Chemistry of Natural Compounds, Vol. 35, No. 4, 1999

INFLUENCE OF A STRUCTURAL TRANSFORMATION OF FIBROIN MOLECULES ON THE MORPHOLOGICAL DYNAMICS OF THE JET—FIBER TRANSITION

A. A. Kholmuminov, T. V. Voronina, Yu. N. Mirkhaidarova, K.A. Akhundzhanov, S. V. Zalyalieva, and B. D. Kabulov

UDC 541.64:539.667.371

The phenomenon of the jet—fiber transition in the biotechnology of natural silk has served as a basis for the development of methods of obtaining artificial fibers [1]. However, until now the qualitative indices of the morphology of artificial fibers have differed greatly from those of natural fibers. This is connected, above all, with the dynamics of the structural organization of the fibroin molecules during the jet-fiber transition, when the gel-like secretion of the silkworm gland first passes into a fluid elastoviscous state and then, when the jet produced is drawn out, is formed into fibers, with the appearance of a syneretic effect.

In order to reveal structural features of the macromolecules in the jet—fiber transition, we have made comparative investigations of the gel-like secretion and the elastoviscous solutions of fibroin obtained in solvents containing a lithium salt: 2.5 M LiCl DMFA and 6.3 M LiBr—water. Jet-like flow of the secretion was achieved by forcing it from the reservoir of the gland through the capillary of the twin excretory duct. Jet-like flow of the prepared solutions and gels was realized with the aid of a Kuvshinskii capillary viscometer [2]. The structural transformation of the fibroin molecules were monitored by methods involving birefringence (BRF) and circular dichroism (CD) [3, 4]. The degrees of crystallinity (C_{Cr}) of samples of the fiber obtained were determined by reversed-phase gas chromatography.

The experiments showed that the macromolecules of the fibroin of the secretion from the gland reservoir had α-helical sections. This permitted us to consider that nodes of gel structure are formed in parts of the nonhelicized sections through hydrogen bonds, since such intermolecular bonds are extremely likely.

The secretion in the twin excretory duct exists in the form of an elastoviscous solution. Jet-like flow of the secretion is accompanied by a transition of the α-helix into the β-form and by organization of the supermolecular structure of the fiber.

It can be seen from the experimental results given in the Table 1 that during the transformation of the elastoviscous solution into a fiber the orientation factor ($\Delta n/\Delta n\ \infty$) was considerably lower than in the gel-like solution and the secretion. This is connected with an ordering of the α-helical section of the macromolecule on gel formation.

In jet-like flow, on passing from the gel-like state to the elastoviscous state, the macromolecules are oriented in parallel and the α-helices are broken down and then restored in the form of a β-structure. The same is observed in the jet-like flow of an elastoviscous solution, but in this case the amount of β-structure is considerably lower than in the case of the gel-like solution, in spite of the fact that, in the jet, the macromolecules are oriented to a fairly high degree. This shows that in the gel-like solution the macromolecules are arranged relative to one another in the most suitable way for the formation of the supermolecular β-structure. This does not apply in the case of the jet-like flow of the initial elatoviscous solution because of the appearance of random contacts and the multiplicity of macromolecular bonds formed by the sections of disintegrated α-helices.

The results obtained by reversed-phase gas chromatography show the appearance of a comparatively high degree of crystallinity when the fibers are formed from a gel-like solution. Thus it may be concluded that the structural transformation of macromolecules in a secretion and a solution with the formation of intermediate gel-like structures is the most suitable for the organization of intermolcular hydrogen bonds in the jet—fiber transition, and this is reflected in the morphology of the fiber.

Institute of the Chemistry and Physics of Polymers, Academy of Sciences of the Republic of Uzbekistan, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 534—535, July-August, 1999. Original article submitted November 28, 1998.

0009-3130/99/3504-0477$22.00

TABLE 1. Some Structural Characteristics of Fibroin During the Jet—Fiber Transition

Sample	Initial indices		Final indices		
	$\Delta n/\Delta n_\infty$	α-, %	$\Delta n/\Delta n_\infty$	β-, %	C_{cr}, %
Secretion	0.18	42	0.85	38	45
Gel of fibroin in 2.5 M LiCl-DMF	0.20	36	0.70	28	34
Elastoviscous solution of fibroin in 2.5 M LiCl-DMF	0.12	38	0.75	20	22

REFERENCES

1. S. Ya. Frenkel' and G. K. El'yashevich, *Vysokomol. Soedin.*, **23A**, No. 2, 493 (1971).
2. L. L. Sul'zhenko and E. B. Kuvshinskii, *Vysokomol. Soedin.*, **11A**, No. 11, 23 (1969).
3. M. R. Macklye and A. Keller, *Philos. Trans. R. Soc. London*, **279**, 20 (1975).
4. S. D. Kostyuk, in: *The Physical Chemistry and Technologu of Natural Silk* [in Russian], Tashkent (1978).
5. A. E. Nesterov and Yu. S. Lipatov, *Reversed-phase Gas Chromatography in Polymer Thermodynamics* [in Russian], Naukova Dumka, Kiev (1978), p. 128.