

# Molecular structure of spider silk in various conditions of liquid crystal spinning

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Spider silk is known as fiber with high strength, stiffness and toughness. Spinning dope of spider is present as liquid crystalline at the spider's body. Therefore, the spider can spin silk with less metabolic cost [1]. Among several different kinds of spider silk, the dragline constituted by fibroins from major ampullate gland is considered as the most functional silk. In the study of structure of spider silk, infrared and Raman spectroscopy have been used in respect of sampled dragline with constant spinning speed [2]. In this study, we obtained samples with controlled spinning speed of dragline of *Nephila clavata* at range of 0.5–100 mm/s. The study on molecular structure has been applied by microscopic polarized FT-IR spectroscopy.

IR spectra of draglines with spinning speed of 0.5 and 100mm/s are shown in Fig. 1. In the obtained infrared spectra, the shoulder band around  $1690\text{ cm}^{-1}$ , which is assigned to antiparallel  $\beta$ -sheet of Amide I band, intensified with increasing of spinning speed in case of  $0^\circ$  polarized measurement. On  $90^\circ$  polarized spectra, the feature at  $1630\text{ cm}^{-1}$  assigned  $\beta$ -sheet appeared. These results indicate that  $\beta$ -sheet structure grew with increasing spinning speed. Consequently, it is revealed that the relationship between the variation of spinning speed of spider dragline and molecular orientation of protein by polarized FT-IR spectroscopy.

[1] Vollrath, F., *et.al.*, "Liquid crystalline spinning of spider silk," *Nature*, **410**, 541-548, 2001.

[2] Paquet-Mercier, F.; Lefèvre, T.; Auger, M. and Pérolet, M., "Evidence by infrared spectroscopy of the presence of two types of  $\beta$ -sheets in major ampullate spider silk and silkworm silk," *Soft Matter*, **9**, 208-215, 2013.

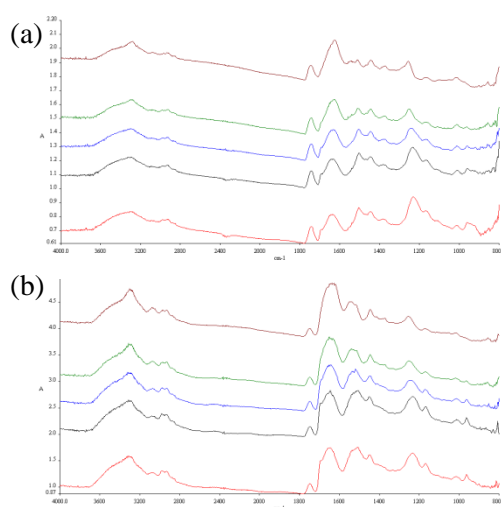


Fig.1. IR spectra of draglines with spinning speed of (a) 0.5 mm/s and (b) 100mm/s. Each line shows the spectrum with polarized angle of  $0^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$  and  $90^\circ$  from the bottom to top, respectively.