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

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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.

Keywords: Lattice model; Orientation; Extensional flow

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

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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

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

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

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

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 energy of mixing:

$$\begin{aligned}\frac{\Delta G}{RT} &= n_1 \ln v_1 + n_2 \ln(v_2/\bar{x}) + (n_1 + \bar{x}n_2)[(1 - 1/\bar{x})v_2 \\ &\quad - (1 - Q)\ln(1 - Q) - Q - v_c \ln z_c + \chi v_1 v_2] \\ &\quad - nn_2(\ln \bar{y}^2 + C) + \frac{1}{16} nn_2 \xi \Gamma b^2 (x^3 + 3x^2 \\ &\quad + 2x)\langle \sin^2\psi \rangle \end{aligned} \tag{4}$$

where v_1 and v_2 denote the volume fraction of solvent and solute molecules, respectively, n_1 and n_2 are their corresponding number of molecules. We consider only a monodisperse system in which all the chains have equal length. Each chain has n rodlike blocks and n coiled blocks. $\bar{x}$ is the total length of the chain, $v_h = \theta_h v_2$ and $v_c = (1 - \theta_h)v_2$ are the volume fractions of rigid and random coiled segments, respectively. θ_h is the fraction of rigid segments in all solute molecules, $v_2 = v_c + v_h$ is the volume fraction of the solute in the mixture, and

$$Q = v_h(1 - \bar{y}/x) \tag{5}$$

where $\bar{y}$ is the average disorientation for all sequences and x is the length of a rodlike sequence. In Eq. (4), z_c is the internal configuration partition function for a coil segment relative to $z_h = 1$ for a rodlike segment and χ is the familiar interaction parameter. In the limit of small average disorientations, C is given by $C = 2\ln(\pi e/8) = 0.131$. The elastic free energy of the coiled parts have not been included in Eq. (4) in as much as they do not induce additional orientation in the rodlike sections.

The expected number of situations accessible to the jth solute molecule added to the lattice is obtained as

$$\begin{aligned} v_j &= \left(n_0 - \sum_1^{j-1} x_i\right) \\ &\quad \times \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0}\right]^{x_j^c + y_j - 1} \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0 - \sum_1^{j-1}(x_i^h - y_i)}\right]^{x_i^h - y_j} \end{aligned} \tag{6}$$

where n_0 is the total number of sites in the lattice, y_i which also serves as a measure of disorientation of molecule i along the preferred axis, is the number of sub-sequences required to make the rodlike sections of molecule i conformable to the cubic lattice. x_j^c and x_j^h are the numbers of random coil and rigid segments, respectively. For n_2 molecules, this equation becomes

$$v_{n_2} = \frac{n_0(1 - v_2)^x}{[1 - v_2 + v_2(\sum y_i/xn_2)]^x}[1 - v_2 + v_2(\sum y_i/xn_2)]^y \tag{7}$$

where

$$\sum_1^{n_2} y_i$$

is given as

$$\sum_1^{n_2} y_i = \theta_h \bar{x} n_2 \left(\frac{\bar{y}}{x}\right) \tag{8}$$

The final form of Eq. (6) becomes

$$v_{n_2} = \frac{n_0(1 - v_2)^x}{[1 - v_2 + v_2(\bar{y}/x)]^x}[1 - v_2(1 - \bar{y}/x)]^y \tag{9}$$

The orientation distribution n_{2y}/n_2 at the equilibrium disorder is obtained as

$$\frac{n_{2y}}{n_2} = A\exp(-\alpha \sin\psi)w_y \tag{10}$$

where A is the denominator in Eq. (10), and w_y is the a priori probability for the interval of orientations associated with disorientation index y. It is given by

$$w_y = \sin\psi \frac{d\psi}{dy} \tag{11}$$

The relationship between ψ and y is as

$$y = \left(\frac{4x}{\pi}\right)\sin\psi \tag{12}$$

Previously, [18], the form of the constant A in Eq. (10) was found to be

$$A \approx f_n = \int_0^{\pi/2} \sin^n\psi \exp(-\alpha \sin\psi)\, d\psi \quad (n = 1, 2, \ldots) \tag{13}$$

α in Eq. (10) is

$$\alpha = \frac{-4}{\pi} x \ln[1 - v_2(1 - \bar{y}/x)] \tag{14}$$

Eq. (10) is the form of the orientation distribution and Eq. (14) gives α for no flow. In case of flow, there will be an additional term for α. To find this additional term, Eq. (4) can be differentiated with respect to y and equated to zero to get the orientation distribution n_{2y}/n_2 at equilibrium. The form of the orientation distribution is the same as Eq. (10), but the new form of α becomes

$$\begin{aligned}\alpha &= \frac{-4}{\pi} x \ln[1 - v_2(1 - \bar{y}/x)] + \frac{1}{16}\xi \Gamma b^2 (x^3 + 3x^2 \\ &\quad + 2x)\sin\psi \end{aligned} \tag{15}$$

The average $\langle \sin^2\psi \rangle$ required to calculate the flow energy term in Eq. (3) is obtained as

$$\langle \sin^2\psi \rangle = f_3/f_1 \tag{16}$$

where f_3 follows from Eq. (13) with $n = 3$.

4. Chemical potentials and conditions for phase equilibrium

The chemical potential of the solvent obtained by differentiation of Eq. (4), with y assumed to have its equilibrium value so that $\partial \Delta G/\partial y = 0$, is

$$(\mu_1 - \mathring{\mu}_1)/RT = \ln v_1 + (1 - 1/x)v_2 - \ln(1-Q) - Q + \chi v_2^2 \tag{17}$$

where μ_1 is the chemical potential of the solvent. The chemical potential of the solute obtained similarly by differentiating Eq. (4) with respect to n_2 is

$$\begin{aligned}(\mu_2 - \mathring{\mu}_2)/RT &= \ln(v_2/x) + (1 - 1/\bar{x})xv_2 - [x - (x \\ &\quad - y)\gamma_{x>y}]\ln(1-Q) - Qx + x(n-1)\ln z_c \\ &\quad - \gamma_{x\le y}\ln x^2 - (\ln y^2 + C)\gamma_{x>y} + x\chi v_1^2 \\ &\quad + \frac{1}{16}\xi \Gamma b^2(x^3 + 3x^2 + 2x)\frac{f_3}{f_1}\end{aligned} \tag{18}$$

where μ_2 is the chemical potential of the solute. In Eq. (18), we introduced the notation $\gamma_{x>y}$ and $\gamma_{x\le y}$ denoting the number of rigid rods in a chain with $x>y$ and $x \le y$, respectively. The orientational distribution function changes with increasing G or increasing flow rate. For some values of v_2, the system separates into two phases. Conditions for phase equilibrium are

$$\mu_1' = \mu_1 \quad \mu_2' = \mu_2 \tag{19}$$

The ordered and disordered phases are distinguished by appending a prime to quantities for the disordered phase where distinction is required. By the application of phase equilibrium conditions, two equations are acquired.

$$\begin{aligned}\ln[(1 - v_2')/(1 - v_2)] &= (1 - 1/\bar{x})v_2 - (1 - 1/\bar{x}')v_2' - 1 + 2/y \\ &\quad + \exp(-2/y) + \chi v_2^2 - \chi'(v_2')^2\end{aligned} \tag{20}$$

$$\begin{aligned}\ln[(1 - v_2')/(1 - v_2)] &= x[(1 - 1/\bar{x})v_2 + (1 - 1/\bar{x}')v_2' + 1 - 2/y \\ &\quad - \exp(-2/y) - \chi(1 - v_2)^2 + \chi'(1 - v_2')^2] \\ &\quad - \gamma_{x>y}[2(x/y - 1) - 2\ln(x/y) + C] \\ &\quad - \frac{G}{2}(x^3 + 3x^2 + 2x)\frac{f_3}{f_1}\end{aligned} \tag{21}$$

where the flow parameter G is defined as

$$G = \frac{1}{8}\xi \Gamma b^2 \tag{22}$$

The flow parameter is proportional to the flow field Γ.

4.1. Procedure for solving Eqs. (20) and (21)

The Eqs. (20) and (21) were solved by an iterative method using two loops; one of these loops increments v_2 and the other increments v_2'. Another loop is used within these two loops that calculates the value of y for each v_2 and v_2'. $\bar{x}$ and $\bar{x}'$ are set equal to each other and kept constant throughout the calculations of each system, assuming the same average dimensions in the isotropic and anisotropic states. Similarly χ and χ' were set equal to each other. (χ and χ' were always set to '0' except the first figure in which χ is the changing parameter). The ratio f_3/f_1 was calculated from Eq. (13) using quadrature integration. All the terms in Eqs. (20) and (21) were taken to the lefthand side and the errors were calculated. Care was taken to check that all solutions are the real solutions at which the error changes sign from positive to negative or vice versa, for both equations.

5. Results

Numerical calculations of phase equilibrium are performed for two systems of block copolymers: The first system consists of $\bar{x} = 15$ with rod length of $x = 10$ and coil length of $x_c = 5$ repeat units. For this system, calculations are performed for $n = 1$, 3, and 5, where n = number of blocks (= number of coils) in a chain. The second system consists of $\bar{x} = 20$, with $x = 15$ and $x_c = 5$ repeat units. For this system, n is again taken as 1, 3, and 5. The notation used in the paper is presented in Table 1.

In order to see the effects of the polymer solvent

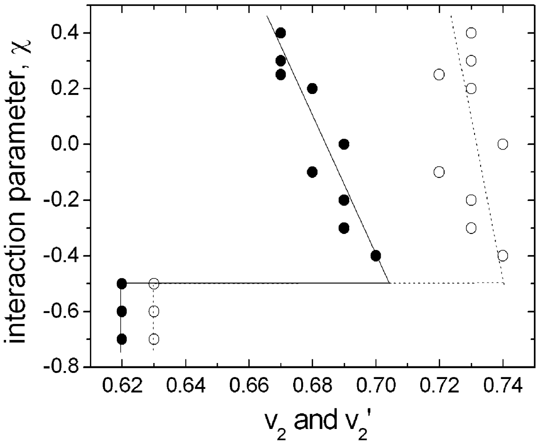

Fig. 1. Phase diagram for a binary system consisting of a solvent and a solute having single, rodlike sequence with axial ratio 15 and appended tail of a coil with five repeat units.

Table 1
Notation used for the different block copolymers used in calculations

Sample	$\bar{x}$	x	x_c	n
A1	15	10	5	1
A3	45	10	5	3
A5	75	10	5	5
B1	20	15	5	1
B3	60	15	5	3
B5	100	15	5	5

interaction parameter χ on phase equilibrium, calculations are first performed for different values of χ for sample B1 in the absence of flow. Results of calculations for the other samples in the absence of flow showed similar tendencies, and hence are not presented. Results of calculations for B1 are presented in Fig. 1. The ordinate denotes the χ parameter, and the abscissa denotes the volume fraction of polymer, the primed quantities denoting the more concentrated phase. The filled circles indicate the values for the less concentrated phase, and the unfilled circles are for the more concentrated phase. The solid and dashed lines are drawn through the calculated points to guide the eye. The scatter in the points show the degree of accuracy in simultaneously finding the roots of Eqs. (20) and (21). The parameter χ is taken to be the same in the two phases (i.e. $\chi'=\chi$) is plotted against the volume fractions v_2 and v'_2 of solute in two phases.

The biphasic region in Fig. 1 shows a sharp narrowing for $\chi\leq-0.5$. For larger values of χ, ie. as the solvent becomes poorer, the biphasic region becomes wider, as can be seen from the figure.

Fig. 2 shows the phase diagrams of the two systems A1 and B1 on which flow is applied. The ordinate in Fig. 2 is the flow parameter G and the abscissa is the volume fraction of rods.

The curves denote the biphasic boundaries, the filled circles indicate the less concentrated phase, and the empty circles are for the more concentrated phase. For the system B1, the biphasic region terminates at the top at $G=0.10$. Inside the curves, the system consists of two anisotropic phases in equilibrium. Outside, the systems consist of a single anisotropic phase, the anisotropy resulting from the orientation of the chains due to flow. Although the curve for the system B1 in which $\bar{x}=20$ intersects the x-axis (i.e. there is a biphasic region when there is no flow), there is no phase separation for the zero flow case for the system A1 in which $\bar{x}=15$. This is shown in more detail in the inset of Fig. 2. For both systems A1 and B1, the biphasic region shifts towards lower values of v_2 with increasing flow. The largest shift in the biphasic region towards more dilute solutions takes place at very low flow fields, as may be verified from Fig. 2. Stated in another way, a very small perturbing flow field generates strong changes in the phase stability of such materials. The v_2 values for which the system is phase separated are significantly smaller for the system B1 than the system A1.

It can be seen from a comparison of Figs. 2 and 3 that the biphasic regions are shifted to the right (to higher concentrations) as the number of rigid blocks in the chain increases from 1 to 3. One also observes that the equilibrium behavior of the two systems is not the same. For the system B3, there is a solution of Eqs. (20) and (21) for no flow (the curve begins on the x-axis). On the other hand, for the system A3, there is no solution of Eqs. (20) and (21) below $G=0.02$. The solutions of Eqs. (20) and (21) for A3 exist only for very large flow parameter values (on the order of 10^{-2}).

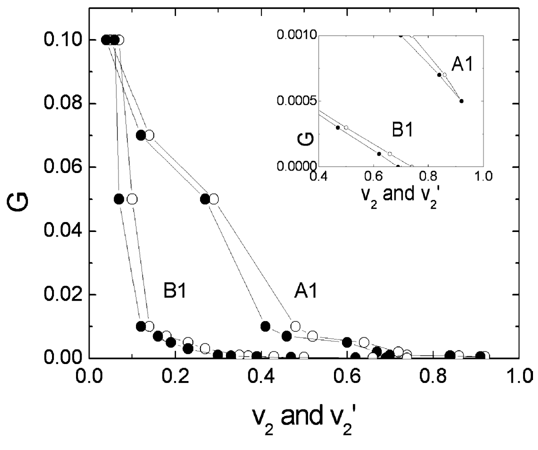

Fig. 2. Flow parameter G vs. polymer volume fractions for a binary system consisting of a solvent and a solute for samples A1 and B1.

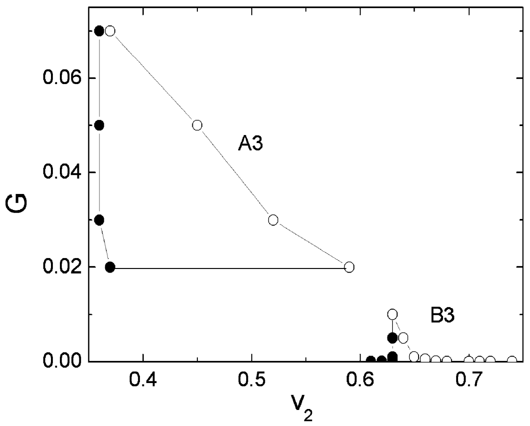

Fig. 3. Flow parameter G vs. polymer volume fractions for a binary system consisting of a solvent and a solute having three rodlike sequences with $\bar{x}=45$ (sample A3) and another with $\bar{x}=60$ (sample B3).

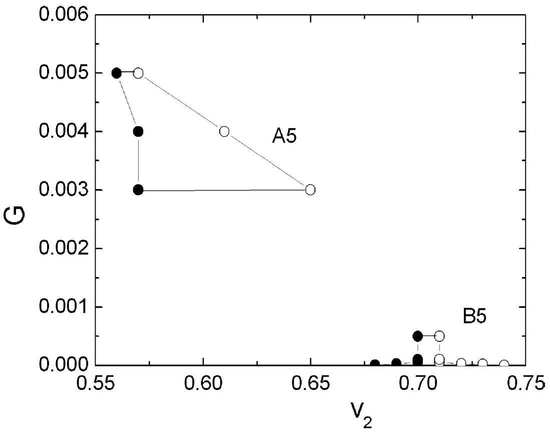

Fig. 4. Flow parameter G vs. polymer volume fractions for a binary system consisting of a solvent and a solute having five rodlike sequences with $\bar{x}=60$ (sample A5) and another with $\bar{x}=100$ (sample B5).

Fig. 4 shows the same systems, but this time there are five rodlike sequences and randomly coiled units that are connected to each other. Both curves are shifted to higher volume concentrations than the systems shown in Figs. 2 and 3. For the system A5 in Fig. 4, a biphasic region is calculated for values of G in the range 3–5×10^{-3}. Outside of this range, the system is anisotropic and single phase. The area within the curves for A5 is smaller than its counterpart A3 of Fig. 3. For the system B5, with largest molecular length $\bar{x}=100$, the solutions to Eqs. (20) and (21) were found only for small flow parameters, the results of which are shown in Fig. 4. Biphasic phase equilibrium is observed for $G=0$ as may be seen from the figure.

6. Orientation function

The orientation function S is defined as

$$S=\frac{1}{2}(3\langle\cos^2\psi\rangle-1) \qquad (23)$$

where $\langle\cos^2\psi\rangle=1-f_3/f_1$. Results of the orientation function calculations for the system B1 in which the axial ratio of the rigid sequence is $x=15$ and $x_c=5$ are shown in Fig. 5. The orientation function is plotted against flow parameter for two different concentrations, for $v_2=0.1$ and 0.2. For the curve corresponding to $v_2=0.1$, the biphasic region occurs between $0.025\leq G\leq 0.05$, as may be verified from Fig. 2. The value of G at the onset of phase separation is marked by the arrow on the left in the figure. The termination of the biphasic region is indicated with the arrow on the right. At the onset of phase separation, the orientation function $S=0.6$. At the end of the phase separated region marked by the arrow at the right in Fig. 5, $S=0.95$. One therefore sees that there is already a significant degree of anisotropy ($0\leq S\leq 0.6$) in the single phase region before bipahasic region starts. For $G\geq 0.05$, the material is again in the single phase region, and $S\geq 0.95$.

For $v_2=0.2$, the biphasic gap is very narrow, starting at $G=0.004$ and extending up to only $G=0.006$, as can be seen from Fig. 2. The value of S for $G=0.004$ is already as large as 0.90. Fig. 5 shows that the main body of segmental orientation takes place either before the biphasic region is entered or within the biphasic region.

In Fig. 6, results of calculations of the orientation function S against flow parameter G are presented for the system A1 ($x=10$, $x_c=5$) for three different volume fractions of the polymer. The arrows on each curve indicate the termini of the biphasic regions. For the curve corresponding to $v_2=0.5$, three different regimes are observed. The first corresponds to the range $0<G<6\times 10^{-3}$. In this region, S increases abruptly from 0 to 0.2. This region corresponds to the single phase, anisotropic region as can be seen from Fig. 2. In the region $6\times 10^{-3}<G<10^{-1}$, S increases from 0.2 to about 0.9. This region extends through the biphasic region as can be verified from Fig. 2. Above $G=0.01$, the system is single phase and highly anisotropic with $G>0.9$. When $v_2=0.3$, the biphasic region starts at $G=0.04$ and ends at $G=0.048$. When $v_2=0.2$, the

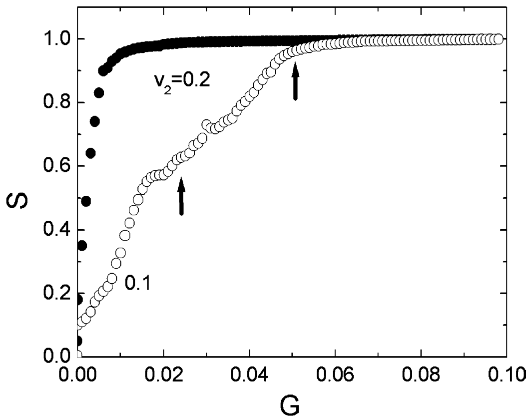

Fig. 5. Orientation function S calculated as a function of the flow parameter G for the indicated volume fractions of the polymer, for the system B1 in which the axial ratio of the rigid sequence is $x=15$ and $x_c=5$.

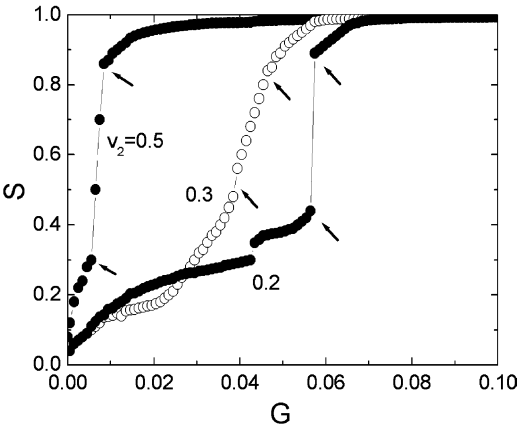

Fig. 6. Orientation function S calculated as a function of the flow parameter G for the indicated volume fractions of the polymer, for the system A1 in which the axial ratio of the rigid sequence is $x=10$ and $x_c=5$.

orientation function makes a large jump at $G=0.058$ which corresponds to exactly the onset of biphasic regime as can be verified from Fig. 2.

7. Conclusion and discussion

All rodlike sytems exhibit phase transitions and self organization at suitable compositions and temperatures. However, rod-coil block copolymers may not exhibit self-organization at equilibrium conditions due to the presence of coils that have large conformational entropies. One needs to impose an external orientational field that helps orient the rodlike components. The entropy decrease associated with the orientation of the rodlike components then counterbalances the excess entropy coming from the presence of the unoriented coils. An elongational flow field imposed on a stationary solution of such systems is one possibility, and is employed in the present work. In the lattice model of Matheson and Flory, the system consists of rigid sequences whose lengths and locations are fixed by its structure within each macromolecule. These sequences are separated by various numbers of random coiled units. As an extension of the Matheson–Flory model, here an excess free energy other than the equilibrium Gibbs free energy is introduced by an elongational flow field. Depending on the magnitude of the flow, it is shown that biphasic states, which are not attainable at equilibrium, may be reached under flow. The effects of composition, polymer–solvent interaction, size of the co-polymer and flow rates on phase transitions are investigated. Dependence of the shape and concentration of biphasic regions on the interaction parameter between solvent and polymer are demonstrated. 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. In general, very small values of flow velocities result in large changes in the phase behavior of the systems studied. The degree of orientation is studied in reference to flow, concentration and biphasic conditions. Orientation of the rodlike components increases sharply if the system is biphasic. For larger flows, where the system turns into an anisotropic single phase system, the value of the orientation function becomes very close to unity that is perfect orientation.

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