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Deformation induced hydrophobicity: implications in spider silk formation

Ashish K. Lele[a,1], Yogesh M. Joshi[a], R. A. Mashelkar[b,*]

[a] *Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India*
[b] *Council of Scientific and Industrial Research, Anusandhan Bhavan, New Delhi 110 001, India*

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Abstract

A theoretical framework, which considers the effect of strong inter-polymer associations on phase separation of a deforming polyacrylamide solution is presented. It is shown that deformation induces effective hydrophobicity in the stretched polymer chains resulting in the formation of strong cooperative hydrogen bonding between the polymer chains. This finding has implications in providing insights into the mechanisms of the way spiders spin silk by rapidly deforming a freshly secreted protein solution. It has been argued that in a manner analogous to the model system showed here, it is likely that a rapid deformation induces phase separation of the solution into a polymer rich phase, which eventually forms the fiber. This work also naturally provides strategic hints for making silk like strong fibers by synthetic means at mild conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Associating polymer solutions; Flow induced separation; Hydrophobicity and hydrogen bonding

1. Introduction

There is a growing interest in spider silk because of its exceptional mechanical and thermal properties. The spider silk is thermally stable to 230°C. Further, the modulus and tensile strength of spider silk threads are comparable to some of the strongest man-made fibres (Kitagawa & Kitayama, 1997). The strength of the fiber lies in stronger inter-polymer associations such as hydrogen bonding between the protein chains. However, the most interesting aspect about the 300 million year old technology of making silk is that the process involves very mild processing conditions such as an aqueous medium and takes place at room temperature. This is in sharp contrast to the extreme processing conditions, such as very high temperature, corrosive and toxic solvents, etc. that are required for making man-made fibers. Nature can indeed provide important clues in understanding how stronger fibers could be synthesized from milder processing conditions. The reader is referred to the recent paper of Vollrath and Knight (2001) and the references therein for a detailed discussion on the exciting potential of 'synthetic' spider silk, its properties, applications and production.

Spider silk is, however, a complex fiber involving many different layers of structural morphologies. For example, at a molecular level the fiber consists of strongly associated protein chains, while at a mesoscopic level the fibers cooperatively form beta-sheets containing tiny crystallites staggered in between amorphous oriented regions (Kummerlen, van Beek, Vollrath, & Meier, 1996). Recent studies have tried to investigate which amino acid sequences could be responsible for the formation of the beta-sheets (Fukushima, 2000). Dragline silk fiber also contains nanofibrils, bundles of nanofibrils, helical structures and a layered structure containing crossangle between the nanofibril sheets (Putthanarat, Stibeck, Fossey, Eby, & Adams, 2000). The basic mechanism of fiber formation has been a subject of intense investigation, but some mysteries have remained unresolved.

The best way to describe the concerns is by quoting some of the most recent literature. We quote from a recent publication by Fox (1999), "But how does the spider transform this mix of water and protein into a fiber that isn't washed away by the rain?… freshly made

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[*] Corresponding author. Tel.: +91-11-371-0472; fax: +91-11-371-0618.

E-mail address: dgcsir@csir.res.in (R. A. Mashelkar).

[1] Current address: Chemical Engineering Department, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK.

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spidroin balls (i.e., concentrated protein solutions secreted by the spider) are stable in water because their charged, water-loving parts are on the outside, while their uncharged water-hating segments are hidden inside. But then something extraordinary happens. The curled-up proteins must straighten out, to reveal their water-hating interiors, and in the process transform into insoluble nanocrystals". A further clue to the mechanism of 'straightening out' of protein molecules has been provided recently by Knight and Vollrath (1999) who indicate that the elongational flow occurring in the gland ducts may be important in destabilizing the spidroin balls and that the high rate of elongation may fold the spidroin, 'squeezing' the water out. This work clearly hints that firstly, the opening-up of the proteins exposes the hydrophobic interior and hides the hydrophilic exterior, thus rendering the protein insoluble. Secondly, the elongational flow plays a crucial part in making this happen. An even more recent reference by Vollrath and Knight (2001) describes the key role played by deformation-induced phase separation process in spider silk formation. We quote from Vollrath and Knight (2001). "The high stress forces generated during this stage of processing probably bring the dope molecules into alignment and into a more extended conformation, so that they are able to join together with hydrogen bonds like zip fasteners to give the anti-parallel beta conformation of the final thread. As the silk protein molecules aggregate and crystallize, they will become more hydrophobic, which should induce phase separation and hence the loss of water from the surface of the solidifying thread".

One of the ways by which we can understand the basic mechanism of silk fiber formation is to examine a much simpler model system, say of a linear flexible polymer chain, which also has hydrophilic and hydrophobic groups and which can be stretched in an elongational flow field. One would then expect that by a similar mechanism, a soluble polymer chain, on extending in an elongational flow field, would undergo phase transition into a solid fiber, which will be essentially insoluble. Fortunately, we do have experimental data on model systems displaying these basic features.

For instance, deformation induced fiber formation has been experimentally observed for aqueous polyacrylamide (PAm) solution. Metzner, Cohen, and Rangel-Nafail (1979) observed that when an aqueous PAm solution was forced through a porous disc, fibers were formed which could not be re-dissolved in water or any other stronger solvents such as aq. solution of 2 N NaCl or 2 M urea, even when boiled. The X-ray data for these fibres provided by Rangel-Nafail (1982) in fact points out the existence of a "stretched and highly oriented structure" and attributes the phenomena to "an interesting morphological structure developed by the way molecules aggregate". The mechanism for forming such "an oriented and stretched structure" and also a "molecular aggregate", has not, however, been explained. In an even more direct suggestion, a possible physical mechanism was proposed by Ferguson, Hudson, Warren, and Tomatarian (1987) on the basis of a very simple experiment, in which a drop of an associating polymer solution (A copolymer of t-butyl styrene-and a monomer containing *associating* groups also called the 'FM9 copolymer' in dipropylene glycol monoethylether) was allowed to fall under its own weight from a burette and the resulting thread was observed by polarized microscopy. The authors observed that the elongational flow affected a phase separation, in which the polymer rich phase forming the inner core was surrounded by the solvent rich phase. The solvent evaporated rapidly to leave a thread of solid polymer behind. The authors speculated that spiders use a similar process of deformation induced association and phase separation for synthesizing the silk. The similarities between the formation of PAm fibres, the work of Ferguson et al. (1987) on associating polymers, and the phenomenon involved in the formation of spider silk are strikingly similar and suggest (the existence of at least same) common underlying physical phenomena.

Fig. 1 shows a schematic of polymer chains undergoing strong deformation. It is possible that sufficient stretching of the chains induces a "zipping" of hydrogen-bonds between polymer chains due to proximity, orientation and cooperativity. Strong inter-polymer associations such as these can possibly drive phase separation since the polar groups on the chains will no longer be available for association with the solvent molecules. Moreover, only the relatively hydrophobic main chain of the polymer will be exposed to the solvent. This can perhaps explain why the PAm fibers observed by Metzner et al. (1979) could not re-dissolve in water.

In this paper, we build a theoretical model based on the above picture for the PAm solution. We begin by using the concept of a flow-induced semi-flexible chain as has done by Vrahopoulou-Gilbert and McHugh (1984), who used the original theory of Flory (1956) for semiflexible

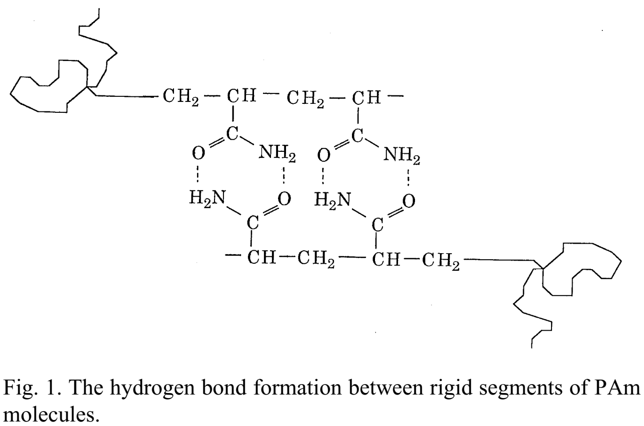

Fig. 1. The hydrogen bond formation between rigid segments of PAm molecules.

chains. We build upon this concept by also incorporating hydrogen-bonding interactions and deformation-induced enhancement of hydrophobicity of the polymer. We show that both flow induced hydrogen-bonding and hydrophobicity can affect phase separation of the PAm solution. The theory outlined here is based on mean-field approximation, which implies that long range order is not described. Thus, the phase separation predicted by the theory is not due to the phenomenon such as flow induced crystallization.

We realize that the use of an equilibrium approach in any deforming system is not sound (Larson, 1992; Agarwal, Dutta, & Mashelkar, 1994). However, in the absence of a simpler theoretical formalism that can bring together the contradictory concepts of equilibrium thermodynamics and non-equilibrium flows, we have chosen to make an engineering approximation by assuming that instantaneous equilibrium conditions exist even in deforming flows. We argue that the local association of functional groups during flow would occur in a very short time scale, since they involve rapid segmental motions as compared to the time scales of the flow itself.

2. Theory

Following Vrahopoulou-Gilbert and McHugh (1984), we begin by considering that deformation (Strong shear or extension) causes a stretching of macromolecular coils, the extent of which is determined by the intensity of the flow. Thus, the state of the solution under investigation is that of semiflexible (stretched) coils mixed with the solvent molecules. Following Flory (1956), the reference states are considered to be pure solvent and pure ordered polymer chains. The total change in free energy in the path consisting of firstly disordering the chains, followed by stretching them (deformation) and finally mixing them with solvent molecules is

$$\Delta G = \Delta G_d + \Delta G_{\mathrm{mix}}, \tag{1}$$

where ΔG_d is the free energy change associated with disorientation and deformation, while ΔG_{mix} is the free energy change associated with mixing the polymer chains with solvent molecules. The free energy of mixing can be considered to be given by

$$\Delta G_{\mathrm{mix}} = \Delta G_{\mathrm{I.F}} + \Delta G_{HB}, \tag{2}$$

where ΔG_{HB} is the free energy change associated with hydrogen-bonding interactions, which are over and above the mean-field nearest neighbor van der Waal like interactions that are considered in the ΔG_{LF} term. Eq. (2) follows from the assumption that the partition function for the lattice-fluid (LF) interactions and that for the hydrogen-bonding interactions can be de-coupled. (Panayiotou & Sanchez, 1991).

The ΔG_d term is given by the Flory's theory of semiflexible polymer, wherein a fraction $f n_2(X-2)$ of the bonds in the chains are allowed to be placed randomly on the lattice while the rest are constrained to be placed in a linear manner. Here f is the flexibility of the polymer molecule, n_2 is the number of polymer molecules and X is the degree of polymerization. Assuming monodisperse polymers, ΔG_d is given by

$$\begin{aligned} \Delta G_d = RT \Bigg[& -n_2 \ln\left(\frac{Xz}{2}\right) + n_2(X-1) + n_2(X-2) \\ & \times \Bigg\{ f\ln(f) - (1-f)\ln(1-f) \\ & -f\ln(z-2) + \frac{f\varepsilon}{kT} \Bigg\} \Bigg], \end{aligned} \tag{3}$$

where R is the gas constant, k is the Boltzmann's constant, T is the absolute temperature, z is the lattice co-ordinate number ($z \sim 6$) and ε is the energy by which the sites containing the linear sequences of monomer links is more than the lattice energy.

ΔG_{LF} is calculated as per mean field approximation in which the interactions other than hydrogen-bonding are considered as nearest neighbor interactions for calculating the lattice energy. We assume ΔG_{LF} to be Flory–Huggin's expression.

$$\Delta G_{LF} = RT[n_1 \ln(\phi_1) + n_2 \ln(\phi_2) + \chi n_1 \phi_2]. \tag{4}$$

Here n_1 is the number of solvent molecules, ϕ_1 and ϕ_2 are volume fractions of solvent and polymer units and χ is the Flory–Huggin's interaction parameter representing interactions other than hydrogen bonding.

The contribution from hydrogen bonding interactions ΔG_{HB} is calculated following the development of Panayiotou and Sanchez (1991), which has been successfully used by our own school (see, Lele, Hirve, Badiger, & Mashelkar, 1995, 1997; Badiger, Lele, Bhalerao, Varghese, & Mashelkar, 1998; Varghese, Lele, & Mashelkar, 2000) to understand the role of hydrophilicity and hydrophobicity in polymeric gels. Let there be i ($i = \mathbf{1}, m$) types of proton donors and j ($j = 1, n$) types of proton acceptors in the system. The total number of donors and acceptors are given by

$$N_d^t = \sum_k d_i^k n_k \quad \text{and} \quad N_a^j = \sum_k a_j^k n_k, \tag{5}$$

where d_i^k and a_j^k are the number of donors of type i and acceptors of type j in component k. Also n_k is number of molecules of component k. If N_{ij} are the total number of hydrogen-bonds formed between $i-j$ donor–acceptor pair, then number of undonated donors of type i and unaccepted acceptors of type j are given by

$$N_{i0} = N_d^i - \sum_j N_{ij} \quad \text{and} \quad N_{0j} = N_a^j - \sum_i N_{ij}. \tag{6}$$

If E_{ij}^0, S_{ij}^0 and V_{ij}^0 are the changes in energy, entropy and volume due to formation of an $i-j$ hydrogen-bond, then the fraction of $i-j$ bonds formed is given by

$$v_{ij}=\left[v_d^i-\sum_k^n v_{ik}\right]\left[v_a^d-\sum_k^m v_{kj}\right]\exp\left(-G_{ij}^0/RT\right), \quad (7)$$

where

$$\begin{aligned}v_{ij}&=\frac{N_{ij}}{(n_1+Xn_2)},\\ v_d^i&=\frac{N_d^i}{(n_1+Xn_2)},\\ v_d^j&=\frac{N_a^j}{(n_1+Xn_2)},\\ G_{ij}^0&=E_{ij}^0+PV_{ij}^0-TS_{ij}^0.\end{aligned} \quad (8)$$

The free energy contribution ΔG_{HB} is given by

$$\Delta G_{HB}=RT(n_1+Xn_2)\times\left\{\sum_i\sum_j v_{ij}+\sum_i^m v_d^i\ln\left(\frac{v_{i0}}{v_d^i}\right)+\sum_i^m v_a^j\ln\left(\frac{v_{0j}}{v_a^j}\right)\right\}. \quad (9)$$

The cooperativity in inter-polymer hydrogen bonding should be related to the entropy change ($-\Delta S_{ij}^0$). If the rigid (linear) sequences of two polymer chains come close within the certain bond forming distance, the loss in entropy during cooperative zipping of hydrogen bonds is expected to be small since the groups are forced to be close to each other. Comparatively, the entropy change associated with the bonding between disoriented segments of the chains is expected to be much greater.

In the above formalism, the interactions represented by χ can be considered as representing the effective 'hydrophobicity' of the polymer chains since the hydrophilic interactions are considered separately through the hydrogen bonding terms. In terms of the physical picture represented by Fig. 1, we propose that the hydrophobicity of the polymer chains increases on stretching the chains since the polar solvent is exposed mainly to the hydrophobic backbone of the chain. We therefore assume that the interaction parameter can be given by

$$\chi=\chi_0+\alpha f, \quad (10)$$

where χ_0 and α are model parameters.

Finally the extent of chain stretching given by $(1-f)$ can be linked to the intensity of the deformation by comparing the root mean square (RMS) end to end distance of the semiflexible chain with that given by an appropriately chosen rheological model. We consider shear flow as an example and assume that the polymer molecule can be modeled using elastic dumbbell model for sake of simplicity. The RMS end to end distance of a semiflexible chain is given by Flory's theory as

$$(Q\cdot Q)=Xl^2\frac{2-f}{f} \quad (11)$$

and that by the elastic dumbbell model as

$$(Q\cdot Q)=xl^2\left[1+\tfrac{2}{3}(\lambda\dot{\gamma})^2\right], \quad (12)$$

where λ is typical relaxation time of the dumbbell, l is the length of monomer unit and $\dot{\gamma}$ is scalar strain rate (second invariant of strain rate tensor). Comparing Eqs. (11) and (12) gives

$$f=\left[1+\tfrac{1}{3}(\lambda\dot{\gamma})^2\right]^{-1}. \quad (13)$$

In reality, the polymer rich phase might be better modeled by a transient network theory, for which the flexibility of the segment would be given by

$$f=2\left[1+\frac{G_0 g}{kTh}\left(1+\frac{2}{3h^2}\beta^2\right)\right]^{-1}, \quad (14)$$

where G_0 is entanglement modulus, while h and g are rates of network formation and loss, respectively and $\beta=\lambda\dot{\gamma}$ is the dimensionless shear rate. However, since inclusion of such a function complicates the computations, and since we are interested in qualitative predictions, we will prefer to use Eq. (13). We also propose that equations similar to Eqs. (12) and (14) above can be used for elongation flows, which despite being unsteady in a Lagrangian sense, can be considered to be steady in an Eulerian sense. Thus at every local position in an elongation flow, molecules would be assumed to experience a certain strain and hence an associated local extent of semi-flexibility.

At any given strain rate $\dot{\gamma}$ an 'equilibrium' value of f and ΔG will be reached which can be calculated by setting $\partial\Delta G/\partial f=0$. Using Eqs. (3), (4) and (9) it can be shown that the minimization yields

$$\alpha\phi_1+\ln\left(\frac{f}{(1-f)(z-2)}\right)+\frac{\varepsilon}{kT}+\frac{\partial\Delta G_{HB}}{\partial f}=0. \quad (15)$$

Substituting Eq. (15) in Eq. (3) and rewriting Eqs. (3), (4) and (9) in terms of dimensionalized excess free energy per unit volume, we get

$$\frac{\Delta G_{LF}/RT}{n_1+Xn_2}=\phi_1\ln(\phi_1)+\frac{\phi_2}{X}\ln(\phi_2)+(\chi_0+\alpha f)\phi_1\phi_2, \quad (16)$$

$$\frac{\Delta G_d/RT}{n_1+Xn_2}=\frac{\phi_2}{X}\left\{\ln(X)+\ln\left(\frac{z}{2e}\right)+(X-2)\times\left[\alpha\phi_1 f-\ln((1-f)e)+\frac{\partial\Delta G_{HB}}{\partial f}\right]\right\}-\phi_1\Delta G_{d,1}^0-\phi_2\Delta G_{d,2}^0, \quad (17)$$

$$\frac{\Delta G_{HB}/RT}{n_1 + Xn_2} = \sum_i \sum_j v_{ij} + \sum_i v_d^i \ln\left(\frac{v_{i0}}{v_d^j}\right)$$

$$+ \sum_j v_a^j \ln\left(\frac{v_{0j}}{v_a^j}\right) - \phi_1 \Delta G^0_{HB,1} - \phi_2 \Delta G^0_{HB,2}, \qquad (18)$$

where $\Delta G^0_{d,1}$ and $\Delta G^0_{d,2}$ represent the free energy due to disorientation and deformation of the pure solvent and the pure polymer, respectively. For pure solvent this term is zero and for pure polymer it can be obtained by inserting $n_1 = 0$ in Eq. (3) and equating it to zero. $\Delta G^0_{HB,1}$ and $\Delta G^0_{HB,2}$ represent hydrogen-bonding free energy of pure solvent and pure polymer. Eqs. (16)–(18), Eqs. (7) and (8) are the main equations of our model.

A rigorous solution of the above set of equations demands intense computational work since all the equations are highly non-linear and coupled. Our motivation in this work is not to provide a rigorous solution to the above set of equations, but mainly to demonstrate the possible existence and manifestation of the flow induced effective hydrophobicity of the polymer. Therefore, we propose here a simplified solution procedure, which although somewhat approximate, captures all the important insights into the main results of the paper. An approximate solution can be obtained by estimating the magnitudes of the individual terms in Eq. (15), which are shown in Fig. 2. It is seen that for low polymer volume fraction, which is really the domain of interest in this paper, the term $\partial \Delta G_{HB}/\partial f$ is small compared to the sum of the first two terms in Eq. (15) by about an order of magnitude. We therefore drop this term as a first approximation. This simplifies the set of equations to be solved as well as the solution procedure. The results described in the following section are based on this simplification.

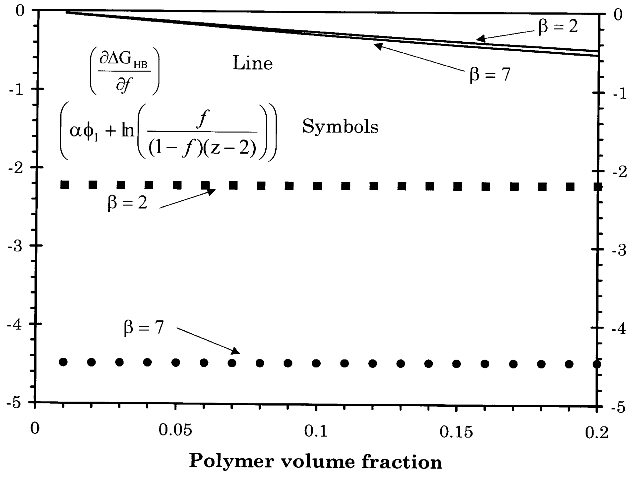

Fig. 2. Comparison of two terms in Eq. (15). The values of S_{ij}, E_{ij} and V^0_{ij} are as per given in Table 2. Also $T = 298$ K, $\alpha = -0.1$ and $X = 1000.0$.

3. Results and discussion

We will present results of our theory for the model system of aqueous polyacrylamide (PAm) solution. In our theory, the polymer–polymer and polymer–solvent interactions are dictated by the lattice fluid interactions (i.e. the non-hydrophilic interactions given by χ), the hydrogen bonding interactions (given by $E^0_{ij}, S^0_{ij}, V^0_{ij}$) and the deformation rate β. We will now consider the effect of these parameters on the phase behaviour of semiflexible PAm–water solution.

We assume that there are three types of proton donor groups and three types of proton acceptor groups in the deforming PAm–water solution as given in Table 1. The proton donor groups are the –NH_2 on the flexible segments of the chain, the –NH_2 on the rigid linear segments of the chain and the –OH groups on water. Similarly, the proton acceptor groups are the $-C=O$ group on the flexible segments, the $-C=O$ group on the rigid segments, and the –OH group on water. The hydrogen-bonding parameters (E_{ij}, V^0_{ij}, S_{ij}) are tabulated in Table 2. These parameters are selected so that PAm is ensured to remain soluble in water under no-flow conditions at all temperatures and concentrations as found experimentally. It is to be noted that there is no unique set of values for these parameters and that our choice is based on earlier reported values (Panayiotou & Sanchez, 1991) and on our own previous work on polyacrylamide-like polymers (Lele et al., 1995, 1997).

For a given value of β, the flexibility f is calculated using Eq. (13) and then the value of ΔG was calculated at various values of polymer fraction (ϕ_2) by solving Eqs. (16)–(18) and Eqs. (7) and (8). Under no flow condition ($\beta = 0$), the excess free energy ΔG was always negative and convex at all concentrations. However, as β

Table 1
Proton donors and acceptors in the system

i or $j =$	1 (rigid)	2 (flexible)	3 (solvent)
Proton donors (i)	$-NH_2$	$-NH_2$	$-OH$
Proton acceptor (j)	$-C=O$	$-C=O$	$-OH$

Table 2
Values of E_{ij}, V^0_{ij} and S_{ij} used in the model

i	j	$-E_{ij} \times 10^{-3}$(J/mol)	$-V^0_{ij} \times 10^6$(m^3/mol)	$-S_{ij}$(J/mol K)
1	1	3.24	0.85	5.0
1	2	3.24	0.85	15.0
1	3	10.5	0.85	7.8
2	1	3.24	0.85	15.0
2	2	3.24	0.85	13.65
2	3	10.5	0.85	7.8
3	1	12.0	0.85	15.8
3	2	12.0	0.85	15.8
3	3	16.595	4.2	10.6

was increased, free energy ΔG increased and also showed inflection points which corresponds to the spinodal points. Thus, the solution tends to phase separate with increasing β.

The chemical potentials of polymer μ_2 and solvent μ_1 were calculated by differentiating Eq. (1) with respect to number of moles of polymer and solvent, respectively. When the chemical potentials are plotted against polymer volume fraction, the maximum and the minimum values of μ_2 and μ_1 correspond to the spinodal points. The loci of all such spinodal points at various values of β will give a spinodal curve with respect to β. We will now present the effect of hydrogen bonding and hydrophobic parameters on the spinodal curves.

The entropy change for hydrogen-bond formation ($-\Delta S^0_{ij}$) between '$-NH_2$' donor and '$-C=O$' acceptors on the flexible segments of the chains is taken to be higher than that for the hydrogen bonding between the same groups of the rigid segments of the chains. The difference in the $-\Delta S^0_{ij}$ values between the flexible and the rigid segments indicate the effect of the 'cooperativity' of hydrogen bonding between rigid segments. The larger the difference, the larger is the effect of cooperativity. Fig. 3 shows spinodal curves for various values of entropy change associated with hydrogen-bond formation between two rigid segments. The entropy change for the hydrogen bonding between flexible segments is kept constant (at -13.65 J/(mol K)). It can be seen that as the difference between $-\Delta S^0_{ij}$ values for the flexible and rigid state is increased, spinodal shifts downwards. This implies that phase separation occurs more easily at smaller deformation rates. The shift in spinodal is significant, indicating the strong effect of cooperativity on phase separation.

It is possible to calculate the number of inter-polymer hydrogen bonds by solving the set of Eqs. (5)–(8). Fig. 4 shows the increase in number of hydrogen bonds with shear rate (β) at any polymer concentration. Fig. 4 also shows that the main contribution to the inter-polymer hydrogen bonds is from the cooperativity of the rigid segments. The number of inter-polymer hydrogen bonds between the flexible segments is comparatively much fewer. The theory predicts that the phase separation is a result of strong associations between the deforming polymer chains.

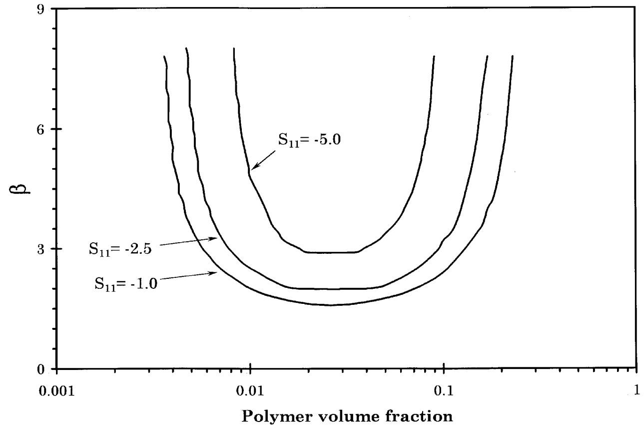

Fig. 3. Spinodal curves with respect to β for various values of S_{11}. The values of S_{ij}, E_{ij} and V^0_{ij} except S_{11} are as per given in Table 2. Also $T=298$ K, $\alpha=-0.1$, $X_0=0.4$ and $X=1000.0$.

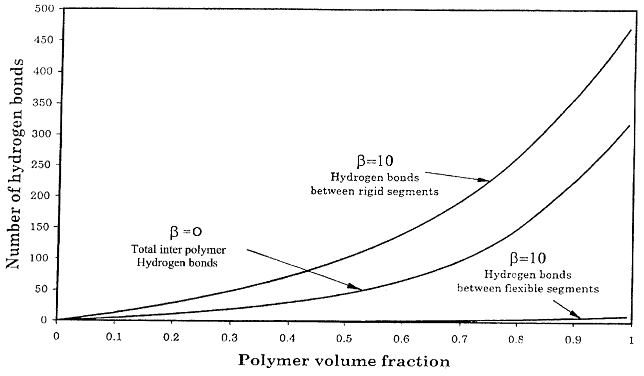

Fig. 4. Inter polymer hydrogen bonds Vs mole fraction of polymer for various values of β. The values of S_{ij}, E_{ij} and V^0_{ij} are as per given in Table 2. Also $T=298$ K, $\alpha=-0.1$, $\chi_0=0.4$ and $X=1000.0$.

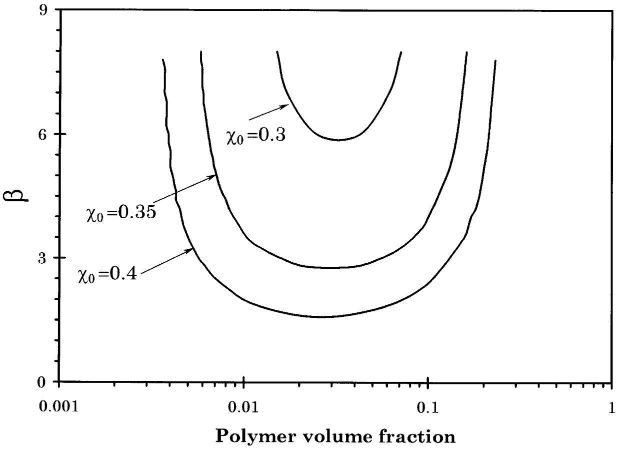

Fig. 5. Spinodal curves with respect to β for various values of χ_0. The values of S_{ij}, E_{ij} and V^0_{ij} are as per given in Table 2. Also $T=298$ K, $\alpha=-.0.1$ and $X=1000.0$.

For a given value of the lattice-fluid hydrophobicity parameter χ_0, phase separation occurs above a critical value of β as seen in Fig. 5. Increasing χ_0 causes the spinodal curve to shift vertically downwards and phase separation occurs at lower β. This is obvious since increasing the hydrophobicity will lead to greater inter-polymer interactions, thus driving the system closer to phase separation.

Finally, we would like to comment on some of the approximations in the present model and possible improvements in the current approach. It is important to note that in reality, the increase in inter-polymer hydrogen bonds would increase the effective hydrophobicity of the PAm molecule. Thus, the effect of hydrogen bonding and hydrophobicity is essentially coupled. However, the model described here inherently assumes a decoupling of the hydrogen bonding and other interactions. The essence of flow induced hydrophobicity is captured in our model by the parameter α, which in a more realistic but complex model should depend on the number of hydrogen bonds formed under the given experimental conditions. Further, the phase separation that is driven by flow will in turn affect the flow conditions. In essence, our model is applicable only until the point of *incipient phase separation stage*. The effects of phase separation on flow will start becoming dominant as the phase separation proceeds to form the polymer-rich and polymer-lean phases. We feel that upon phase separation the polymer-rich phase will take up most of the stress to form the fibre. Our model provides a preliminary foundation for incorporation of such complex effects.

4. Conclusions

We propose that an aqueous solution of flexible polyacrylamide molecules can be used as a model system for understanding the mechanism of formation of complex spider silk fibres. We have shown that deformation can induce strong cooperative interpolymer hydrogen bonds between stretched polymer chains. This can affect a phase separation of the solution above a critical value of dimensionless deformation rate. Further, the zipping of hydrogen bonds also increase the effective hydrophobicity of the chains, which can possibly prevent re-dissolution of the fibres in water. Our work also provides a potential explanation for the observation in the literature that PAm fibres could not redissolve in the solvent, in which PAm was earlier soluble. Our theory suggests that a polymer having a semiflexible configuration, strong proton donor and acceptor groups and a hydrophobic backbone can, in principle, show a tendency to form strong fibres. The semiflexibility can be induced physically by either strong shear/elongation flows, or chemically by copolymerizing flexible and rigid comonomers. This strategy can be adopted for making silk like strong fibres by synthetic means at mild conditions.

Notation

d_i^k	number of proton donors of type i in component k
E_{ij}^0	change in energy due to formation of an $i-j$ hydrogen-bond
f	flexibility of the polymer molecule
g	rate of network loss
G_0	entanglement modulus
ΔG	total change in free energy
ΔG_{d}	free energy change associated with disorientation and deformation
ΔG_{HB}	free energy change associated with hydrogen-bonding interactions
ΔG_{LF}	free energy change associated with the lattice-fluid (LF) interactions
ΔG_{mix}	free energy change associated with mixing
h	rate of network formation
k	Boltzmann constant
l	length of a monomer unit
n_1	number of solvent molecules
n_2	number of polymer molecules
n_k	number of molecules of component k
N_a^j	numbers of proton acceptors of type j
N_d^i	number of proton donors of type i
N_{0j}	number of unaccepted proton acceptors of type j
N_{i0}	number of undonated proton donors of type i
N_{ij}	total number of hydrogen-bonds formed between $i-j$ donor–acceptor pair
R	universal gas constant
S_{ij}^0	change in entropy due to formation of an $i-j$ hydrogen-bond
T	absolute temperature
V_{ij}^0	change in volume due to formation of an $i-j$ hydrogen-bond
X	degree of polymerization
z	lattice co-ordination number ($z \sim 6$)

Greek letters

α	model parameter in Eq. (10)
α_j^k	number of proton acceptors of type j in component k
β	dimensionless shear rate ($\lambda\dot{\gamma}$)
$\dot{\gamma}$	scalar strain rate (second invariant of strain rate tensor)
ε	energy by which the sites containing the linear sequences of monomer links is more than the lattice energy
λ	relaxation time of the dumbbell
ν_a^j	$\frac{N_a^j}{(n_1+Xn_2)}$
ν_d^i	$\frac{N_d^i}{(n_1+Xn_2)}$
ν_{ij}	$\frac{N_{ij}}{(n_1+Xn_2)}$
ϕ_1	volume fraction of solvent
ϕ_2	volume fraction of polymer units
χ	Flory–Huggin's interaction parameter
χ_0	model parameter in Eq. (10)
ν_{ij}	fraction of $i-j$ bonds formed

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