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Effect of flow on solutions of rod-coil block co-polymers

Sezen Curgul, Burak Erman*

College of Engineering, Koc University, Rumelifeneri Yolu, 34450 Istanbul, Turkey

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Abstract

An elongational flow field is imposed on a solution of block copolymers consisting of semirigid macromolecules with rigid, rodlike sequences of units in combination with random coil (flexible) units. The problem is formulated according to the lattice treatment of Matheson and Flory. In this formulation, the system consists of rigid blocks whose lengths and locations are fixed by the structure within each macromolecule. These blocks are separated by random coiled units. An excess free energy other than the equilibrium Gibbs free energy of the quiescent solution has to be considered due to the flow field that tends to align the rods. This excess free energy is calculated from the potential energy of rods when a steady-state, homogeneous and irrotational flow field is applied to the solution. The effects of composition, polymer–solvent interaction, size of the co-polymer and flow rates are investigated. Depending on the size and number of rods, some of the chains studied exhibit a biphasic region at equilibrium that shifts to lower concentrations with increasing flow. Longer chains with shorter rods that are isotropic at equilibrium, exhibit a biphasic region at finite values of flow. The degree of orientation increases sharply when the system is biphasic. For larger flows, the orientation function is very close to unity which is perfect orientation.
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1. Introduction

The problem of flow induced alignment of block copolymers is an important technological problem. There have been important advances in the understanding and production of these systems, which are now well documented in the literature [1]. Of particular significance is the nanostructured engineering of block copolymers based on self assembly and microphase equilibria [1]. Use of block copolymers of two different types, such as sequences of rigid and flexible components, introduces the advantage of controlling the compositions of phases, which is otherwise difficult in mixtures of different polymers due to their limited miscibilities [2]. As a general rule, in a phase separated mixture of rodlike and coiled polymers, although the isotropic phase may tolerate some amount of the rodlike species, the anisotropic phase excludes the flexible chains completely [3]. The different phases in rod-coil block copolymers may further be oriented and reorganized by applying external fields. An efficient way of creating desired nano-structures in such systems is by applying a flow field, most commonly by shear or extensional flow [1]. Although flow induced orientation is a widely used method in polymer processing and manufacture, the relationship of a flow field to the phase behavior of block copolymers at the molecular scale is not yet fully understood. One way of studying these dependences at the molecular level is by the use of lattice models of solutions of polymers. Equilibrium lattice theories of polymers of different flexibilities are widely studied in the literature, based on the works of Flory, Abe, Matheson, Ballauf and Lin [4–14]. In the present paper, we employ the lattice model of Matheson and Flory [7] to study the effects of an extensional flow field on the orientability of block copolymer chains, and their phase separation behavior and the stability of different phases. We also study the effect of the size and number of repeating blocks in the chains and the effects of thermodynamic variables such as the polymer–solvent interaction for these systems when they are subject to an extensional flow field.

The present study rests on evaluating the orientational

* Corresponding author. Tel.: +90 212 338 1704; fax: +90 212 338 1548.
E-mail address: berman@ku.edu.tr (B. Erman).

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entropies of the rodlike sequences of rod-coil block copolymers in a small molecule solvent. The lattice theory of binary mixtures of a rigid, rodlike solute with a small-molecule solvent has been formulated by Flory [15] and Flory and Ronca [16]. Although the theory is in good agreement with experimental results for some polymers, departures from the theory are exhibited for some other polymers, especially for high molecular weight ones. This can be attributed to the deviations from perfect rigidity that was assumed in the theory. Recently, Abe and collaborators improved the theory by assigning flexibilities to the rodlike components in a mixture of rod-coil-solvent system [9]. Previously, it was shown [6] that a system of identical rods joined by flexible connections should exhibit nematic-isotropic phase equilibria that very nearly coincide with the equilibria for disconnected rods of the same length. Semirigid chains which contain inherently flexible units or sequences of such units, at certain locations along the otherwise rigid chain have been examined by Matheson and Flory [7]. They considered solutes that incorporate both features in the same molecule, i.e. rigid, rodlike sequences whose orientations are mutually independent and intervening sequences of random coiled units of variable length. The system was modeled with lattice theory and the partition function, free energy of mixing, chemical potentials and conditions for phase equilibrium have been formulated. Our flow field model is based on the Matheson–Flory treatment.

The effects of a steady state extensional flow field on a solution of rodlike particles were first studied by Marucci and Ciferri [17]. They formulated the contribution to the Gibbs free energy of the solution under the aligning effect of the flow field. The treatment of Marucci and Ciferri [17] was extended by Bahar and Erman [18] to include the effect of any homogeneous flow field on a solution of rodlike particles. They adopted the improved formulation [16] of the exact lattice treatment for the equilibrium free energy and calculated the degree of flow induced orientation in terms of the orientation function.

In the present study, we combine the equilibrium lattice model of Flory and Matheson [7] with the lattice flow model of Bahar and Erman [18] to analyze the behavior of block copolymers in an extensional flow field.

2. Review of the lattice model and formulation of the problem

The copolymer chain consists of n rigid blocks and n flexible chains, joined together to form an alternating block copolymer. We consider the case where all the rodlike segments have equal length. When the chain is placed in an extensional flow field, the forces coming from the flowing solvent will be transmitted to each segment of the copolymer through frictional forces. These forces will tend to distort the overall conformations of the chain by (i) rotating the rods along the direction of flow, and (ii) translating the rods relative to each other. Relative translations of two rods connected by a flexible coil will store strain energy into the coil. However, under flow fields that are small perturbations from the quiescent solution, the dominant effect of the flow field will be the direct rotational effect on the rigid sequences. In the present treatment, we ignore the loss of configurational entropy of the coils, and assume that the only contribution comes from the direct rotational effect of the flow field on the rods.

The problem then becomes similar to the kinematics of disconnected rodlike molecules subjected to an irrotational flow field, which has been considered by Bahar and Erman [18].

It is also worth noting that there is a basic analogy between the present model and the uniaxial stretching of network chains embedded on a lattice, which has previously been introduced by Mark and collaborators [19–22].

2.1. Free energy change in elongational flow

The center of mass of the rod is situated at the origin and the rod is divided into x segments, each of length b. According to the conventional lattice theory, the size of segments is such that each of them occupies one cell of the lattice. An ensemble of n_2 randomly oriented rodlike molecules in the flow field possess an additional free energy ΔG_{F}, compared to the quiescent solution, given by

$$\Delta G_{\mathrm{F}} = 2\xi n_2 \langle \sum_{m=1}^{x/2} \phi(r_m)|_0^{\psi} \rangle \tag{1}$$

where r_{m} denotes the location of the m'th segment relative to the origin, ξ is the friction coefficient, ϕ is the velocity potential and ψ is the angle which the rigid rod makes with respect to a preferred orientational axis which is the direction of the elongation flow. Angular brackets in Eq. (1) denote the ensemble average over all possible orientations, and the subscript F indicates flow. The potential for the m'th segment is derived as [18]

$$\phi(r_m) = \frac{1}{4}\Gamma(mb)^2(3\sin^2\psi - 2) \tag{2}$$

When Eq. (2) is substituted into Eq. (1), the expression for the free energy due to elongational flow is obtained as

$$\Delta G_{\mathrm{F}} = \frac{1}{16} n_2 \xi \Gamma b^2 (x^3 + 3x^2 + 2x)\langle \sin^2\psi \rangle \tag{3}$$

where Γ is the stretching rate.

3. The total free energy

The change in free energy, ΔG, due to mixing and flow of a system of block copolymers consisting of rodlike and flexible sequences in solution is obtained by addition of the free energy due to elongational flow ΔG_{F} and the Gibbs free

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