Relaxation of Silk Fibroin's Uncoiling Molecules in a Longitudinal Flow

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Abstract: The relaxation properties of strained chains of silk fibroin in a longitudinal flow have been studied. A birefringence in a longitudinal hydrodynamic field was used to determine the degree of uncoiling of fibroin molecules; antiparallel β-structure in the fibers was assumed. A comparative study of fibroin solutions in longitudinal flow demonstrated that uncoiling of the macromolecules is largely controlled by their initial conformational state, which is a function of the quality of the solvents used.

Key words: Uncoiling · relaxation · birefringence · longitudinal flow · silk fibroin solution

INTRODUCTION

Investigation of dynamic phenomena in solution of fiber-forming polymers is especially important for fiber spinning because the quality of the final products is largely controlled by the effects due to external force fields and the properties of the solvents. The goal of this study was to examine the effect of these factors on the uncoiling and relaxation behaviors of the macromolecules of silk fibroin in a longitudinal hydrodynamic field.

MATERIALS AND METHODS

The samples of silk fibroin were obtained in washing of silk cocoon from sericin and wax with used hot water and alcohol. The binary systems of LiCl in dimethylformamide (DMF) and NaNCS in water were used as solvents to the preparation of solutions.

During longitudinal flow of polymer solutions, the molecular chains sustain strong orientational and deformational action of the hydrodynamic field. In a certain range of rate gradients G, a dynamic phase transition occurs that leads to an anisotropic state of the macromolecules [1, 2]. Each polymer-solvent system is characterized by an inherent critical rate gradient G_{cr}, at which the macromolecules start uncoiling and the anisotropic state is formed. The multiplication of rate gradient (G_{cr}) and relaxation time (τ) of strained chains is constant size: $G_{cr}\tau \approx 0.5$ [2].

As is known, the mean degree of uncoiling of polymer chains <β> is determined from the reduced birefringence $\Delta n/\Delta n_\infty$ at different G

$$<\beta>^2 \approx \Delta n/\Delta n_\infty \qquad (1)$$

where; Δn is the birefringence of the anisotropic region of the solution, which is determined from the phase difference $\Delta\varphi$ between the ordinary and extraordinary beams that pass through an anisotropic region of thickness d. For this purpose the device of Frank-Keller is used [1, 2]

$$\Delta n \approx \lambda\Delta\varphi/180d \qquad (2)$$

($\lambda \approx 0.56 \times 10^{-4}$ cm is the wavelength of a monochromatic light beam).

The quantity Δn_∞ corresponds to the maximally attainable birefringence of the uncoiled chains; it is defined by the following relationship

$$\Delta n_\infty \approx 2\pi(n^2+2)^2(9n)^{-1}(a_1-a_2)N' \qquad (3)$$

where; n is the refractive index of solution, $N' = \rho N_A/M_0$ is the number of repeat units in a unit volume, N_A is the molecular mass of a repeat unit, ρ is the density of a polymer (for solutions, concentration of the polymer in solution c is used instead of ρ) and (a_1-a_2) is the optical anisotropy of a repeat unit.

Although (a_1-a_2) was tabulated for many polymers [3]; there is no such data reported for fibroin. It is known that, in the fiber, the macromolecules of fibroin acquire an antiparallel alignment stabilized by hydrogen bonds (Fig. 1a), that is, they form a β-structure. When the fiber dissolves, the hydrogen bonds dissociate. Macromolecules in solution occur predominantly in the
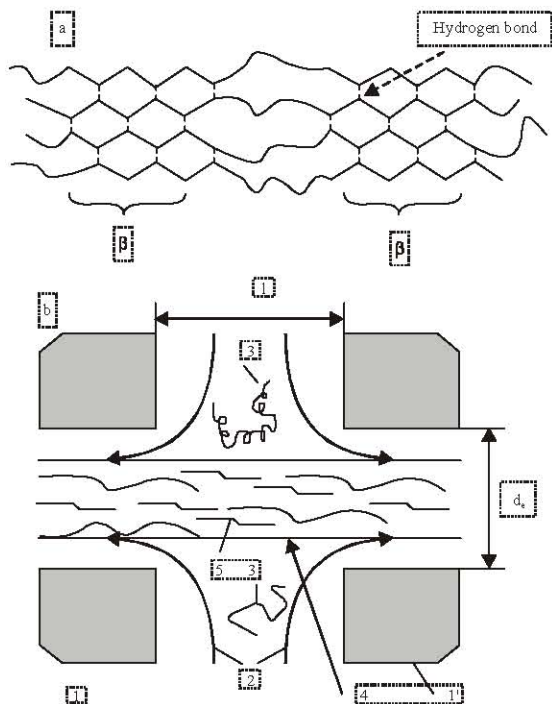
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Fig. 1: Schematic presentation of conformational states of fibroin: (a) in the fiber, (b) in a longitudinal hydrodynamic field. (1, 1') coaxial capillaries, dc is the capillary diameter, 1 distance between the capillaries; (2) lines describing the flow patter; (3, 3') molecules in the coiled or α-helical states; (4) anisotropic region; (5) uncoiled and oriented macromolecules

coiled or in the α-helical states [4]. However, in longitudinal flow, the molecular chains uncoil and align parallel to the axis of a hydrodynamic cell (Fig. 1b). The anisotropic region is observed as a thin "thread".

The parallel alignment of fibroin chains in the fiber makes it possible to assume that the fiber corresponds to the maximally extended state of macromolecules. Then, the birefringence

$$\Delta n_f \approx \Delta n_\infty \qquad (4)$$

In this case, $n \approx n_p$ (n_p is the refractive index of the polymer). In solutions where $n \neq n_p$, it is also necessary to consider the contribution to Δn_∞ of the refractive index of the solvent. This feature and the long time required to dissolve fibroin (more than 20 h at 80-90°C) were taken into account and Δn_f was measured using the 0.0036 cm thick fiber immersed in the solvent. For 2.5 M LiCl in DMF, $\Delta n_f \approx 8.34 \times 10^{-3}$; for 7.7 NaNCS in water, $\Delta n_f \approx 8.55 \times 10^{-3}$.

The values of (a_1-a_2) were calculated using Δn_f and expressions (3) and (4)

$$(a_1-a_2) \approx 9n \, \Delta n_\infty \, M_0 / [2\pi(n^2+2)^2 \rho N_A] \qquad (5)$$

where; $M_0 \approx 345$ and $\rho \approx 1.33$ g cm^{-3}, were taken from [5, 6].

Thus, $(a_1-a_2) \approx 4.2 \times 10^{-25}$ and 4.4×10^{-25} cm^3 for dimethylformamide and aqueous NaNCS solutions, respectively.

Using these values for (a_1-a_2) and substituting c for ρ in equation (3), the coefficients relating Δn_∞ to the concentration of fibroin in solutions were obtained: $\Delta n_\infty \approx 6.16 \times 10^{-3}$ g cm^{-3} for 2.5 M LiCl in DMF and $\Delta n_\infty \approx 6.43 \times 10^{-3}$ g cm^{-3} for 7.7 M NaNCS in water.

RESULTS AND DISCUSSION

To determine Δn, semidilute fibroin solutions ($c[\eta] \approx 1.3$, where $[\eta]$ is intrinsic viscosity) were subjected to longitudinal flow in a hydrodynamic cell consisting of two coaxial capillaries (Fig. 1b, were d_c = 0.1 cm and 1 = 0.21 cm). Figure 2 shows the plots of $\Delta n / \Delta n_\infty$ versus G for fibroin solutions.

As is seen from curve 1, the uncoiling of fibroin chains in 2.5 M LiCl in DMF begins at $G_{cr} \approx 970$ s^{-1}. At $G \approx 25000$ s^{-1}, the maximum magnitude $\Delta n / \Delta n_\infty \approx 0.8$ is reached; this corresponds to $\beta \approx 0.9$. This means that in a longitudinal hydrodynamic field, the macromolecules of fibroin acquire an almost completely, extended
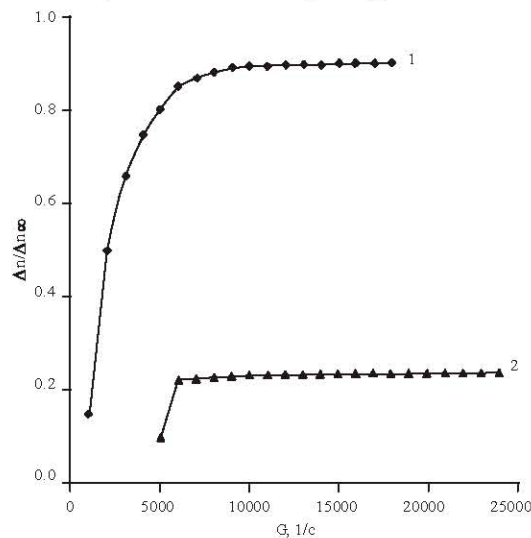

Fig. 2: Plots of reduced birefringence $\Delta n / \Delta n_\infty$ vs. velocity gradient G for solutions of fibroin in different solvents: (1) 2.5 M LiCl in DMF, (2) and 0.7 M NaNCS in water

conformation. In the case, the degree of uncoiling is 60% of the maximally attainable. However, the transition to an anisotropic state begins at higher G ($G_{cr} \approx 5200$ s^{-1}) than in a DMF solution.

The high degree of chain uncoiling and the lower critical magnitude of the rate gradient G in the case of fibroin ($M_w = 34.5 \times 10^4$) solution in 2.5 M LiCl in DMF are due to the high viscosities of the solvent ($\eta_0 \approx 0.11$ poise) and the solution ($\eta \approx 0.47$ poise at c = 0.01 g cm^{-3}). For the solution of fibroin in aqueous NaNCS solution these parameters are somewhat smaller ($\eta_0 \approx 0.058$ poise and $\eta \approx 0.26$ poise even at c = 0,028 g cm^{-3}). In a solution of high viscosity, the residence time of a macromolecule in a longitudinal field is longer and, consequently, the force field imposes a greater effect on fibroin in saline DMF solution is $[\eta] \approx 130$ cm^3 g^{-1}, which is significantly greater than that of fibroin in an aqueous NaNCS solution $[\eta] \approx 46$ cm^3 g^{-1}, This implies that, in DMF, the macromolecules of fibroin acquire a more extended conformation than in an aqueous medium because, other conditions being the same, $[\eta]$ is proportional to the third power of the mean-square radius of chain [3]. The differences between curves 1 and 2 in Fig. 2 become easily understandable when the proportionally $G_{cr} \sim [\eta]^{-1}$ is taken into account\$ the attainment of high degrees of uncoiling of fibroin macromolecules largely depends on the initial state of macromolecules in solution.

For fibroin solutions examined in this study, relaxation time τ for weakly strained chains was determined from the condition $\tau \approx 0.5/G_{cr}$ and the strain relaxation time of chain molecules τ_k was calculated [8, 9]

$$\tau_k \approx M(\eta - \eta_0)/RTc \qquad (6)$$

where; R = 8,31$\times 10^7$ g cm^3/(s^2 mol K) is the universal gas constant and T = 298 K is absolute temperature.

The values of τ were found to be close:

Solvent	$\tau \times 10^4$ s	$\tau_k \times 10^4$ s
2.5 M LiCl in DMF	5.5	1.0
7.7 M NaNCS in water	5.0	0.9

These data demonstrate the accuracy of the values obtained for the critical rate gradients of a longitudinal field.

CONCLUSION

Thus, transition the fibroin chains to the uncoiled state, occurring in a longitudinal hydrodynamic field, is strongly influenced by the initial conformational state of macromolecules; this state is, in its turn, controlled by solvent quality. Optical anisotropy dates of a repeat unit of silk fibroin thus are determined which was used for account extreme maximally attainable birefringence of the uncoiled chains. Doing experiences on the device of Frank-Keller investigated of transition of fibroin molecules in the uncoiled and oriented state in a longitudinal hydrodynamic field and determined of relaxation time of strained chains on critical sizes of a rate gradient. The certain meanings of relaxation time in experiences will well be coordinated to the settlement data.

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