Electronic Supplementary Information

Hydrophilicities of Amylose and Natural Cellulose Are Regulated by the Linkage between Sugar Rings

Yu Bao,[1] Duo Xu,[2] Lu Qian,[1] Li Zhao,[3] Zhong-yuan Lu[2] and Shuxun Cui*,[1]

[1] Key Lab of Advanced Technologies of Materials, Ministry of Education of China, Southwest Jiaotong University, Chengdu 610031, China.

[2] Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

[3] College of Life Sciences, Jilin University, Changchun 130012, China

*E-mail: cuishuxun@swjtu.edu.cn

Tel/FAX: +86-28-87600998

Part I: Details of Experiments and MD Simulations

Materials and chemicals: The ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl), is synthesized following the literature.[1] Five polysaccharides are used in this study, i.e., amylose (Type III from potato, Sigma-Aldrich), CMA (Kelong Chemical Ltd.), NC (Product No. C6288; Sigma-Aldrich), MC (Product No. M0512; degree of substitution: 1.5-1.9; Sigma-Aldrich) and CMC (Product No. 419338; degree of substitution: 0.8-0.95; Sigma-Aldrich). The primary structures of these polysaccharides are shown in Scheme S1. PBS buffer (phosphate buffered saline, 150 mM, pH = 7.4) is used to dissolve CMC and CMA. Deionized (DI) water (>15 MΩ·cm) is used when water is involved. Other chemicals are analytically pure and used without further treatment.

Sample preparation. NC is dissolved in AMIMCl by stirring the mixture at 60 °C for ~ 2 h to a concentration of 10 mg/L. Amylose is dissolved in hot DI water (~ 90 °C) to a concentration of 10 mg/L. MC is dissolved in DI water to a concentration of 10 mg/L. Both of CMC and CMA are dissolved in PBS buffer to a concentration of 10 mg/L. The low concentrations mentioned above are helpful to realize the single-chain

measurements later. The quartz slides, which are treated by a hot piranha solution (98% H_2SO_4 and 35% H_2O_2, 7:3, v/v) for 30 min and then rinsed by abundant DI water, are used as the substrates. (*Warning: piranha solution is extremely oxidizing and should be handled with extreme care!*) A drop of the target polysaccharide solution (~ 10 μL) is deposited on a clean quartz slide for 30 min. Then, the sample is thoroughly rinsed with abundant DI water, followed by drying with air flow.

Force measurements. The sample is mounted in the AFM (NanoWizard II, JPK Instruments, Germany). Prior to the measurements, a drop of liquid is introduced between the V-shaped Si_3N_4 AFM cantilever (MLCT model, Bruker Corp., CA) and the sample. Then during the force measurements, the data are collected at the same time and converted to F-E curves later. The spring constant of the AFM cantilever is measured by the thermo excitation method, which ranges from 30 to 50 pN/nm. The stretching velocity applied is 2.0 μm/s, if not mentioned otherwise. The resulting F-E curves were analyzed with Igor Pro 6.05 software with custom procedures. The details of the instrumentation can be found elsewhere.[2-4]

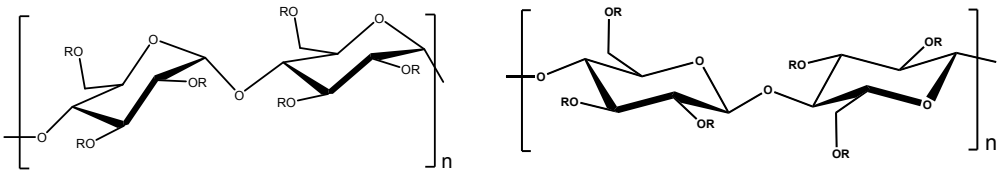
Molecular dynamics simulations.

MD simulations were carried out with GROMACS 5.0.2, using the force field parameter set GROMOS $53A6_{carbo}$.[5] In the simulations, both the amylose and NC molecules contain 9 sugar units, respectively. The initial conformation of the amylose was build according to the data reported by Imberty et al.[6] Following Ref. [7], the simulation of NC was started from the conformation with the angles $\varphi = \angle(O5,C1,O4',C4') = -120°$ and $\psi = \angle(C1,O4',C4',C5') = -120°$. The simulation system consists of one solute molecule solvated by the simple-point-charge (SPC) water molecules within a cubic simulation box. The box side lengths are 7 nm for NC and 4 nm for amylose, respectively. The systems were simulated under periodic boundary conditions at a temperature of 300 K. The steepest-descent energy minimization was performed first to relax the unfavorable solute-solvent contacts. Electrostatic interactions were treated using the particle-mesh Ewald (PME) method with a real-space cutoff of 1.0 nm. Van der Waals interactions were cut off at 1.0 nm with the long-range dispersion correction for both energy and pressure. All bond

lengths were constrained by the LINCS algorithm. The initial velocities of the atoms were assigned from a Maxwell distribution centered at 300 K. The densities of the systems reached 0.990 g/cm^3 for NC and 0.978 g/cm^3 for amylose, respectively, after the equilibration run in 100 ps NVT followed by 200 ps NPT ensemble. The production runs of amylose and NC were carried out in an NVT ensemble for 10 ns with 1 fs integration timestep, respectively. The RMSDs were always around 0.04 for NC and 0.038 for amylose, which indicated that during the production run the conformations of amylose and NC did not change much. The number of hydrogen bond between O bridge atom and water in 9-10 ns was calculated setting the distance between the O atom in water (donor) and O bridge atom (acceptor) in amylose or NC at 0.35 nm and the angle H-O(donor)-O(acceptor) at 30°.[8]

Part II: Additional Data

Scheme S1. (A) Primary structures of amylose (black) and CMA (red). (B) Primary structures of NC (black), MC (blue) and CMC (red).



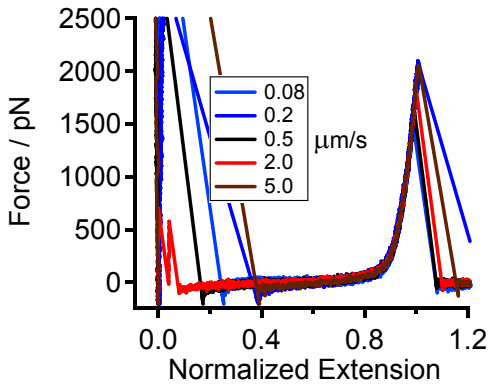


Fig. S1. The normalized F-E curves of amylose obtained in octane at various pulling speed.

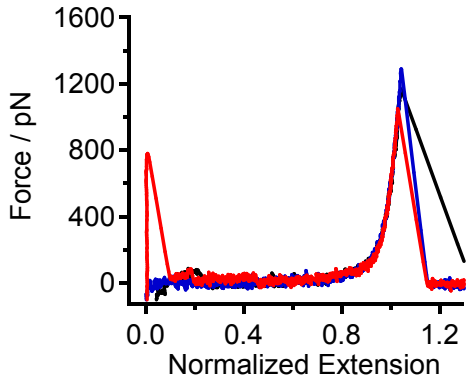


Fig. S2. The normalized F-E curves of amylose obtained in TCE.

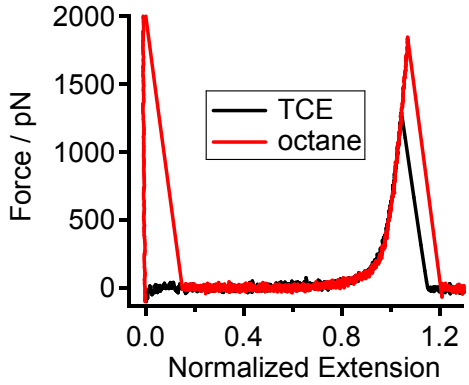


Fig. S3. The normalized F-E curves of amylose obtained in TCE (black) and octane (red).

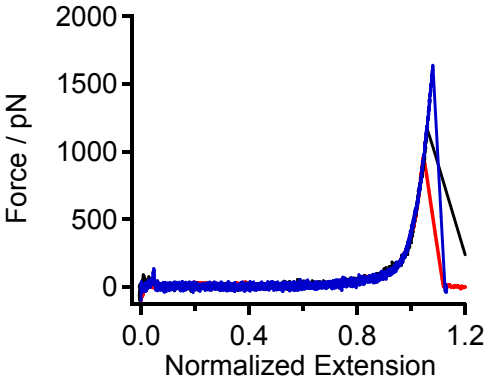


Fig. S4. The normalized F-E curves of CMA obtained in octane.

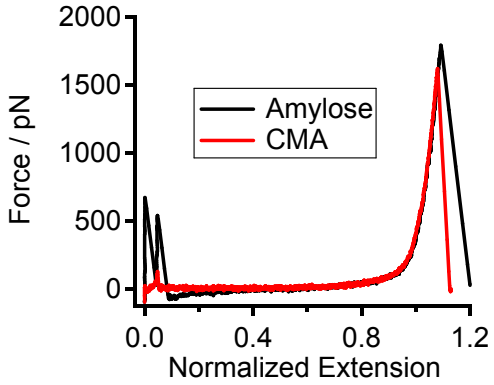


Fig. S5. The normalized F-E curves of amylose (black) and CMA (red) obtained in octane.

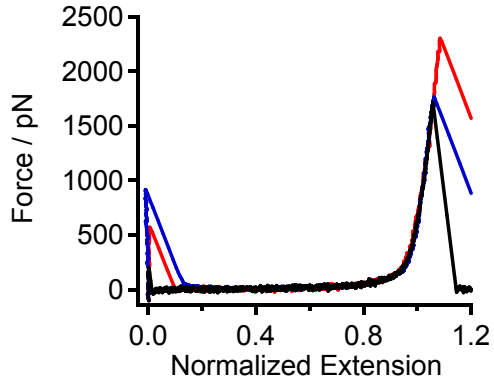


Fig. S6. The normalized F-E curves of NC obtained in octane.

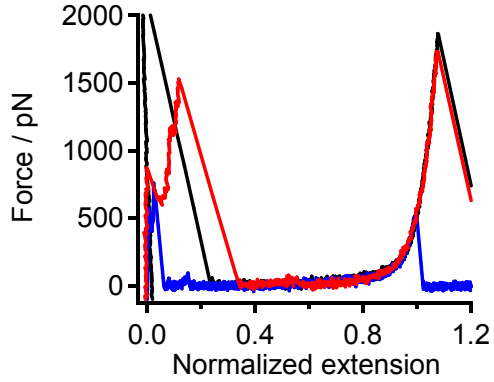


Fig. S7. The normalized F-E curves of MC obtained in octane.

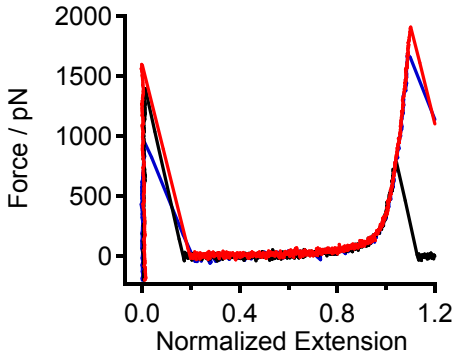


Fig. S8. The normalized F-E curves of CMC obtained in octane.

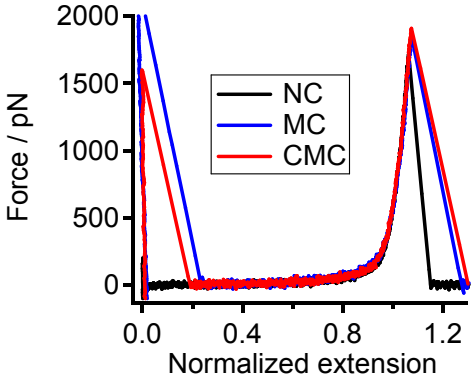


Fig. S9. The normalized F-E curves of NC (black), MC (blue), and CMC (red) obtained in octane.

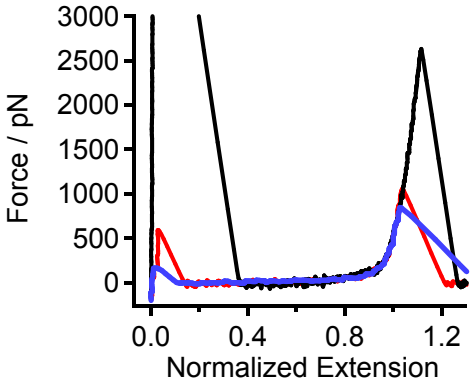


Fig. S10. The normalized F-E curves of NC obtained in TCE.

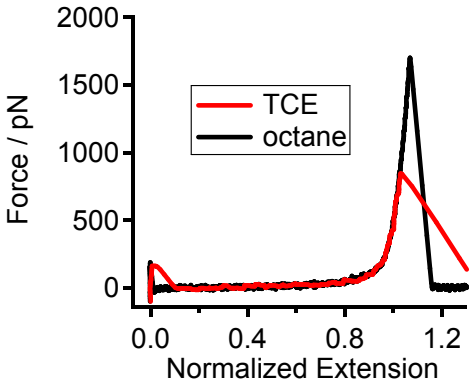


Fig. S11. The normalized F-E curves of NC obtained in TCE (red) and octane (black).

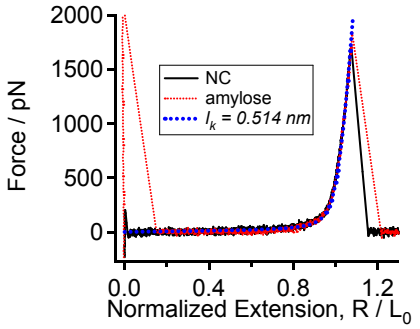


Fig. S12. QM-FJC fitting curve with l_k = 0.514 nm vs. the normalized F-E curves of amylose and NC obtained in octane.

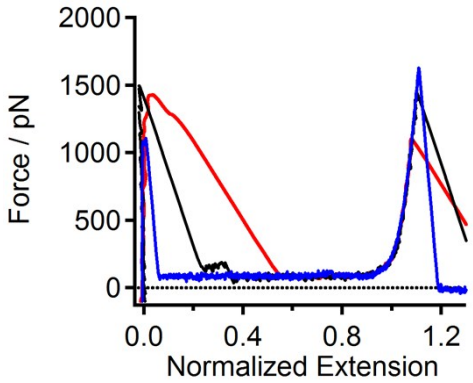


Fig. S13. The normalized F-E curves of NC obtained in water.

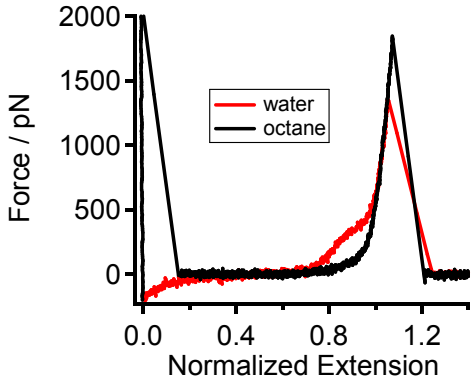


Fig. S14. The normalized single-chain F-E curves of amylose obtained in water (red) and in octane (black).

References

1. H. Zhang, J. Wu, J. Zhang and J. S. He, *Macromolecules*, 2005, 38, 8272-8277.
2. A. Janshoff, M. Neitzert, Y. Oberdorfer and H. Fuchs, *Angew. Chem., Int. Ed.*, 2000, 39, 3213-3237.
3. Y. R. Xue, X. Li, H. B. Li and W. K. Zhang, *Nat. Commun.*, 2014, 5, 4348.
4. B. Cheng, S. G. Wu, S. X. Liu, P. Rodriguez-Aliaga, J. Yu and S. X. Cui, *Nanoscale*, 2015, 7, 2970-2977.
5. H. S. Hansen and P. H. Huenenberger, *J. Comput. Chem.*, 2011, 32, 998-1032.
6. A. Imberty, H. Chanzy, S. Perez, A. Buleon and V. Tran, *J. Mol. Biol.*, 1988, 201, 365-378.
7. M. C. Winger, M.; van Gunsteren, W. F., *Int. J. Carbohyd. Chem.* , 2009, 307695.
8. A. Luzar and D. Chandler, *Nature*, 1996, 379, 55-57.