of interface formed in his experiments. We try to demonstrate the interfacial evolution theoretically by the C–H equation. We restrict our calculations on the local properties of the interfaces. In this view the effects of the interfacial curvature are omitted and a single planar interface is considered. Thus we can focus on the time evolution of the interface and the calculation is one-dimensional.

In the modeling of the blends, PEH and PEB are labeled as polymers A and B. The polymerization degrees are N_A and N_B, respectively. The segment lengths are the same as b. The volume fraction of polymer A is $\phi(x)$. According to the incompressible condition implicated by Flory–Huggins theory, the local volume fraction of polymer B is $1 - \phi(x)$. The excess free energy of the mixture can be written in the Flory–Hugggins–de Gennes form, in which the structure of the interface between the coexisting phases is well described: two semi-infinite polymer phases ϕ_α and ϕ_β separated by a planar interface (at $x = 0$) and the composition $\phi(x)$ across this interface. The relevant functional ΔF for the free energy of mixing per site volume V (taken as equal to the average segmental volume V of both blend components) and the area S of the interface is given by

$$\frac{\Delta F}{S k_B T} = \int \mathrm{d}x \left\{ f[\phi(x)] - \Delta\mu\phi(x) + \kappa[\phi(x)] |\nabla\phi(x)|^2 \right\}. \tag{1}$$

The Flory–Huggins mixing free energy $f[\phi(x)]$ describing the bulk phase is given by

$$\begin{aligned} f[\phi(x)] = {} & \left\{ \frac{1}{N_A}\phi(x)\ln\phi(x) + \frac{1}{N_B}[1-\phi(x)]\ln[1-\phi(x)] \right\} \\ & + \chi\phi(x)[1-\phi(x)], \end{aligned} \tag{2}$$

where $\kappa[\phi] = b^2/[36\phi(1-\phi)]$ characterizes the non-local properties and $\Delta\mu$ is the difference of the two bulk phases chemical potential

$$\Delta\mu = \mu_{\mathrm{PEH}} - \mu_{\mathrm{PEB}} = \left.\frac{\delta\Delta F}{\delta\phi}\right|_{\mathrm{bulk}}. \tag{3}$$

By Euler–Lagrange equation applied to the functional ΔF, we obtain the equilibrium solution

$$\phi(x) = \frac{1}{2}\left[(\phi_\alpha + \phi_\beta) + (\phi_\alpha - \phi_\beta)\tanh\left(\frac{x}{l_e}\right) \right], \tag{4}$$

where the characteristic width of the tanh-profile l_e is defined as the interfacial width. In fact the mean field theory [16,17] shows that the interfacial width is in the order of fluctuation correlation length in coexistence phase ($l_e = 2\xi$) with the form of

$$l_e = \frac{\sqrt{2}b}{3}\left(\frac{1}{\chi - \chi_c}\right)^{1/2}, \tag{5}$$

where $\chi_c = (1/\sqrt{N_A} + 1/\sqrt{N_B})^2/2$.

The time dependence of interfacial profile during LLPS is studied with C–H equation, which characterizes the local conservation of order parameter,

$$\frac{\partial\phi(x,t)}{\partial t} = -\nabla\cdot\mathbf{J}(x) + \eta(x,t). \tag{6}$$

Here, $\phi(x,t)$ is the volume fraction of polymer A at position x and time t, and $\mathbf{J}(x)$ is the local current of polymer A. Usually, it is postulated that the local current varies linearly with local chemical potential difference $\mathbf{J}(x) = -M\nabla\mu(x)$, where M is the mobility. The local chemical potential is given by the functional derivative of the excess free energy functional ΔF,

$$\mu(x) = \frac{\delta\Delta F[\phi(x)]}{\delta\phi(x)}, \tag{7}$$

and the thermal noise η satisfies the fluctuation–dissipation theorem

$$\langle \eta(x,t)\eta(x',t') \rangle = -2k_B T M \nabla^2[\delta(x-x')\delta(t-t')]. \tag{8}$$

Hence, the equation of the composition profile $\phi(x)$ can be written as

$$\begin{aligned} \frac{\partial\phi}{\partial t} = {} & M k_B T \nabla^2 \left[\frac{1}{N_A}\ln\phi + \frac{1}{N_B}\ln(1-\phi) - 2\chi\phi \right. \\ & \left. + \frac{(1-2\phi)b^2}{36\phi^2(1-2\phi)^2}(\nabla\phi)^2 - \frac{b^2}{18\phi(1-\phi)}\nabla^2\phi \right] + \eta. \end{aligned} \tag{9}$$

This equation is a nonlinear stochastic partial differential equation. In our calculations, the noise term is ignored, then Eq. (9) converts to a fourth order nonlinear parabolic equation for ϕ. Usually it can be solved with the finite difference scheme [18–20] and the cell dynamical scheme (CDS) [21–23]. Here we adopted the former method. The evolution of the interface starting from the initial profile is described by applying a second-order accurate Crank–Nicolson method to update at every time step. As demonstrated in Fig. 2, the interfacial thickness $l(t)$ can be determined from the interfacial profile. It corresponds to the projection of interfacial tangent with maximal slope on the normal of interface, i.e.,

$$l(t) = \frac{\phi_\alpha - \phi_\beta}{2}\left|\frac{\partial}{\partial x}\phi(t)\right|_{\max}^{-1}. \tag{10}$$

To compare with the experiments [7–10], a mean field theory fitting of the phase diagram of experiments is performed to determine the phenomenological parameter. Firstly we calculated the number-average degree of polymerization of the PEH and PEB used in the experiments: $\overline{N}_A = 1980$ as well as $\overline{N}_B = 1250$. To ensure the chains satisfied the Gaussian model we re-scale them with $N_i = 0.4\overline{N}_i$, i.e., the degree of polymerization in our coarse grain model is $N_A = 792$ and $N_B = 500$, respectively. Consequently, the coexistence curve ϕ vs χ can be determined with

$$\left.\frac{\partial f(\phi)}{\partial\phi}\right|_{\phi_\alpha} = \left.\frac{\partial f(\phi)}{\partial\phi}\right|_{\phi_\beta}, \tag{11}$$

where the $f(\phi)$ is the Flory–Huggins mixing free energy for the bulk system. Comparing with the experimental binodal curve ϕ vs T, a relation between χ and T can be concluded. The linear fitting of this relation shows that the Flory–Huggins interaction parameter χ is $\chi = -A + B/T$ with $A = 0.0033$, $B = 2.7431$.

An unstable interfacial profile, of which the width is four times of that of the equilibrium state, is imputed as an initial condition of Eq. (9). The initial profile has the same shape with the equilibrium profile of Eq. (4). The parameters in Eq. (4) are determined at the LLPS temperature $T = 135$ °C with $\phi_\alpha = 0.2445$, $\phi_\beta = 0.6537$. For the simplicity, we choose the non-flux boundary condition $\mathbf{J}|_b = \nabla\mu|_b = 0$, i.e., $\nabla\phi|_b = \nabla^3\phi|_b = 0$. A more reasonable boundary condition to the numerical integrate of the equation is the chemical equilibrium between the interphase and coexistence phase $\mu|_b = 0$. Practically, if a large enough system were considered in the calculation, the non-flux boundary condition would always be feasible.

We re-scale the system length with equilibrium interfacial thickness l_e, i.e.,

$$x = \frac{x'}{l_e} = x'\frac{3}{\sqrt{2}b}\sqrt{(\chi - \chi_c)}, \tag{12}$$

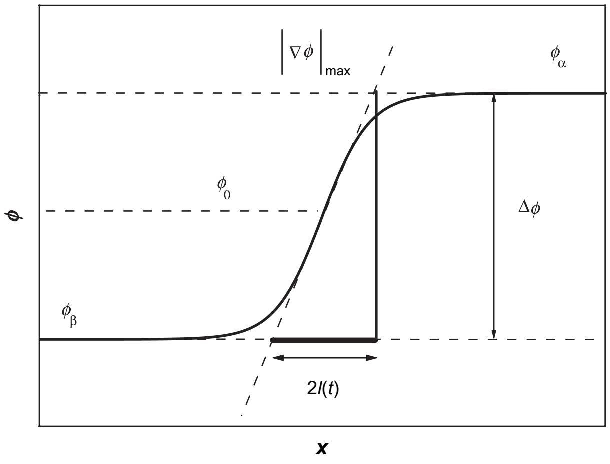

Fig. 2. Interfacial profile and quantitative measure for the interfacial evolution.

and re-scale the time by time unit τ

$$t = \frac{t'}{\tau} = t'\frac{9Mk_{\mathrm{B}}T(\chi - \chi_{\mathrm{c}})}{2b^2}. \tag{13}$$

The unit of time $\tau = 2b^2/9Mk_{\mathrm{B}}T(\chi - \chi_{\mathrm{c}})$, is the time in which the fluctuation diffuses through a length of equilibrium interfacial thickness, l_{e}, in the polymers A and B mixture.

3. Results and discussion

Fig. 3 shows the time-dependent interfacial profile of the PEH–PEB blends. An initial interface, which is much more diffused than the equilibrium one, is quenched to 135 °C. The interfacial regions are unstable, and the PEH and PEB chains, respectively, in these regions interdiffuse into the PEH and PEB rich domains automatically. The coexistent phase domains grow and the interfacial regions sharpen gradually. Finally the interfacial profile crosses over to the equilibrium one. In this process, the interdiffusion of polymer chains makes the profile asymmetry, but does not change the interfacial position. In the asymmetry polymer blend systems, some authors reported the interdiffusion of polymer chains making the interfaces move [24,25]. Actually in the frame of Flory–Huggins–de Gennes model and C–H equation theoretical system, a single planar interface cannot move only with the help of interdiffusion of chains. Only the interfacial curvature and the mutual interactions of different interfaces can make interfaces move, and then the domains coarsening can be investigated. The movement of the single planar interface in the results of the C–H equation is attributed to the ignorance of the higher order contributions, such as $(\nabla\phi)^4$ and $(\nabla\phi)^2\nabla^2\phi$, etc.

To investigate the evolution of the interfacial profile, the interfacial thicknesses at selected time steps have been calculated with the Eq. (10). The results are showed in Fig. 4. To demonstrate the power law of the interfacial thickness dependent on the LLPS time, the data have been analyzed in the double-logarithmic plot. It can be found that the evolution process includes two steps: an initially rapidly sharpening process and a smooth ending process towards the equilibrium thickness. The data of initial stage were analyzed with linear fitting in the double-logarithmic plot. The integral of C–H equation shows the process of a single planar interface recover its equilibrium shape satisfies the scaling law $l(t) \sim t^{-\alpha}$ with $\alpha = 0.47$. According to the explanation mentioned above, the nucleation rate is proportional to the thickness of the interface. Consequently the LLPS time-dependent nucleation rate follows the same power law of the interfacial evolution. In present calculational model, nucleation rate of different samples depends on their kinetic history of the LLPS with $R(t) \sim t^{-0.47}$. This theoretical prediction coincides well with the experimental result $\alpha = 0.42$.

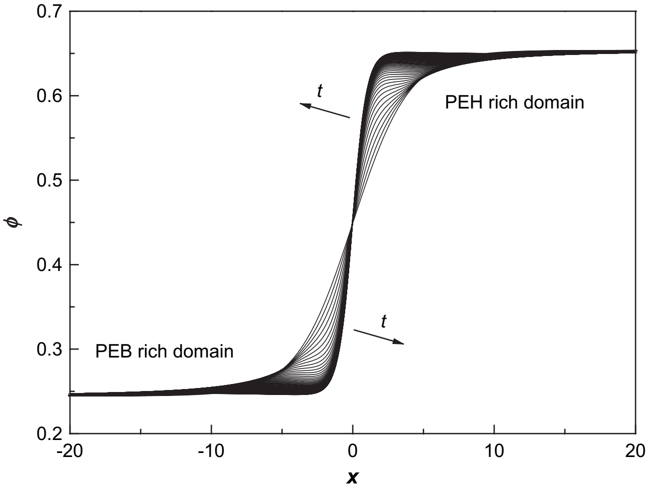

Fig. 3. Time evolution of the composition profiles for PEH–PEB blends at 135 °C.

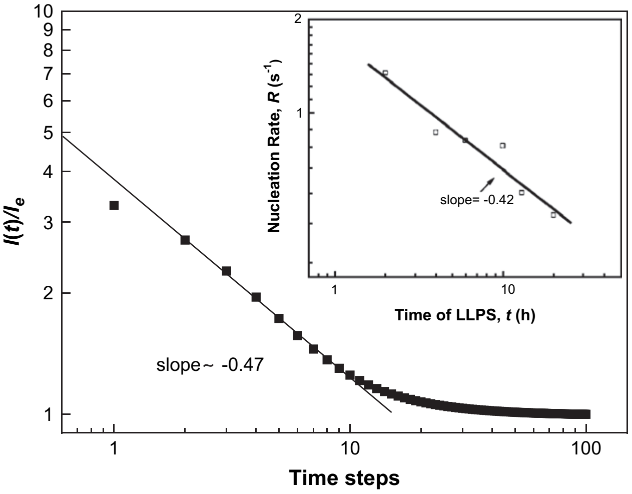

Fig. 4. Time evolution of the interfacial thickness for PEH–PEB blends at 135 °C. The inset plot is the experimental results of LLPS time-dependent nucleation rate.

In fact, the C–H equation and the Flory–Huggins–de Gennes model, which usually have been applied widely in the field of polymer blends, are phenomenological coarse grained theory. They are mainly used to demonstrate the diffusion of the order parameter in the mesoscopic scale. For the polymer LLPS problem, the order parameter is the volume fraction. The details of interdiffusion of polymer chains in the LLPS processes, such as the orientation and the stretch, are hardly understood in the frame of Flory–Huggins' excess free energy of mixing. For the crystallization problem, however, the local and microscopic properties are crucial. Therefore, the interplay between the LLPS and the crystallization is a typical two-scale stage involved problem. To understand these phenomena generally, a new effective method connecting volume fraction evolution and the microscopic conformation is necessary. However, the knowledge of the multi-scale dynamics of polymer is not known well at present. It is expected that the theory of the phase separation dynamics in the molecular scale may come into being in the future.

4. Conclusions

We have studied the phase separation of the PEH/PEB blend system and developed the conformation-assistant fluctuation explanations for the novel properties of nucleation rate varying with the LLPS time. The numerical results show that the interfacial evolution relation from theoretical calculations is consistent with the experimental evolution of nucleation rate well. From this theoretical investigation it can be concluded that the conformation-assistant fluctuation explanations for the nucleation in LLPS processes are reasonable even in a quantitative test.

Acknowledgments

The authors would like to acknowledge helpful discussions with Dr. Shuang Yang and Dr. Hongge Tan. This work is supported by the National Natural Science Foundation of China (NSFC) 20490220 and the foundation from Chinese Academy of Sciences KJCX2-YW-206.

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