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論 文 內 容 要 旨

Abstract

In this thesis, using the static and dynamic Self Consistent Field (SCF) theories, we investigated the physical properties of polymeric materials especially for diblock copolymers. To perform large scale simulations, we also proposed a dynamic density functional theory based on the Ginzburg-Landau free energy model with the random phase approximation (GRPA).

An order-order transition from a bicontinuous double gyroid (G) structure to a hexagonally packed cylinder (C) structure induced by an external flow is simulated using real-space dynamical SCF technique. When a shear flow in [111] direction of the G unit cell is imposed, a nucleation of the C domains followed by a stable coexistence between the G phase and the C phase is observed. We confirm that the generated C domains grow epitaxially, where the {220} planes of the G structure coincide with the {10} planes of the C structure (so called epitaxial growth), while the experimental studies suggest {211} to {10} transition. In a steady state under the shear flow, the G structure shows different splitting and reconnection processes when the direction of the velocity gradient of the shear flow is changed. Thus, the kinetic pathway from the initial G phase to the final C phase is determined not only by the commensurability between the positions and the lattice constants of the initial and the final domain structures (epitaxial condition) but also by the stability of the phase coexistence that depends on the direction of the velocity gradient.

A similar epitaxial transition is studied but an external electric field is imposed instead of the shear flow. G to C transition in a diblock copolymer melt under an electric field is studied by real-space dynamical SCF theory. Starting from an equilibrium gyroid structure, we apply an electric field along [111], [1-10], [11-2] directions of the conventional unit cell of the gyroid structure. Under sufficiently high value of the electric field, an epitaxial transition to cylinders occurs. Contrary to the case of similar transition under the shear flow, we observe 5-fold connections as intermediates in the transition. We found a critical behavior of the life time of the initial gyroid structure, which can be accounted for using mean field argument. Numerically obtained scattering function explains the unclarified intermediates experimentally observed in the thermal relaxation of a sheared gyroid.

The high-impact modified poly-styrene (HIPS) is studied. HIPS is a major polymeric materials and is known to have a typical micro domain structures induced by the chemical reaction (polymerization of styrene monomers). The mechanism of the domain formation is discussed on many aspects. The phase inversion and the typical morphology named salami structure of HIPS can not be reproduced in the dynamic SCF simulation coupled with the chemical reaction of polymerization. But the static SCF simulation can reproduce the salami-like structure by using a mixture of a grafted polymer and a homopolymer. This result is in good agreement with experimental report.

The dynamic SCF theory and the Navier-Sokes equation are coupled and the hydro dynamics effect to the dynamic SCF theory is studied. Diblock copolymer melts are used for this study under the condition of the

viscosities: $\eta = 1.0, 0.1, 0.01$. The simulation results show that in the low viscosity $\eta = 0.01$ the micro domain formation of diblock copolymers from disordered states is clearly accelerated.

A high-speed and accurate hybrid dynamic density functional theory is proposed for the simulations of the phase separation processes of polymer melts and blends. The proposed theory is a combination of the dynamic SCF theory and the dynamic GRPA theory. To make the accuracy of the SCF theory and the high-performance of the GRPA theory compatible, we adjust the chemical potential of the GRPA theory by using the SCF theory every constant time steps in the dynamic simulations. The performance of the GRPA and the hybrid theories is tested by using several systems composed of an A/B homopolymer, an AB diblock copolymer, or an ABC triblock copolymer. Using the hybrid theory, we succeeded in reproducing the metastable complex phase-separated domain structures of an ABC triblock copolymer observed by experiments.

論文審査の結果の要旨

異種のモノマーからなる高分子ブロックを結合したブロック高分子は、種々の興味深い自己組織構造を作ることが知られている。その形成機構を明らかにすることは、学問的にも応用的にも、極めて重要である。

本田隆は、ブロック高分子のつくる種々の自己組織構造をシミュレーションする汎用のプログラム(SUSHI)を開発した。本論文はSUSHIの実装と、それを用いた研究結果をまとめたものである。

2章ではSUSHIの実装法が議論されている。SUSHIのベースになっている高分子の平均場理論は1960年代にできあがったものであるが、本田隆は(1)任意の分子構造の高分子の任意の組成に対して(2)ずり、電場、壁などの外場の影響を考慮して、(3)球、円柱などの対称性を考慮して、(4)構造形成の時間発展をシミュレーションすることのできるきわめて汎用的なプログラムを開発した。このような汎用的な条件で使えるプログラムは世界的に見ても他に例がなく、計算科学的にも非常に先進的なものであるということが出来る。

3章、4章、5章ではSUSHIを用いた応用例を議論している。3章では、ずりによるジャイロイド構造からシリンダー構造への転移、4章では電場によるジャイロイド構造からシリンダー構造への転移、5章では重合によるサラミ構造の出現を議論している。これらの知見は本プログラムによって初めて可能になったことであり、すでに論文として発表されている。

6章と7章はSUSHIの新しい展開に関するものである。6章では流体力学的相互作用を取り入れる方法について、7章では密度汎関数法と自己無撞着法の混合法による新規なアルゴリズムを提案し、開発実装している。特に、密度汎関数法と自己無撞着法の混合法は大幅な計算時間の短縮が期待される新規な方法である。

以上のように、本論文は新規なシミュレーションプログラムの開発とその応用を示した優れた研究であり、学問的にも応用的にも大きな意義を持っているものである。この論文は、本田隆が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって、本田隆提出の博士論文は、博士(理学)の学位論文として合格と認める。