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Computer Simulation Studies of the Conformations of Polymeric Systems Near Surfaces as a Basic Research of the Elastomer

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고무의 기초 연구로써 표면에 위치한 고분자 시스템 거동에 관한 수치모사 연구

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ABSTRACT: In this study as a basic research of the elastomer, we show the results of the behavior of the two different chain length polymers in the melt confined between two impenetrable planes. The cubic lattice simulations are conducted in the canonical ensemble with a method that is a combination of reptation and crackshaft bond flip motions. A total of 680 chains which are 544 short chains comprising 10 beads and 136 long chains comprising 160 beads were placed in 20 lattice layers. It was assumed that there is no energetic interactions between covalently connected beads, while all other neighbors will interact with a truncated 6-12 Lennard-Jones potential. From the analysis of the simulation results, it was shown that purely entropic effects caused the shorter chains to partition preferentially to the surface. We also showed that the center of mass density of the shorter chains shows maximum near the surface. This is the opposite phenomena when compared to that of the longer chains. However, the segments of the shorter and the longer chains did not display any significant changes in bond order.

요 약: 본 연구에서는 elastomer의 기초 연구로써 두개의 침투할 수 없는 평판사이로 국한시킨 용융상태에서 두개의 다른 사슬 길이를 가진 고분자의 거동에 대한 결과를 보여 주었다. 입방 격자 시뮬레이션은 reptation과 crankshaft bond flip 이동의 조합에 따른 방법으로 유도되었다. 10개의 구슬로 엮어진 544개의 짧은 사슬과 160개의 구슬로 엮어진 136개의 긴 사슬로 구성된 전체 680개의 사슬은 20개의 격자 층에 투입되었다. 공유결합으로 연결된 구슬사이의 energetic 상호인력은 없고 반면에 모든 다른 이웃들은 truncated 6-12 Lennard-Jones 포텐셜로서 상호작용하고 있다고 가정하였다. 수치모사 결과의 분석으로부터 순수한 entropic 효과로 인하여 짧은 사슬이 우선적으로 표면에 도달하는 것을 보여 주었다. 또한 짧은 사슬의 질량밀도중심은 표면근처에서 최

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고값을 보여주었다. 이것은 긴 사슬의 경우와 상반되는 현상이다. 그러나 짧은 사슬과 긴 사슬의 segment는 결합 정렬에 있어서는 큰 변화를 주지 않았다.

Keywords : monte carlo simulation, entropic effect, segregation, radius of gyration.

I. Introduction

The behavior of polymeric systems in the vicinity of surfaces has important consequences in many different contexts. Typical examples include the stabilization of colloidal suspensions with adsorbed polymer chains,[1] and the use of polymer melts as lubricant films.[2,3] These situations are also useful in studying the fundamental physics that drives the observed behavior of polymer systems in the bulk. Such studies include the interdiffusion of polymers across an interface (useful in studying the phenomenon of crack healing of the elastomer).[4]

In all these cases, the phenomena under consideration involve the behavior of polymeric systems in the presence of a surface. A surface presents a constraint on the system and is thus expected to perturb strongly the properties of the chain molecules in its vicinity. In the case of a model homopolymer melt system that is confined into a thin-film between two impenetrable surfaces, Kumar et al.[5] have demonstrated this perturbative effect of a wall through an Off-lattice Monte-Carlo simulation approach. They have shown that the effect of the surface is to force chains in its proximity to adopt pancake-like shapes. Properties such as the radius of gyration perpendicular to the wall and the order parameter of these chains are thus modified in comparison to the unperturbed coils. Further, this perturbative effect persists on all chains that have their centers of mass within a distance of ca. 2RG (twice the unperturbed radius of gyration of the chains) from the wall. However, the model considered in this case is a simple, idealized polymer melt that is confined between impenetrable surfaces, a system that is not representative of a experimentally reliable system.

Frequently, real macromolecular systems are characterized by several other factors such as the presence of a distribution of molecular weights, and energetic interactions between specific moieties and the surface. In addition, the presence of polymerization initiators and terminators as the end-groups on a chain transforms even a simple homopolymer system into a copolymer system. All of these factors are expected to affect the interfacial behavior of a polymeric system.

In this paper, we will consider the effect of the presence of a molecular weight distribution in a polymer sample on its interfacial behavior. To date, analytical calculations[6,7] have been performed on the surface segregation demonstrated by a binary mixture of monodisperse melt-polymers near an impenetrable surface to study the effects of polydispersity on the surface behavior of a polymer melt. Such calculations cannot yield a quantitative description of the situations of interest. In our lattice simulations, the effects of the surface on the conformations of the two chain length polymers in its vicinity will be studied to understand the surface segregation phenomenon from a molecular viewpoint.

The lattice simulation is advantageous in that they can be performed relatively rapidly to obtain accurate information for the conformations of the macromolecules in the interface.

Ⅱ. The Model

The technique adopted in simulating the effects of polydispersity on the behavior of a polymer molecules in a melt confined between two parallel plates was involved a modified Metropolis Monte-Cárlo scheme.[8] In such a scheme the chains were simulated in the Canonical ensemble, i.e., at conditions of constant temperature, total volume and the number of particles.[9] It has been shown that the probability of a fluctuation in this ensemble at equilibrium is

$$P_{fluc} \propto \exp(-\triangle E_t/k_BT), \qquad (1)$$

where $\triangle E_t$ is the change in the total energy of the system due to the fluctuation, k_B is the Boltzmann's constant, and T the absolute temperature.

The lattice was constructed so that its planes are parallel to the surface with its first layer coincident with the wall. Connections to the other layers are then provided through the presence of bonds in the interlayers perpendicular to the wall. The surfaces of interest were modelled as planes normal to the z-axis. The planes were located at z=1 and z=20. During the simulations the chains are not allowed to cross these planes. In the x and y directions, periodical boundary conditions were assumed as illustrated in Fig. 1. The periodical boundaries were located at x=1, x=40 and y=1, y=40. Polymer chains were represented in these simulations as a necklace of 160 and 10 connected beads, respectively. In this study, the polymer density was 0.85 (i.e., 15% of the lattice sites were empty). A total of 680 chains which are 544 short chains (=ns) comprising 10 beads (= M_s) and 136 long chains (=n$_l$) comprising 160 beads (= M_l) were placed in 20 lattice layers. It was assumed that there is no energetic interactions between covalently connected beads, while all other neighbors will interact with a truncated 6-12 Lennard-Jones poten-

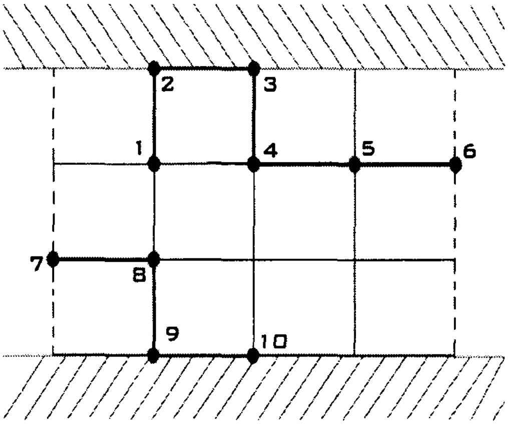

Fig. 1. A schematic representation of boundary conditions.

tial.[5]

One technique to allow a system to attain its equilibrium state denoted by a minimum in its Helmholtz energy,[10] is to use the technique that was proposed by Metropolis et al.[8] In this scheme, new configurations are generated from an initial, feasible state as is described below. Subsequently, the change in the total interaction energy of the system due to this change, $\triangle E_t$, is calculated. If this quantity is smaller than zero, denoting a decrease in the Helmholtz energy of the system, the new configuration is stored and a new set of moves attempted on it. However, if this quantity is larger than zero, then a quantity P_α [$=\exp(-\triangle E_t/kBT)$] is computed. A random number between 0 and 1, ξ, is then generated. If ξ is larger than P_α, then the new configuration is stored as the new starting point. Otherwise, the old configuration is restored and utilized to generate a new configuration.

The initial configuration of chains is generated by randomly placing the chains on the lattice under its geometric constraints. Further, chains are placed so as to have at most a single bead at each occupied lattice site. Subsequently, the beads of the chains were moved through a combination of two different elementary moves (See Fig. 2) : reptation and crank-shaft of bond flip. In the reptation move which has been used previously by several workers,[5,11,12] a chain was chosen at random, and one of its end beads (also chosen at random) moved to the other end of the chain. The new, trial orientation of this bead was chosen randomly.

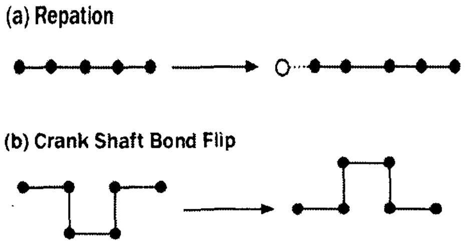

Fig. 2. Illustration of elementary motions : (a) reptation (b) crank shaft of bond-flip.

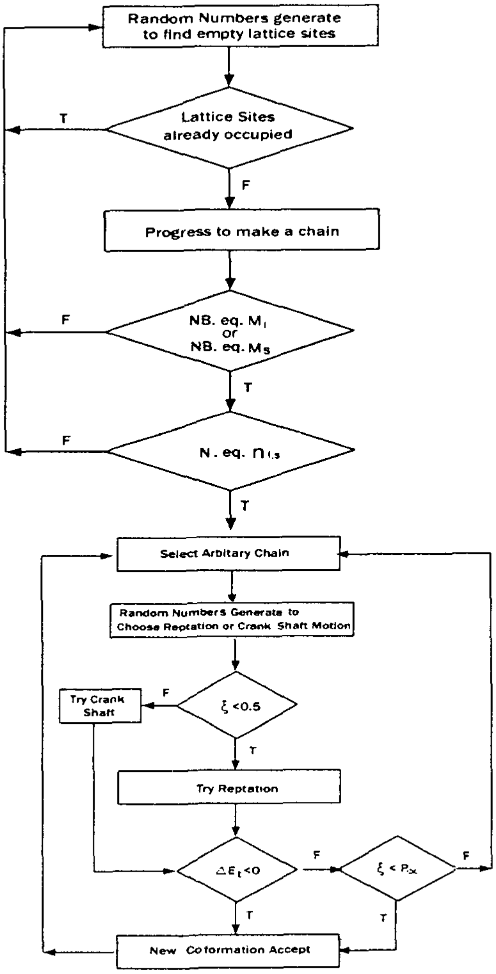

Fig. 3. Flow cart of the simulation procedure. NB and N denote number of beads and number of chains, respectively.

The trial orientation was then tested for acceptance following Eq. (1), and if rejected the old configuration was restored, and stored as the result of the attempted move. In the crank-shaft of bead-flip move, proposed originally by Verdier and Stockmayer,[13] non-collinear beads on a chain are selected at random. The center beads are then flipped so that they occupies the other available sites, also chosen at random. In this fashion a new configuration is generated. The procedure is summarized in Fig. 3. Ten different equilibrium structures were made to reduce the statistical error. Average were calculated, taking the symmetry of the system into account.

Ⅲ. Results and Discussion

Fig. 4 shows total energy as a function of number of steps. It is shown that the elementary moves lead the system to attain a state of thermodynamic equilibrium after 10^7 steps. The polymer bead density as a function of z for the shorter chains comprising 10 beads is plotted in Fig. 5. The concentration of the beads of the shorter chain was found to be maximum on the surface and approached its bulk value at distances characteristic of each system. This result is in agreement with the analytic calculation of Hariharan et al.[6] It suggests that the segregation of the shorter chains to the surface is a purely entropic effect. Consequently the shorter chains are thermodynamically driven to the surface so as to maximize the entropy of the system. In other words, the entropic loss suffered by the longer chains in the vicinity of the surface, in the absence of any energetic interactions, would be greater than that for the shorter chains due to the restriction posed by connectivity of the chain beads. To exam the effect of the surface on the configurations of shorter chain ends as a

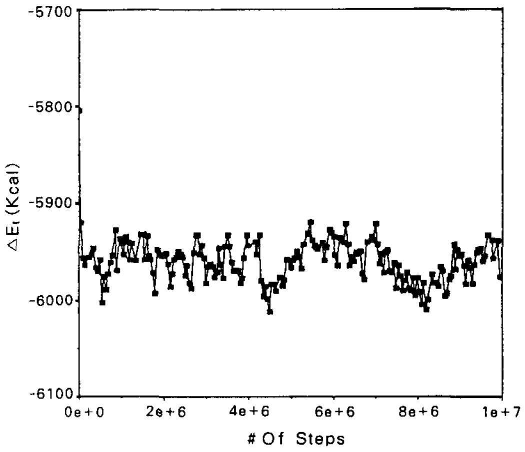

Fig. 4. Total energy as a function of number of steps.

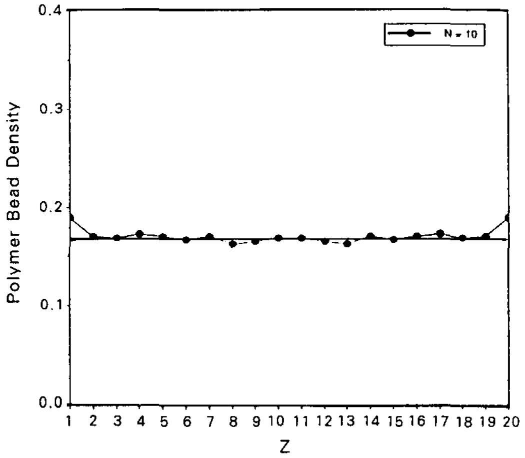

Fig. 5. Polymer bead density as a function of z for the shorter chains.

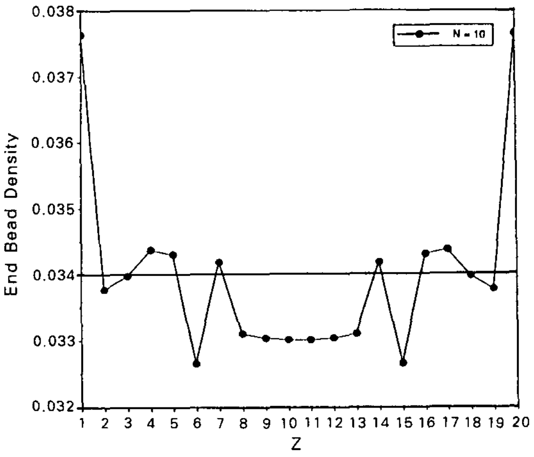

Fig. 6. End bead density as a function of *z* for the shorter chains.

function of *z* from the surface. This is plotted in Fig. 6. It is seen in this figure that we have an enhanced density of shorter chain ends at the surfaces. The presence of chain ends near the surface is less restrictive than having a central bead near the surface. This is because an end is attached to only one unit while each central bead has two bonded neighbors. This effect will be damped out as *z* is extended out of the surface. Subsequently, a bulk structure should be obtained since all the interfacial effects have been screened out.

Having checked the distribution of ends near the surface we proceeded to examine the distribution of centers of mass of shorter chains along the *z* axis for all shorter chains. The vector position of the center of mass (CM) of a chain is the first moment of the spatial distribution of its segments,

$$r_{CM,i} = \frac{1}{M_{s,l}} \sum_{j=1}^{M_{s,l}} r_{j,i}, \tag{2}$$

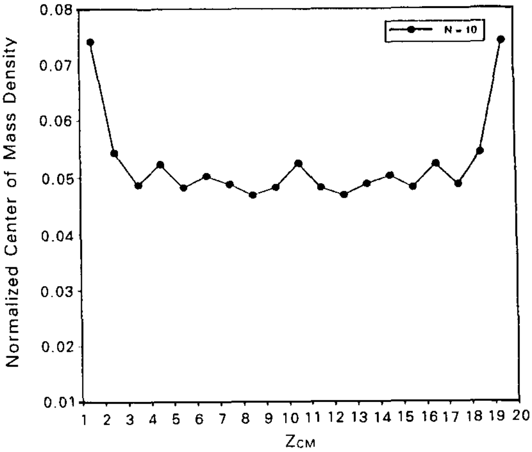

Fig. 7. Normalized center of mass density for the shorter chains.

where $r_{j,i}$ represents the vector position (i.e., *x*, *y*, and *z*) of the *j*th bead of molecule *i* and $M_{s,l}$ are number of beads of short chains and long chains, respectively.

From this, the center of mass position along the *z* axis may be obtained. The density of centers of mass for the shorter chains as a function of their *z* is plotted in Fig. 7 positions. It is seen in this figure that

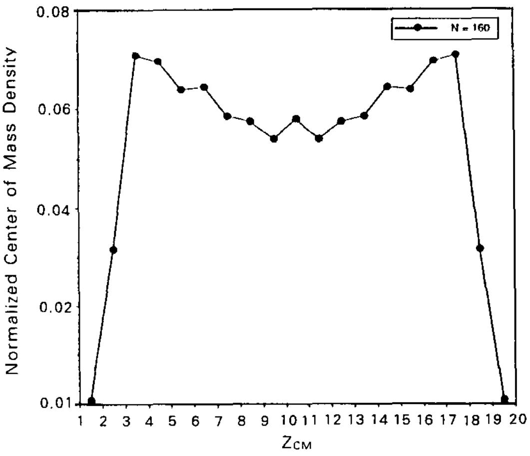

Fig. 8. Normalized center of mass density for the longer chains.

the center of mass density for the shorter chains shows maximum near the surface. In case of the polydisperse system the shorter chains segregated to the surface. As a consequence, we have many shorter chains that have centers of mass in this region. This is the opposite phenomena when compared to that of the longer chains (See Fig. 8).

Next, we consider the radius of gyration (Rg) in the $x-y$ and z directions. It is the second moment about the center of mass. This quantity is the radius of gyration ($R_{g,z}$) in the z direction :

$$R^2_{g,x-y} = \left\{ \frac{1}{M_{s,l}} \sum_{j=1}^{M_{s,l}} (z_j - z_{CM})^2 \right\} \tag{3}$$

Also, the x and y components of the radius of gyration are calculated through similar expressions. The average value in the $x-y$ direction was calculated through the expression

$$R^2_{g,x-y} = \frac{[R^2_{g,x} + R^2_{g,y}]}{2}. \tag{4}$$

In Fig. 9, we plot the z, the average of the x and y components and the total radius of gyration as a function of the z position of the center of mass of the shorter chains. The z component of $R_{g,z}$ is small for chains that have their center of mass near the surface. It suggests that chains that have centers of mass close to the surface must be flattened in a direction parallel to the surfaces. Also, the $x-y$ component of Rg suggests that chains close to the surface must be swollen in a direction parallel to the surfaces. Near the middle of surfaces, a plateau value is reached. In the plateau regime, the parallel component of the radius of gyration is approximately equal to the orthogonal component.

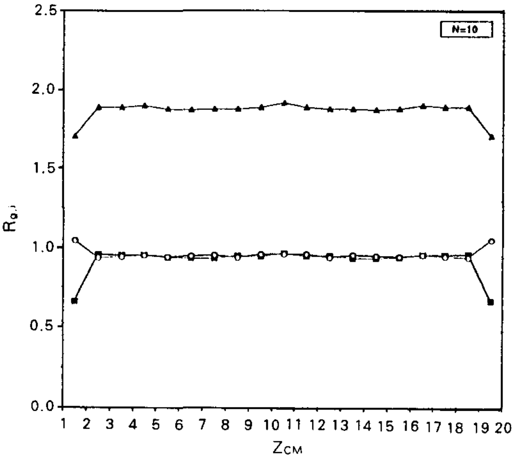

Fig. 9. Radii of gyration of as a function of the position of the center of mass. Filled squares are the z component of R, while circles are averages of the $x-y$ components. Triangles are the total R.

Another technique used in this paper is to study the order parameter associated with each chain. We initially proceeded to calculate the direction cosine of each segment of a chain in relation to the z axis. This was determined by taking the dot product of the unit vector joining the centers of beads j and $j-1$ with the vector defining the z axis, The order parameter of a chain was calculated through the expression

$$S_{c,i} = \frac{3(\cos^2\theta_{j,z})_i - 1}{2}, \tag{5}$$

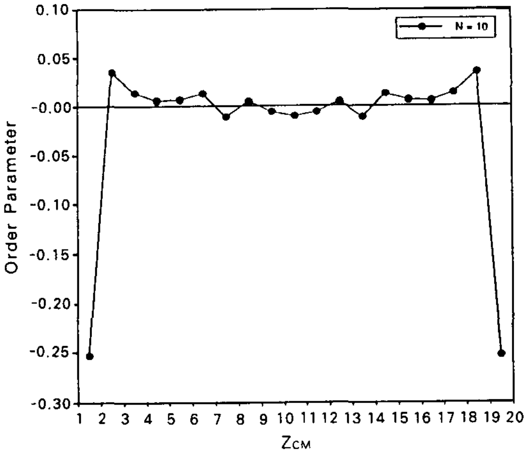

Fig. 10. Order parameter profile of the segments of the shorter chain.

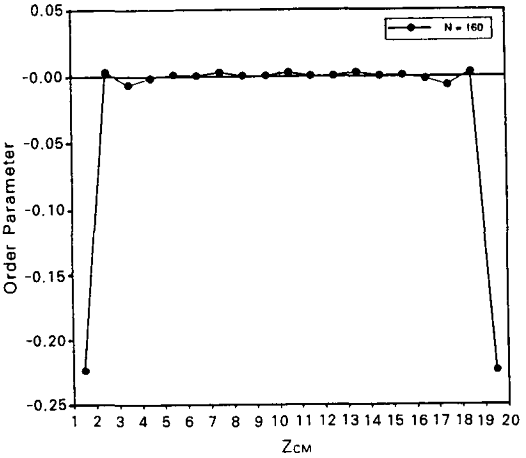

Fig. 11. Order parameter profile of the segments of the shorter chain.

where the ensemble average is taken over all the segments of a single chain i.

The order parameter of chains are plotted as functions of the positions of their centers of mass in Fig. 10 and Fig. 11. The segments of the shorter and the longer chains did not display any significant changes in bond order. That means the changes in bond order in the interface from the case of a pure homopolymer to a bimodal melt were seen to be negligible in our simulations. This order parameter then become smaller and it is zero i.e., the chains have essentially no preferred orientation, and hence constitute isotropic chains.

IV. Conclusions

An advantage of computer simulation techniques 14-16 is that they can be used as predictive tools to determine the dependence of the properties of polymeric interfacial systems on the microscopic architecture of the chains. In this paper, we have simulated, with the aid of a cubic lattice model, the behavior of the two chain length polymers in the melt confined between two impenetrable planes. This includes the segregation of shorter chains to a surface from a bimodal melt composed of shorter and longer chains.

The concentration of the beads of the shorter chain was found to be maximum on the surface and approached its bulk value at distances characteristic of each system. It was shown that purely entropic effects caused the shorter chains to partition preferentially to the surface. The center of mass density of the shorter chains shows maximum near the surface. This is the opposite phenomena when compared to that of the longer chains.

We also showed that the shorter chains near the surface are flattened parallel to the surface. However, the segments of the shorter and the longer chains did not display any significant changes in bond order.

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