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INTRODUCTION

Dissolution is an important part of silk fibroin (SF) reprocessing; it enables the fabrication of SF-based biomaterials in various applicable formats. Cocoon SF produced by the wild silkworm, *Samia cynthia ricini* (*S. c. ricini*) is known to dissolve in ionic solvents and liquids. Recently, we found the possibility of mild dissolution the SF in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). In the current study, we optimized the conditions and clarified the mechanism of dissolution of *S. c. ricini* SF in HFIP.

EXPERIMENTAL

S. c. ricini native fibers were obtained from silkworm larvae reared indoors on an all-instar artificial diet, SilkMate L4M (Nosan Corp., Yokohama, Japan) at 25 °C. The fibers were dissolved in neat HFIP (99.0%; Tokyo Chemical Industry Company Limited, Tokyo, Japan) in sealed screw tubes under varying conditions to obtain SF solution. Films obtained by casting the fibroin solutions were characterised in detail by various analytical techniques.

RESULTS AND DISCUSSION

The native fibers which exhibit a typically β sheet rich spectra (Figure 1A). Empirically, it is not possible to dissolve SF in HFIP once it crystallizes in the β sheet form. However, by the dissolution of *S. c. ricini* native silk in HFIP for a duration of ~2 months under mild agitation at room temperature we obtained a SF solution. Alcohols, especially fluorinated alcohols such as HFIP, denature the native state of proteins by disrupting the hydrogen bonds participating in β sheet formation and induce or stabilize the helical conformation in the unfolded proteins, including silk proteins. The ^{13}C CP-MAS solid-state NMR spectra of films cast from the cocoon-derived HFIP fibroin solution (Figure 1D) are α helix-rich.

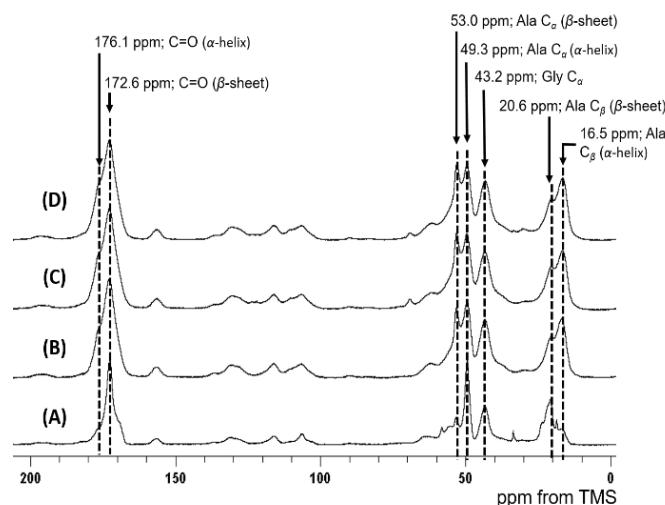


Fig. 1. ^{13}C CP-MAS solid-state NMR spectra in the range 0 to 200 of *S. c. ricini* native silk (A) and LF_{aq} (B), SGF_{HFIP} (C) and cocoon-SF $_{\text{HFIP}}$ (D) as-cast films.

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