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# Three-dimensional analysis of membrane formation via thermally induced phase separation by dissipative particle dynamics simulation

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ABSTRACT

The effects of polymer molecular weight (polymer chain length), polymer molecular weight distribution (polymer chain length distribution) and diluent structure on the membrane formation of polymer–diluent system via the thermally induced phase separation (TIPS) method were analyzed on the basis of a dissipative particle dynamics (DPD) simulation platform. The simulation platform was extended into three-dimensions (3-D) to make sure that the results were more comprehensive. The simulation results proved that both the polymer chain length and polymer chain length distribution had significant influences on the phase separation process. As the polymer chain length increased, phase separation rate first increased when the polymer chain was relatively short and then decreased when the polymer chain length was larger. In addition, as the chain length distribution got wider, the phase separation rate decreased gradually at the middle and last stages of the phase separation process. It was also demonstrated that the interaction between polymer and diluent could be regulated by changing the interaction of the polymer and diluent local part by the local modification on the diluent molecular structure, which was beneficial to the membrane preparation. The information obtained from this study is consistent with the experimental results in literatures, proving that the simulation method could be widely applied in dynamics analysis of the membrane formation process.



## 1. Introduction

Dissipative particle dynamics (DPD) simulation method, as an important bridge between the atomistic and macroscopic description, has been applied to a large number of computer simulations which aim at complex fluid systems, such as polymer melt and solution [1–3]. In the preceding work of our group, the DPD method was firstly carried out to gain a better fundamental understanding about the membrane formation kinetics via the thermally induced separation (TIPS) method which could be regarded as the most important microporous polymeric membrane preparation technique. The simulation results illustrated that this simulation platform could be considered as a supplement on the mesoscale between the microscale theories and the macroscale experiments [4]. As a subsequent work, the effect of adding a second diluent on the membrane formation process of polymer–diluent system via TIPS was investigated based on the simulation platform. The results exhibited that a second diluent would change the membrane structure from a spherulitic to a bicontinuous structure and the interaction between the primary and the second diluent should be considered as the main factor for the second diluent selection [5].

Since the TIPS method was introduced, it has received considerable attention and has become one of the main methods of polymeric membrane preparation [6,7]. Over the past few years, TIPS has been widely applied in many fields, such as combining with the nonsolvent induced phase separation (NIPS) method to prepare a nanoporous membrane, using polymer blend to produce a microporous membrane with special property, preparing particles or scaffolds, and so on [8–13]. Therefore, a better understanding of the fundamental TIPS membrane-formation process mechanism needs to be addressed to develop membranes for new applications. Much attention has been paid to study the phase separation dynamics by using the method of mathematical modeling incorporating Cahn–Hilliard theory and Flory–Huggins theory. The research demonstrated that the droplet morphology changed with the gradient by imposing an external force [14–18]; however, the results were not intuitive and the microscopic information could hardly be included. Some researchers considered the solid–liquid (S–L) TIPS process and incorporated a nucleation and growth model to develop a mathematical model which described the S–L TIPS membrane-formation process and captured the fundamental features of the evolving structure [19–21]. But this model was limited to the S–L phase separation and did not explore the phase

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separation process. Additionally, microscopic simulation methods such as molecular dynamics and Monte Carlo had also been used to study the phase behavior of polymer blends, but it was extremely difficult and even beyond computational capacity to describe these systems at the microscopic level due to the short time scale and the large number of microscopic particles.

In the previous work, it has been concluded that DPD has distinct advantages on the research of the polymer membrane formation process compared to the methods mentioned above. Firstly, DPD is based on the particle method so that the results are more intuitive and the microscopic information can be added into consideration. Secondly, since every particle in DPD represents a group of atoms, this method can calculate much larger systems compared to the microscopic method and improve the computational efficiency. Moreover, the transport and distribution of polymer and diluent are able to be illustrated and the kinetics of phase separation can be clearly studied by the established DPD simulation platform. So this mesoscopic simulation technique is more suitable for the polymer solution included in the TIPS process.

Experimental researches have demonstrated that both polymer molecular weight and diluent have significant influences on the membrane formation process [22–25]. As the third publication of this series work, here the DPD simulation platform is improved through extending the previous two-dimensional (2-D) method to a three-dimensional (3-D) method. On the basis of this 3-D simulation platform, much efforts are paid to investigate the influences of the polymer chain, including chain length (representing polymer molecular weight) and chain length distribution (representing polymer molecular weight distribution), and diluent structure on the membrane formation of polymer–diluent system undergoing TIPS. Simulation results in 3-D are more general and real, and this work extends the application of this simulation method on the field of membrane formation research.

## 2. Simulation method and model construction

### 2.1. DPD method

DPD is based on the particle method in which a "fluid" particle represents a cluster of atoms or molecules and the particle–particle interactions are ultra-soft. The time evolution of the interacting particles is governed by Newton's equations of motion, and GW–VV algorithm [3] is used here;

$$\begin{aligned} r_i(t+\Delta t) &= r_i(t)+\Delta t\, v_i(t)+\frac{1}{2}(\Delta t)^2 f_i(t),\\ \tilde{v}_i(t+\Delta t) &= v_i(t)+\lambda\,\Delta t\, f_i(t),\\ f_i(t+\Delta t) &= f_i(r(t+\Delta t),\tilde{v}(t+\Delta t)),\\ v_i(t+\Delta t) &= v_i(t)+\frac{1}{2}\Delta t(f_i(t)+f_i(t+\Delta t)) \end{aligned} \quad (1)$$

According to our previous work [4], $\lambda=0.65$ and $\Delta t=0.01\tau_0$ ($\tau_0$ is defined in Section 2.2) are adopted in order to ensure that the simulation has high efficiency and good temperature control.

The pairwise interactive force acting on a particle $i$ by particle $j$ is characterized by three parts: the conservative force ($\vec{F}^C_{ij}$), the dissipative force ($\vec{F}^D_{ij}$), and the random force ($\vec{F}^R_{ij}$). The conservative force is given by

$$\vec{F}^C_{ij}=\begin{cases}\alpha_{ij}(1-r_{ij}/r_c)\vec{e}_{ij} & (r_{ij}<r_c)\\ 0 & (r_{ij}\geq r_c)\end{cases} \quad (2)$$

where $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$, $r_{ij}=|\vec{r}_{ij}|$, and $\vec{e}_{ij}=\vec{r}_{ij}/r_{ij}$. $\alpha_{ij}$ is the maximum repulsion between particle $i$ and particle $j$. All of the three forces act within a certain cutoff radius $r_c$ ($r_c$ is chosen as the length unit in the simulations, which will be illustrated in the following sections). The remaining two forces between the interacting particles are dissipative and random forces, which couple together to form a momentum-conserving thermostat. They are correspondingly given by

$$\vec{F}^D_{ij}=-\gamma\omega^D(r_{ij})(\vec{e}_{ij}\cdot\vec{v}_{ij})\vec{e}_{ij}, \quad (3)$$

$$\vec{F}^R_{ij}=\sigma\omega^R(r_{ij})\theta_{ij}\vec{e}_{ij}, \quad (4)$$

where $\vec{v}_{ij}=\vec{v}_i-\vec{v}_j$ and $\theta_{ij}$ is a random number with zero mean and unit variance. The noise level is taken to be $\sigma=3.0$ for good temperature control and the relationship between $\sigma$ and $\gamma$ is given by $\sigma^2=2\gamma k_BT$. The weight functions $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ follow the relation $\omega^D(r)=[\omega^R(r)]^2$ to satisfy fluctuation–dissipation theorem [2]. For simplicity, the general function form of $\omega^R(r)$ is

$$\omega^R(r)=\begin{cases}(1-r) & (r<1)\\ 0 & (r\geq 1)\end{cases}, \quad (5)$$

The polymer chain is constructed by connecting the adjacent particles via a harmonic spring:

$$\vec{F}^S_{ij}=-Kr_{ij}, \quad (6)$$

where $K$ is the spring constant. According to the preceding work [4], $K$ is chosen to be 4.0.

### 2.2. Model construction

Compared with the previous work, although the current simulations do not correspond to any specific system, the results may shed light on the understanding of membrane formation in the TIPS process. In the simulation, the reduced units are used to decrease the computation complexity. Length unit $r_c$ (the cutoff distance of interaction) and mass unit $m$ (particle mass) are chosen to be $r_c=m=1$. The temperature is determined by the energy unit $k_BT$ and the temperature of the simulation system is controlled as follows: $T=273.15$ K is set to be the reference temperature, which means at this temperature $k_BT=1.00$; therefore when $T=473.15$ K, $k_BT=1.73$. Correspondingly, the time scale in the simulation is defined by $\tau_0=r_c(M/k_BT)^{1/2}$. Due to the soft potential used in DPD simulation, the particle number density $\rho$ should be larger than 3 so that the equation of state can be fulfilled [3]. Taking into account the computational efficiency, $\rho=3$ is a reasonable choice. All the above parameters used here correspond with Ref. [3].

This work is separated into two parts to investigate the effects of polymer chain and diluent structure on the membrane formation process. Two different models are adopted in different parts. Fig. 1 shows the model of polymer and diluent used in the first part (Section 3.1) which investigates the effects of polymer chain length and polymer chain length distribution. The diluent is regarded as a single particle and the polymer chain consists of $N$ interconnecting particles. Different $N$ means a different polymer molecular weight. In this work, the conservative interaction parameter between the same type particles $\alpha_{ii}$ equals on $25k_BT$ [3]. The phase separation can take place by adjusting the conservative interaction parameter between polymer and diluent $\alpha_{polymer-diluents\ (p-d)}$ when the system is quenched to 273.15 K. The subscripts "$p$" and "$d$" indicate polymer and diluent, respectively. Table 1 summarizes the conservative interaction parameter $\alpha_{p-d}$ at different temperatures used in Section 3.1. At 473.15 K, $\alpha_{p-d}$ is chosen to be 25.0 so that the polymer chain can relax sufficiently.

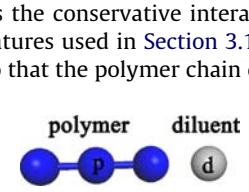


**Fig. 1.** Model of polymer and diluent used in Section 3.1.