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Dynamical Mean Field Calculation of Grafting Reaction of End-Functionalized Polymer

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ABSTRACT: Using a new numerical scheme of dynamical mean field theory, we investigate the kinetics of a grafting reaction of end-functionalized polymers onto a solid surface. We calculate the time evolution of the reaction rate and density profiles during the grafting reaction.

Introduction

Grafting reactions of end-functionalized polymers onto a surface is a complex process which involves chemical reaction and structural change of the reacted polymers. As the grafting reaction progresses, grafted polymers form a brush layer on the surface[1] and prevent the remaining free polymers in the solution from approaching the surface. Consequently a grafting reaction rate decreases gradually. The kinetics of such a process is important in various industrial processes such as reactive polymer blending, surface modification, etc.[2,3] Recently such a diffusion-controlled reaction at polymer interfaces has attracted considerable attention both theoretically and experimentally.[4−8] This is a new area since the earlier works[9,10] on the diffusion-controlled reaction of polymers are for homogeneous systems.

In this paper we study the process by a new numerical scheme which is a extension of that proposed in the previous paper.[11] In this scheme, the time evolution of the system is calculated by using the free energy functional which is obtained by the mean field theory at every time step. The scheme enables us to study various factors affecting the reaction kinetics, such as the polymer molecular weight, polymer concentration, chain architecture, copolymer ratio, etc. In this paper, however, to demonstrate the essence of the method, we report the result of the study of a simple case, i.e., the grafting reaction of end-functionalized linear polymers onto a bare surface. We study the effect of the intrinsic reaction rate on the overall reaction kinetics.

Formulation

We consider a semi-infinite space bounded by a surface at $z = 0$. The space is initially filled by solvent and unreacted free polymers which have a reactive segment at one of their ends. To simplify the analysis, we assume that all free polymers are equivalent. This is a drastic simplification of the real situation of the grafting reaction. In reality, there is a molecular weight distribution, and only a part of the free polymers have reactive segments at their ends. In this paper, we ignore these effects for the sake of simplicity and assume that all polymers have the same length N and have the reactive segments at their ends.

We assume that, at time $t = 0$, the surface starts to react with the reactive segments of the polymer. We divide each polymer into P consecutive subunits, each made of N_α segments ($\alpha = 1, ..., P$).

$$N = \sum_{\alpha=1}^{P} N_\alpha \tag{1}$$

N_α can be chosen arbitrarily depending on the problem. In this paper, we simply set N_α equal to each other, i.e., $N_\alpha = N/P$.

We then ask what is the time evolution of the concentration profiles of each species. Let $\phi_{f\alpha}(z,t)$ be the density of the polymer segments belonging to the αth subunit of the free polymer at point z and time t, where z denotes the distance from the surface. Let $\phi_{g\alpha}(z,t)$ and $\phi_s(z,t)$ be the segment density of the grafted polymer and the segment density of solvent molecules. The concentration profiles of the free polymers $\phi_f(z,t)$ and the grafted polymers $\phi_g(z,t)$ are sums of all $\phi_{f\alpha}(z,t)$ and all $\phi_{g\alpha}(z,t)$ respectively:

$$\phi_f(z,t) = \sum_{\alpha=1}^{P} \phi_{f\alpha}(z,t) \tag{2}$$

$$\phi_g(z,t) = \sum_{\alpha=1}^{P} \phi_{g\alpha}(z,t) \tag{3}$$

The bulk concentration of the free polymers is denoted by ϕ^b.

$$\lim_{z\to\phi} \phi_f(z,t) = \phi^b \tag{4}$$

Let $\sigma(t)$ be the fraction of the surface sites which have reacted with the polymer. Since the reaction rate is proportional to the reactive-segment density at the surface and the number of unreacted surface sites, $\sigma(t)$ satisfies the following kinetic equation:

$$\frac{d\sigma}{dt} = k(1 - \sigma)\phi_f^r(0,t) \tag{5}$$

where k is the intrinsic reactive rate coefficient and $\phi_f^r(z,t)$ is the concentration of the reactive segments at position z and time t.

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We impose the incompressible condition

$$\phi_f(z,t) + \phi_g(z,t) + \phi_s(z,t) = \sum_{\alpha=1}^{P} (\phi_{f\alpha}(z,t) + \phi_{g\alpha}(z,t)) + \phi_s(z,t) = 1 \quad (6)$$

Therefore the concentration profile is described by the $2P$ independent density fields $\Phi_{f\alpha}$ and $\Phi_{g\alpha}$ defined by

$$\Phi_{f\alpha}(z,t) = \phi_{f\alpha}(z,t) - \phi_s(z,t) \quad (7)$$

$$\Phi_{g\alpha}(z,t) = \phi_{g\alpha}(z,t) - \phi_s(z,t) \quad (8)$$

We use the following time evolution equations for the density fields:

$$\frac{\partial \Phi_{f\alpha}}{\partial t} = \nabla M_{f\alpha} \nabla \frac{\delta F}{\delta \Phi_{f\alpha}} - \frac{d\sigma}{dt}\, \phi_{r\alpha}(z,t) \quad (9)$$

$$\frac{\partial \Phi_{g\alpha}}{\partial t}\ \nabla M_{f\alpha} \nabla \frac{\delta F}{\delta \Phi_{g\alpha}} + \frac{d\sigma}{dt} \phi_{r\alpha}(z,t) \quad (10)$$

The first term in eqs 9 and 10 is the usual diffusion term. Here $F[\Phi_{f\alpha},\Phi_{g\alpha}]$ is the free energy functional and $M_{f\alpha},M_{g\alpha}$ are the mobility coefficients, which are generally functions of the local segment density. For the sake of simplicity, we use the "free draining" picture in this paper and assume that $M_{f\alpha},M_{g\alpha}$ are constant, i.e., $M_{f\alpha} = M_{g\alpha} = M$.

The second term on the rhs of eqs 9 and 10 represents the effect of reaction. Here $\phi_{r\alpha}(z,t)$ is the normalized density profile of the free polymer whose end is located at the surface (at $z = 0$). The term $(d\sigma/dt)\phi_{r\alpha}(z,t)$ represents that if the end of a free polymer reacts on the surface, the αth subunit belonging to the free polymer turns into the αth subunit of the grafted polymer.

A main assumption in eqs 9 and 10 is that dynamical processes are slow compared with the Rouse time of the αth subunit, $\tau_{R\alpha} = N_\alpha{}^2 a^2/6\pi^2 M_{i\alpha} k_B T$ ($i = f, g$), where a is the segment length and k_BT is the Boltzmann constant multiplied by the temperature. An advantage of our formulation is that we can freely control a level of a modeling from atomistic ($P = N$) to mesoscopic ($P = 1$).

Our aim in this paper is not to reproduce an exact motion of graft reaction but to check an applicability of our new scheme to the reaction problems at polymer interfaces, especially the diffusion barrier by the brush layer.

As in the previous paper,[11] the free energy functional $F[\Phi_{f\alpha},\Phi_{g\alpha}]$ is divided into the entropic term (the athermal term) $F_0[\Phi_{f\alpha},\Phi_{g\alpha}]$ and the interaction term:

$$\begin{aligned} F[\Phi_{f\alpha},\Phi_{g\alpha}] &= F_0[\Phi_{f\alpha},\Phi_{g\alpha}] + \int_0^\infty \chi \sum_{\alpha=1}^{P} (\phi_{f\alpha} + \phi_{g\alpha})\phi_s\, dz \\ &= F_0[\Phi_{f\alpha},\Phi_{g\alpha}] + \int_0^\infty \frac{\chi}{(2P+1)^2} (2P + \sum_{\alpha=1}^{P} (\Phi_{f\alpha} + \Phi_{g\alpha}))(1 - \sum_{\alpha=1}^{P} (\Phi_{f\alpha} + \Phi_{g\alpha}))\, dz \end{aligned} \quad (11)$$

where χ is the Flory−Huggins interaction parameter between polymer and solvent. Using the Legendre transformation, the free energy can be obtained in terms of the potential fields instead of the density fields:[11]

$$F_0[\Phi_{f\alpha},\Phi_{g\alpha}] = \tilde{F}_0[V_{f\alpha},V_{g\alpha}] - \int_0^\infty (\Phi_{f\alpha} V_{f\alpha} + \Phi_{g\alpha} V_{g\alpha})\, dz \quad (12)$$

where $V_{f\alpha}$ and $V_{g\alpha}$ are the potential field conjugate to $\Phi_{f\alpha}$ and $\Phi_{g\alpha}$. They can be expressed by the potential field $v_{f\alpha}$, $v_{g\alpha}$, v_s each acting on α th subunit of the free polymer, the grafted polymer, and the solvent.

$$V_{f\alpha}(z,t) = v_{f\alpha}(z,t) - v_s(z,t) \quad (13)$$

$$V_{g\alpha}(z,t) = v_{g\alpha}(z,t) - v_s(z,t) \quad (14)$$

The potential field $v_{f\alpha}$, $v_{g\alpha}$ and v_s are determined in such a way that, under these potentials, the density of the αth subunit of the free polymer, graft polymer, and solvent are given by $\phi_{f\alpha}$, $\phi_{g\alpha}$, and ϕ_s respectively. They are determined by the following set of equations (eqs15−33):

The relation between v_s and ϕ_s is

$$\phi_s(z,t) = (1 - \phi^b) \exp(-v_s(z,t)) \quad (15)$$

(In this paper k_BT is taken to be unity.) The density of the free polymer $\phi_{f\alpha}(z,t)$ is given by

$$\phi_{f\alpha}(z,t) = \frac{\phi^b}{N} \int_0^{N_\alpha} \psi_{f\alpha}(z,n,t)\psi^\dagger_{f\alpha}(z,N_\alpha - n,t)\, dn \quad (16)$$

where $\psi_{f\alpha}(z,n,t)$, $\psi^\dagger_{f\alpha}(z,n,t)$ are the solutions of the following Schrödinger type equations:

$$\frac{\partial \psi_{f\alpha}}{\partial n} = \frac{a^2}{6} \nabla^2 \psi_{f\alpha} - v_{f\alpha}\psi_{f\alpha} \quad (17)$$

$$\frac{\partial \psi^\dagger_{f\alpha}}{\partial n} = \frac{a^2}{6} \nabla^2 \psi^\dagger_{f\alpha} - v_{f\alpha}\psi^\dagger_{f\alpha} \quad (18)$$

under the "initial' conditions.

$$\psi_{f1}(z,0,t) = 1 \quad (19)$$

$$\psi^\dagger_{f1}(z,0,t) = \psi^\dagger_{f2}(z,N_2,t) \quad (20)$$

$$\psi_{f\alpha}(z,0,t) = \psi_{f\alpha-1}(z,N_{\alpha-1},t) \qquad 1 < \alpha < P \quad (21)$$

$$\psi^\dagger_{f\alpha}(z,0,t) = \psi^\dagger_{f\alpha+1}(z,N_{\alpha+1},t) \qquad 1 < \alpha < P \quad (22)$$

$$\psi_{fP}(z,0,t) = \psi_{fP-1}(z,N_{P-1},t) \quad (23)$$

$$\psi^\dagger_{fP}(z,0,t) = 1 \quad (24)$$

The densities of the grafted polymer $\phi_{g\alpha}(z,t)$ are given by

$$\phi_{g\alpha}(z,t) = \frac{\sigma(t)}{\int_0^\infty \psi_{g\alpha}(z,0,t)\psi^\dagger_{g\alpha}(z,N_\alpha,t)\, dz} \times \int_0^{N_\alpha} \psi_{g\alpha}(z,n,t)\psi^\dagger_{g\alpha}(z,N_\alpha - n,t)\, dn \quad (25)$$

where $\psi_{g\alpha},\psi^{\dagger}_{g\alpha}$ are the solutions of the following equations

$$\frac{\partial \psi_{g\alpha}}{\partial n} = \frac{a^2}{6}\nabla^2 \psi_{g\alpha} - v_{g\alpha}\psi_{g\alpha} \tag{26}$$

$$\frac{\partial \psi^{\dagger}_{g\alpha}}{\partial n} = \frac{a^2}{6}\nabla^2 \psi^{\dagger}_{g\alpha} - v_{g\alpha}\psi^{\dagger}_{g\alpha} \tag{27}$$

under the initial condition,

$$\psi_{g1}(z,0,t) = \delta_{z,0} \tag{28}$$

$$\psi^{\dagger}_{g1}(z,0,t) = \psi^{\dagger}_{g2}(z,N_2,t) \tag{29}$$

$$\psi_{g\alpha}(z,0,t) = \psi_{g\alpha-1}(z,N_{\alpha-1},t) \qquad 1 < \alpha < P \tag{30}$$

$$\psi^{\dagger}_{g\alpha}(z,0,t) = \psi^{\dagger}_{g\alpha+1}(z,N_{\alpha+1},t) \qquad 1 < \alpha < P \tag{31}$$

$$\psi_{gP}(z,0,t) = \psi_{gP-1}(z,N_{P-1},t) \tag{32}$$

$$\psi^{\dagger}_{gP}(z,0,t) = 1 \tag{33}$$

Finally $\phi^{r}_{f}(z,t)$ in eq 5 and $\phi_{r\alpha}(z,t)$ in eqs 9 and 10 are respectively given by

$$\phi^{r}_{f}(z,t) = \frac{\phi^{b}}{N}\psi_{f1}(z,0,t)\psi^{\dagger}_{f1}(z,N_1,t) \tag{34}$$

$$\phi_{r\alpha}(z,t) = \frac{1}{\int_0^{\infty}\psi_{r\alpha}(z,0,t)\psi^{\dagger}_{r\alpha}(z,N_{\alpha},t)\,dz} \times \int_0^{N_\alpha}\psi_{r\alpha}(z,n,t)\psi^{\dagger}_{r\alpha}(z,N_{\alpha-n},t)\,dn \tag{35}$$

where $\psi_{r\alpha},\psi^{\dagger}_{r\alpha}$ are the solutions of eqs 17 and 18 under the following initial conditions:

$$\psi_{r1}(z,0,t) = \delta_{z,0} \tag{36}$$

$$\psi^{\dagger}_{r1}(z,0,t) = \psi^{\dagger}_{r2}(z,N_2,t) \tag{37}$$

$$\psi_{r\alpha}(z,0,t) = \psi_{r\alpha-1}(z,N_{\alpha-1},t) \qquad 1 < \alpha < P \tag{38}$$

$$\psi^{\dagger}_{r\alpha}(z,0,t) = \psi^{\dagger}_{r\alpha+1}(z,N_{\alpha+1},t) \qquad 1 < \alpha < P \tag{39}$$

$$\psi_{rP}(z,0,t) = \psi_{rP-1}(z,N_{P-1},t) \tag{40}$$

$$\psi^{\dagger}_{rP}(z,0,t) = 1 \tag{41}$$

To solve the self-consistent field equation, we follow the method of Schuetjens–Fleer.[13] To solve the time evolution equation, we use the Crank–Nicholson scheme. The functional derivative $\delta F/\delta\Phi_i$ (i = 1, 2) of the diffusion terms in eqs 9 and 10 are calculated by

$$\begin{aligned}\frac{\delta F}{\delta \Phi_i} &= -V_i - \frac{\chi}{(2P+1)^2}\left(2P - 1 + 2\sum_{\alpha=1}^{P}(\Phi_{f\alpha} + \Phi_{g\alpha})\right) \qquad i = f\alpha, g\alpha \\ &= -V_i - \frac{\chi}{2P+1}(1 - 2\phi_s)\end{aligned} \tag{42}$$

The unit of length is taken to be the segment length a, and the unit of time the segmental diffusion time a^2/Mk_BT, which approximately corresponds to the time that a segment diffuses over the distance a by cooperative diffusion.

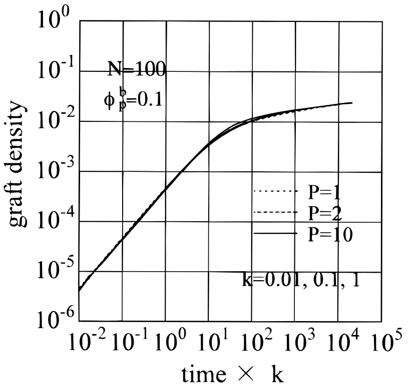

Figure 1. Time development of the graft density when a bare surface is inserted into a polymer solution of concentration of $\phi^b = 0.1$, where the chain length $N = 100$, the subunit length $N_\alpha = 100$, 50, and 10 (i.e., $P = 1$, 2, and 10) polymer–solvent interaction parameter $\chi = 0$ and the reaction rate coefficient $k = 0.01$, 0.1, and 1.0.

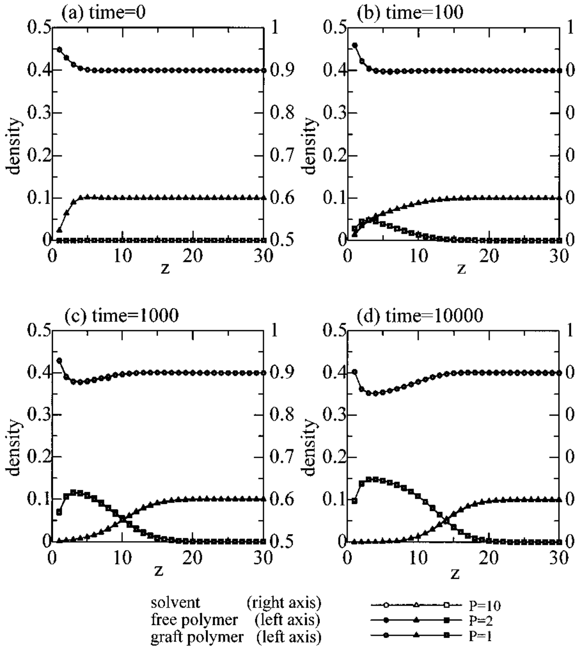

Figure 2. Time evolution of the density profile in the process of a grafting reaction. The density profiles of the segments of graft polymer $\phi_g(z,t)$, the segments of free polymer $\phi_f(z,t)$, and solvent molecules $\phi_s(z,t)$ at (a) time = 0, (b) time = 100, (c) time = 1000, and (d) time = 10 000. The constants are $\chi = 0$, $N = 100$, $P = 1$, 2, and 10, $\phi^b = 0.1$, and $k = 0.1$.

Results and Discussion

As a demonstration of our calculation, we show the results for various intrinsic reaction rate constants k = 0.01, 0.1, and 1.0 and various levels of modeling P = 1, 2, and 10 (i.e., $\tau_{R\alpha} \sim 200$, 50, and 2). The values of the other constants are $\chi = 0$ (good solvent), $N = 100$, and $\Phi^b = 0.1$.

Figure 1 shows the time evolution of the graft density σ, the number of graft chains per unit area created by the chemical reaction. Initially, the graft density σ increases linearly with time, but then it slows down when σ reaches a certain cririal value $\sigma^* \simeq 5 \times 10^{-3}$ which is independent of the intrinsic reaction rate k and the level of modeling P. The slow down occurs when the grafted polymers start to overlap, i.e., when the grafted polymers transform from "mushroom" to "brush". According to the scaling theory,[14] σ^* scales as $\sigma^* \simeq N^{-6/5}$. For $N = 100$, $N^{-6/5} = 4 \times 10^{-3}$ which is well compared with the σ^* obtained from Figure 1.

Figure 2 shows the time evolution of the density profiles of each components, $\phi_g(z,t)$, $\phi_f(z,t)$, and $\phi_s(z,t)$ in the case of $k = 0.1$. At $t = 0$, the free polymers and the solvent molecules are in the equilibrium state and there is no grafted polymer. The depletion layer of the free polymer is observed near the surface. As the reaction progresses, a typical profile of polymer brushes starts to be seen. The brush height increases, and the penetration depth decreases with time and then gradually saturates.

Using the present scheme, we can study not only the reaction rate but also the density profiles of each molecule over a long period of time. Furthermore it is easy to couple the reaction dynamics with phase separation kinetics. These problems are being studied and will be published in the future.

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