

Controlling the growth behaviour of multilayered films via layer-by-layer assembly with multiple interactions

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Characterization of polymer structures

In this study, CHI-g-Ph was synthesized from CHI and phthalic anhydride. The amine groups of chitosan were reacted with phthalic anhydride to obtain the water soluble CHI-g-Ph. Ph-CHI-g-CD was synthesized from CHI-g-Ph and vinyl α -cyclodextrin through Michael addition between the amine group of CHI-g-Ph and the vinyl group of vinyl-CD.

The ^1H NMR spectrum of CHI-g-Ph is shown in Supplementary Figure 1c. Compared with the spectrum of CHI reported in our previous work,¹ new peak appeared at 7.3 and 7.4 ppm in the spectrum of CHI-g-Ph is assigned to phenyl moiety. By comparing the intensity of the peak at 3.4-3.6 ppm (multiplet, assigned to glucosamine unit) with intensity of the peaks at 7.3 and 7.4 ppm, the substitution degree is calculated to be 12%.

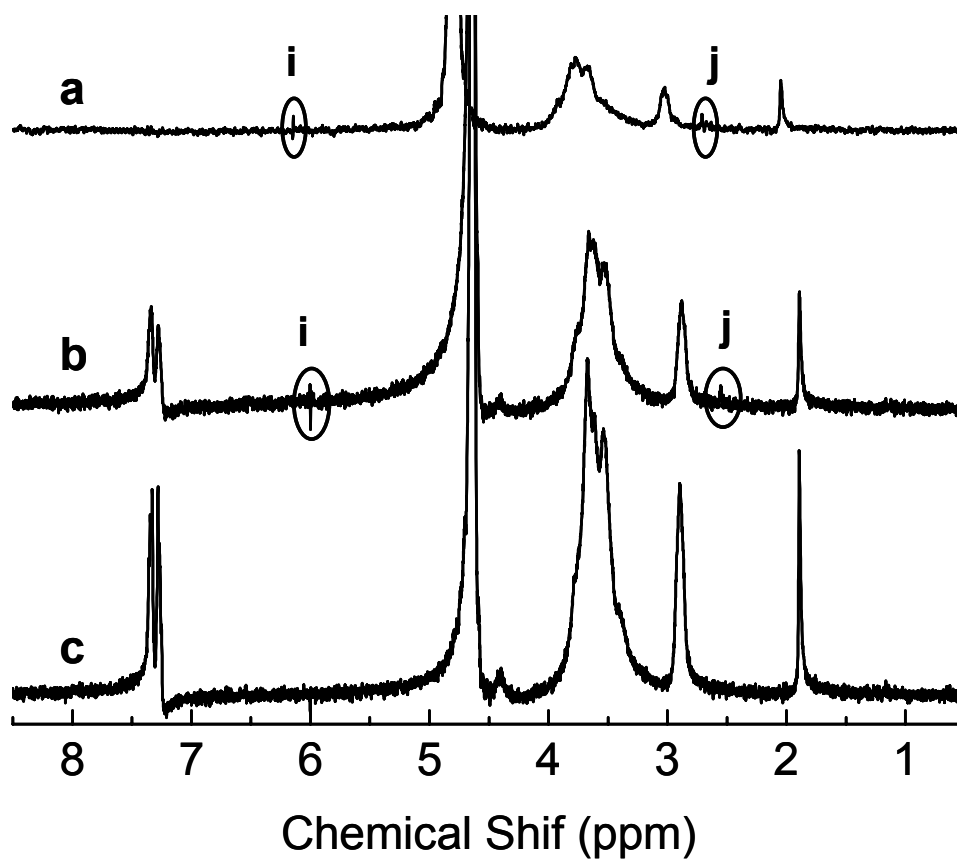
The ^1H NMR spectrum of Ph-CHI-g-CD is shown in Supplementary Figure 1b. Compared with the spectrum of CHI-g-Ph, new peaks appeared at 2.6 (j) and 6.0 (i) ppm in the spectrum of Ph-CHI-g-CD are assigned to α -cyclodextrin moiety. The substitution degree of CD in Ph-CHI-g-CD is calculated to be 1.6%.

The ^1H NMR spectrum of CHI-g-CD is shown in Supplementary Figure 1a. Peaks j and i in the spectrum of CHI-g-CD are assigned to α -cyclodextrin moiety. The substitution degree is calculated to be 1.7%.

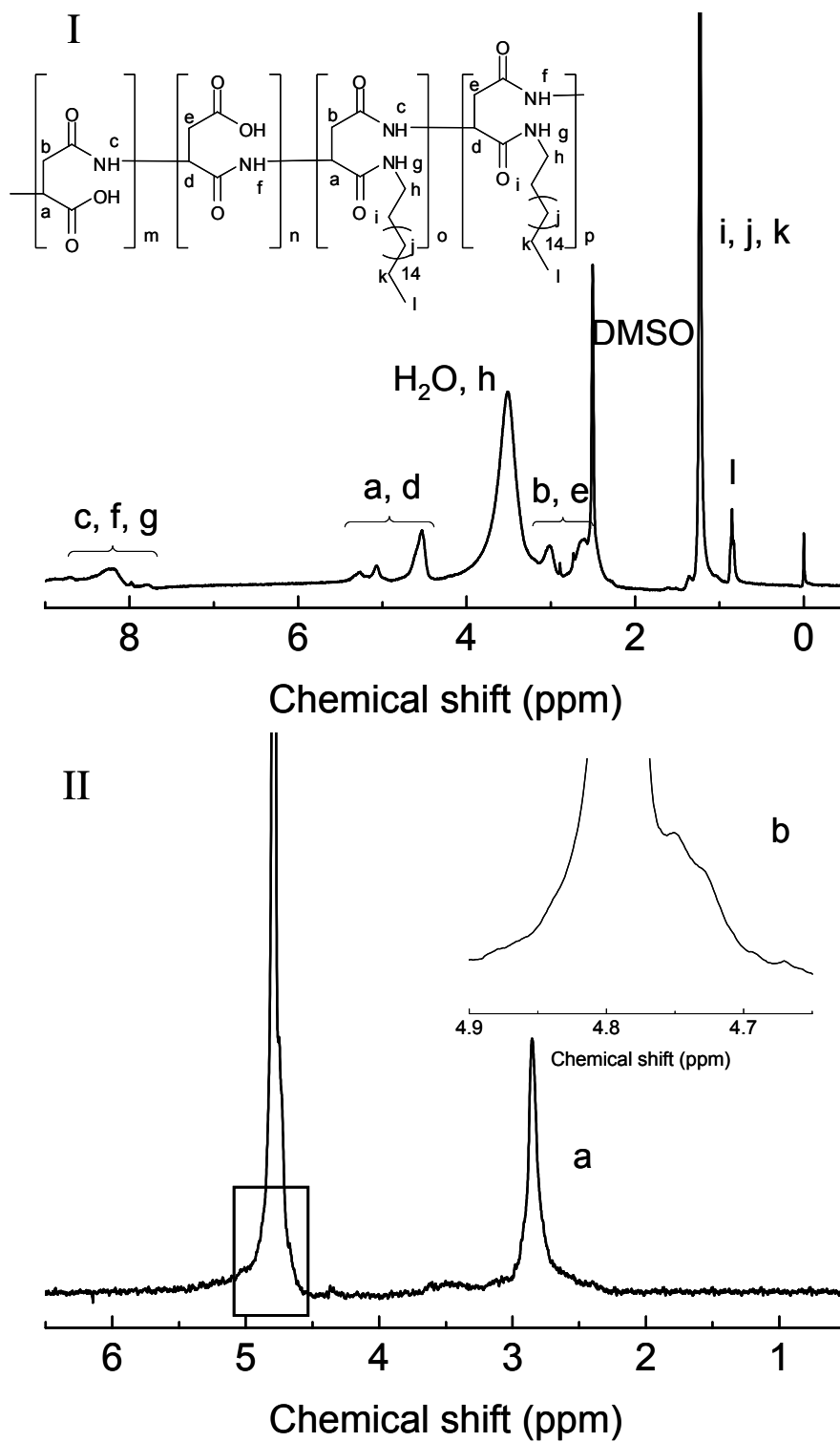
PASP and PASP-g-OD were synthesis from PSI. And the chemical structure of PASP-g-OD is confirmed by ^1H NMR spectrum (Supplementary Figure 2I). The substitution degree is 13% as calculated from the ^1H NMR spectrum of PASP-g-OD with DMSO- D_6 as the solvent.

The ^1H NMR signals originating from both hydrophilic and hydrophobic parts in amphiphilic PASP-g-OD can be detected when using DMSO- D_6 . (Supplementary Figure 2I). Besides the signals of octadecyl chain ($-\text{CH}_3$ protons centered at $\delta = 0.85$ ppm, $-\text{CH}_2$ protons centered at $\delta = 1.2$ ppm and $-\text{NHCH}_2$ protons centered at $\delta = 3.5$ ppm), characteristic signals of PASP chain also appear in Supplementary Figure 3I. In contrast, the use of D_2O as ^1H NMR solvent leads to insufficient mobility and a suppression of the signals of octadecyl chain. As shown in Supplementary Figure 2II, the use of D_2O results

in the total absence of the signals originating from octadecyl chain. This result also indicates the formation of PASP-g-OD micelles.



Supplementary Figure 1. ¹H NMR spectra of (a) CHI-g-CD, (b) Ph-CHI-g-CD and (c) CHI-g-Ph.



Supplementary Figure 2. ^1H NMR spectra of PASP-g-OD in DMSO-D_6 (I) and D_2O (II).

Notes and references

1. B. Lu, X. D. Xu, X. Z. Zhang, S. X. Cheng, R. X. Zhuo, *Biomacromolecules*, 2008, **9**, 2594.