Hydrogen-Bonded Polymers with Bent-Shaped Side Chains and Poly(4-vinylpridine) Backbone: Phase Behavior and Thin Film Morphologies.

Xiaoshan Liu,[†,‡] *Xiaofang Chen*,[*,†] *Jingkui Wang*,[†] *Gang Chen,*[*,§] and *Hailiang Zhang*[*,‡]

[†] College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou 215123, P. R. China

[‡] College of Chemistry, Xiangtan University, Xiangtan 411105, P. R. China

[§]Shanghai Institute of Applied Physics, Chinese Academy of Science, Shanghai 201800, P. R. China

Experimental Section

Materials.3,4,5-trihydroxybenzoicacid methyl ester (98%),1-bromodecane (98%),K_2CO_3, KOH, ethanol (99.5%), ethyl acetate (99.8%), acetone(99.9%), dichloromethane (99.5%), 4-(dimethylamino)pyridine (DMAP, 99%), *N,N*-dicyclohexylcarbodiimide(DCC, 95%), 4-benzyloxyphenyl (99%) and palladium carbon catalyst were used as received from Beijing Chemical Co. 1,4-Dioxaxne (99%) was also purchased from Beijing Chemical Co. and was refluxed over sodium under argon and distilled before use. Poly(4-vinylpyridine)(P4VP, weight-average molecular weight, *M*w 5600) was purchased from Polymer Source Inc. Silicon wafers

[p-doped, (100)-oriented, 0.45 mm thick, and 100 mm in diameter] were from Guangzhou Semiconductor Materials (Guangzhou, China).

Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR) measurements were performed on a Bruker ARX400 MHz spectrometer using with $CDCl_3$ as solvent, tetramethylsilane (TMS) as the internal standard at room temperature.

10CBP: ^{1}H NMR(δ, ppm, $CDCl_3$): 0.86-0.90 (t, 9H, -C*H*$_3$), 1.26-1.51 (m, 42H,-(C*H*$_2$)$_7$-), 1.79-1.86 (m, 6H, 3-OCH$_2$C*H*$_2$-), 4.04-4.09 (t, 6H,3-O-C*H*$_2$-), 4.8 (s, 1H, -O*H*), 6.88-6.91 (d, 2H, Ar-*H*), 7.11-7.14 (d, 2H, Ar-*H*), 7.27-7.31 (m, 2H, Ar-*H*), 7.42 (s, 4H, Ar-*H*), 7.70 (m, 1H, Ar-*H*), 8.46-8.49 (d, 2H, Ar-*H*), 9.02 (s, 1H,Ar-*H*). Elemental Analysis: Anal. Calcd for $C_{57}H_{78}O_{10}$: C, 74.15; H, 8.52. Found: C, 74.17; H, 8.60.

12CBP:^{1}H NMR(δ, ppm, $CDCl_3$): 0.86-0.90 (t, 9H, -C*H*$_3$), 1.26-1.54 (m, 54H,-(C*H*$_2$)$_9$-), 1.73-1.87 (m, 6H, 3-OCH$_2$C*H*$_2$-), 4.04-4.09 (t, 6H,3-O-C*H*$_2$-), 5.14 (s, 1H, -O*H*), 6.87-6.90 (d, 2H, Ar-*H*), 7.09-7.12 (d, 2H, Ar-*H*), 7.27-7.32 (m, 2H, Ar-*H*), 7.41 (s, 4H, Ar-*H*), 7.68-7.71 (m, 1H, Ar-*H*), 8.45-8.47 (d, 2H, Ar-*H*), 9.01 (s, 1H,Ar-*H*). Elemental Analysis: Anal. Calcd for $C_{63}H_{90}O_{10}$: C, 75.11; H, 9.00. Found: C, 75.22; H, 9.16.

14CBP:^{1}H NMR(δ, ppm, $CDCl_3$): 0.86-0.90 (t, 9H, -C*H*$_3$), 1.26-1.54 (m, 66H,-(C*H*$_2$)$_7$-), 1.75-1.86 (m, 6H, 3-OCH$_2$C*H*$_2$-), 4.04-4.08 (t, 6H,3-O-C*H*$_2$-), 6.88-6.90 (d, 2H, Ar-*H*), 7.11-7.13 (d, 2H, Ar-*H*), 7.26-7.33 (m, 2H, Ar-*H*), 7.41 (s, 4H, Ar-*H*), 7.68-7.71 (m, 1H, Ar-*H*), 8.45-8.47 (d, 2H, Ar-*H*), 9.01 (s, 1H,Ar-*H*). Elemental Analysis: Anal. Calcd for $C_{69}H_{102}O_{10}$: C, 75.42; H, 9.42. Found: C, 75.63; H, 9.46.

Electron Density Reconstruction

The reconstruction of relative electron density distribution in real space based on XRD data is calculated according to the literature[1]. Considering the hexagonal columnar phase, three clear peaks can be assigned for PVP(10CBP)$_{0.75}$. These peaks are related to reflection (10), (11), (20). The electron density profiles have been calculated using the suitable phase combinations of "+ – – " for the corresponding reflections.

Supporting Figures

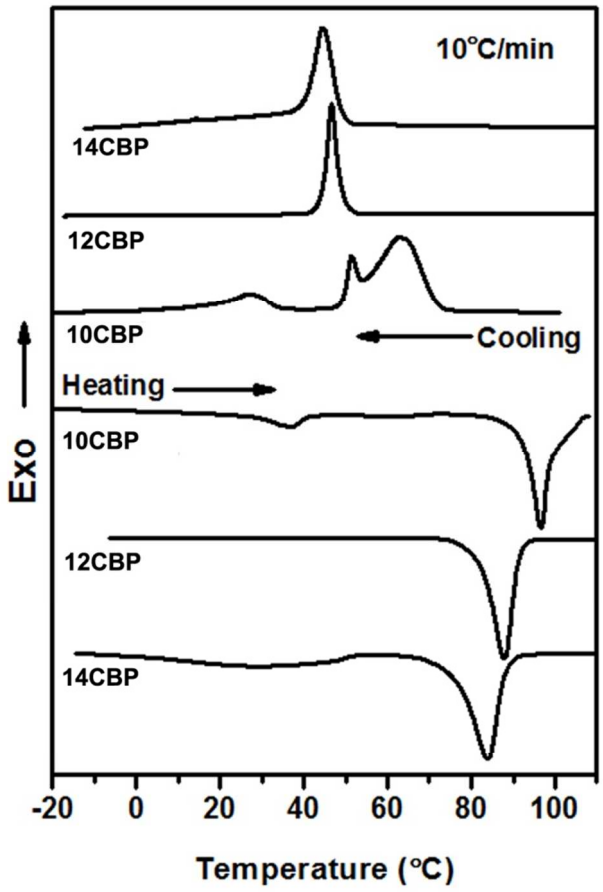

Figure S1.DSC curves of nCBP during first cooling and second heating at a rate of 10 ^{o}C/min under N_2 atmosphere

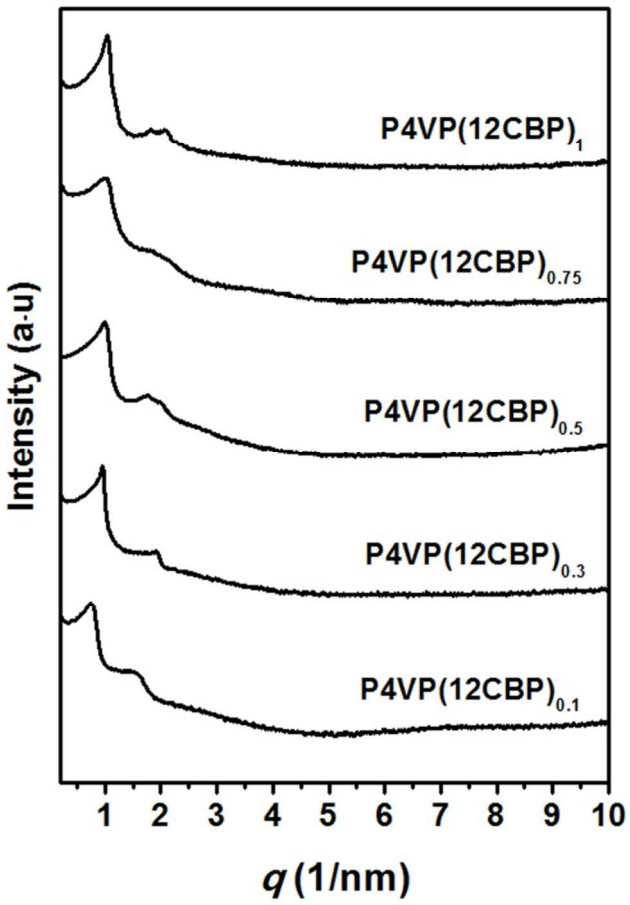

Figure S2. SAXS profiles of P4VP(12CBP)$_x$ complexes recorded at 25 ^{o}C

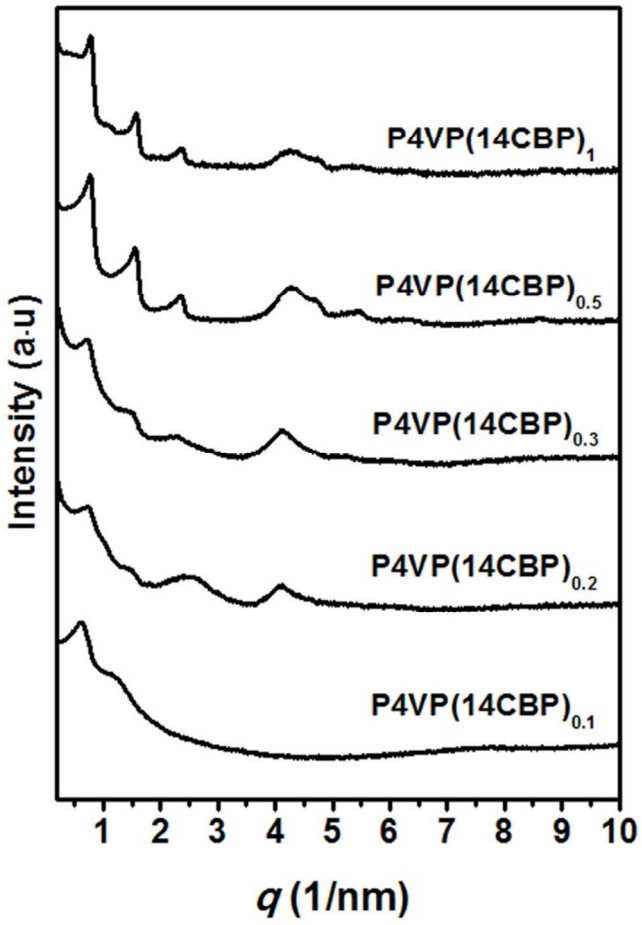

Figure S3. SAXS profiles of P4VP(14CBP)$_x$ complexes recorded at 25 ^{o}C.

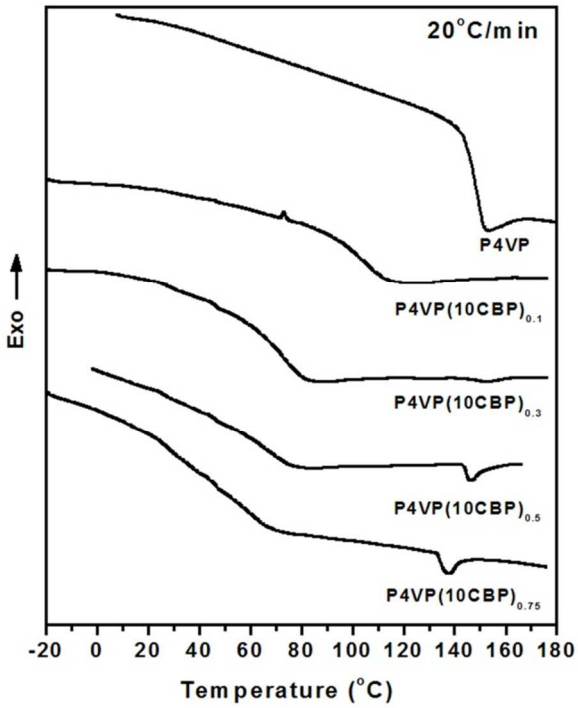

Figure S4. DSC curves of P4VP and P4VP(10CBP)$_x$ during the second heating cycle at a rate of 20 °C/min under N_2 atmosphere.

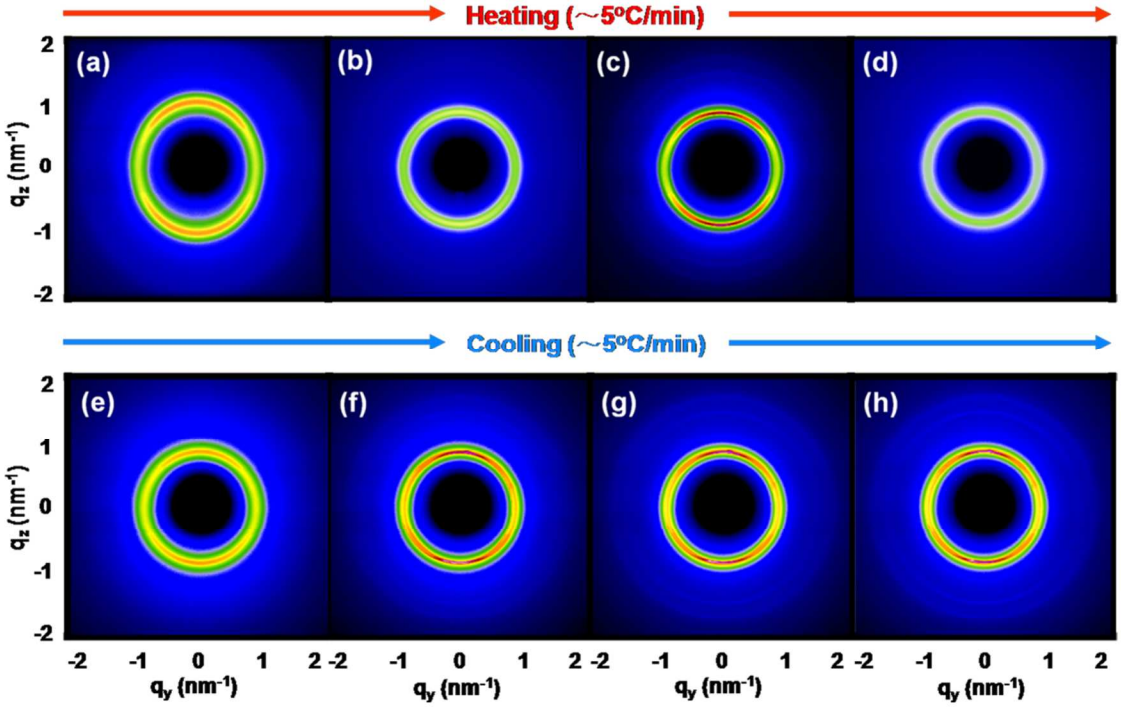

Figure S5. 2D X-ray diffraction patterns of P4VP(12CBP)$_{0.3}$ during the heating and cooling cycles. Data from the heating cycle were taken at (a) 30 ^{o}C, (b) 120 ^{o}C, (c) 140 ^{o}C, and (d)180 ^{o}C. After stabilized ~10 min at 180 ^{o}C, data were collected during the cooling cycle at (e) 160 ^{o}C, (f) 130 ^{o}C, (g) 70 ^{o}C, and (h) 30 ^{o}C. Heating and cooling rates were ~5 ^{o}C/min.

REFERENCE:

(1) Zheng, J. F.; Liu, X.; Chen, X. F.; Ren, X. K.; Yang, S.; Chen, E. Q. *ACS Macro Letters* **2012**, *1*, 641-645.