

Supporting Information for

Intramolecular Cyclization-Induced Crystallization-Driven

Self-Assembly of an Amorphous Poly(amic acid)

Hui Sun^{*,†,‡,§} and Jianzhong Du^{*,†,‡}

[†]Department of Orthopedics, Shanghai Tenth People's Hospital, Tongji University School of Medicine, Shanghai 200072, China.

[‡]Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China. Email: jzdu@tongji.edu.cn; Fax: +86-21-6958 0239; Tel: +86-21-6958 0239

[§]State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China. Email: sunhui@nxu.edu.cn

1. Materials

Hydrazine hydrate (99%), pyromellitic dianhydride (PMDA, 99%), KBr (99.9%), acetone (AR) and dimethyl formamide (DMF, AR) were purchased from Aladdin. DMSO-*d*₆ was purchased from J&K Scientific Ltd.

2. Characterizations

2.1 ¹H NMR

The ¹H NMR spectra of the polymers were recorded using a Bruker AV 400 MHz spectrometer at room temperature with DMSO-*d*₆ as the solvent.

2.2 FTIR

The FTIR spectrum of poly(amic acid) (PAA) was obtained using an IR/Nicolet 6700 spectrometer.

2.3 GPC

The molecular weight and polydispersity of PAA were evaluated using a DMF GPC conducted by an Agilent 1260 Infinity GPC analysis system with two Shedex GPC KD series columns with HPLC grade DMF as the eluent at a flow rate of 0.8 mL min⁻¹ at 40 °C.

2.4 Real Time FTIR

The real time FTIR (RT-FTIR) spectra of PAA were obtained using an IR/Nicolet 6700 spectrometer. The powders of PAA and KBr were mixed and ground to prepare tablet. Then the tablet was fixed in a heating equipment with a heating rate of 10 °C/min. The IR spectrum of the sample was scanned and recorded at different temperatures.

2.5 DLS

The hydrodynamic diameter and polydispersity of the nano-objects were determined by ZETASIZER

Nano series instrument (Malvern Instruments ZS 90) at a fixed scattering angle of 90°.

2.6 TEM

The aqueous solutions of the nano-structures were dropped onto a copper grid and dried at ambient temperature. The images were recorded on a JEOL JEM-2100F instrument at 200 kV equipped with a Gatan 894 Ultrascan 1k CCD camera.

2.7 SEM

SEM was utilized to observe the morphologies of the nano-objects. To obtain SEM images, a drop of solution was dropped onto a silicon wafer and dried at ambient temperature. Then it was coated with gold and viewed by an FEI Quanta 200 FEG electron microscope operated at 10 kV. The images were recorded by a digital camera.

2.8 XRD

The XRD patterns of the samples were obtained using a Bruker D8 ADVANCE X-ray diffractometer. The angle was set from 5° to 50° with a rate of 6°/min.

3. Experimental Section

3.1 Synthesis of PAA

Hydrazine hydrate (1.139 g, 22.5 mmol) was dissolved in 20 mL of DMF. PMDA (4.867 g, 20.00 mmol) was dispersed in 20 mL of DMF and added into the DMF solution of hydrazine hydrate batch by batch in an hour at 0 °C. Then the solution was stirred for an hour to promote the complete consumption of the monomers. The solution of PAA (5.0 mL) was taken out and precipitated in acetone for three times to afford polymer powder, which was dried under vacuum for characterization (NMR, GPC and FTIR).

3.2 Intramolecular Cyclization-Induced Crystallization-Driven Self-Assembly (ICI-CDSA) of

PAA in DMF/Water

The stock solution of PAA was diluted into different concentrations: 5.0, 10, 15, 20, 25 mg mL⁻¹. After thermal treatment at 160 °C for 10 min, the color of the solution turned yellow. Then, water was added into the solutions dropwise under stirring ($V_{\text{water}} : V_{\text{DMF}} = 2 : 1$). After centrifugation and washing by water, the aqueous solutions of the nano-assemblies were obtained.

3.3 ICI-CDSA of PAA in DMF

The stock solution of PAA was diluted into 40 mg mL⁻¹, and thermo-treated at 153 °C for 5 min. The solution is naturally cooled to room temperature. After centrifugation and washing by water, the aqueous solution of the nanofibers was obtained.

4. Schemes and Figures

Scheme S1. Synthesis of PAA and Its Thermo-Induced Imidization Reaction

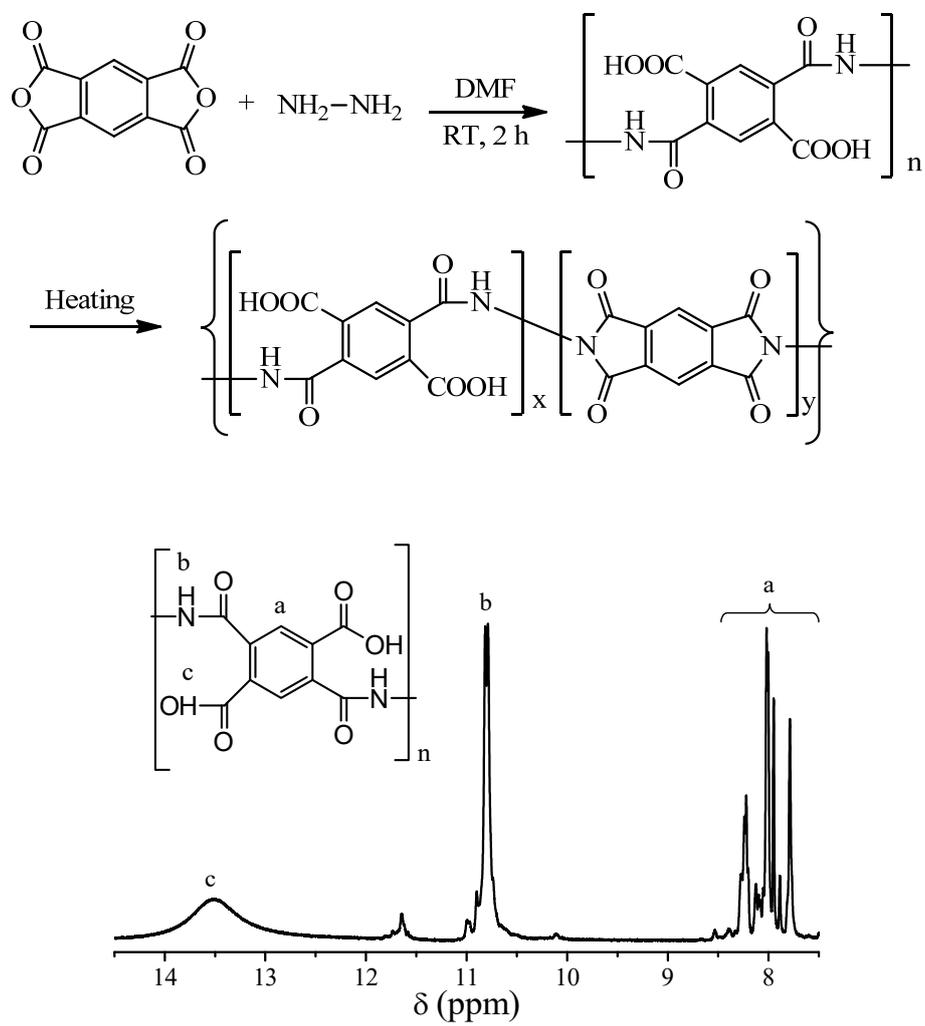


Figure S1. NMR spectrum of PAA in $\text{DMSO-}d_6$.

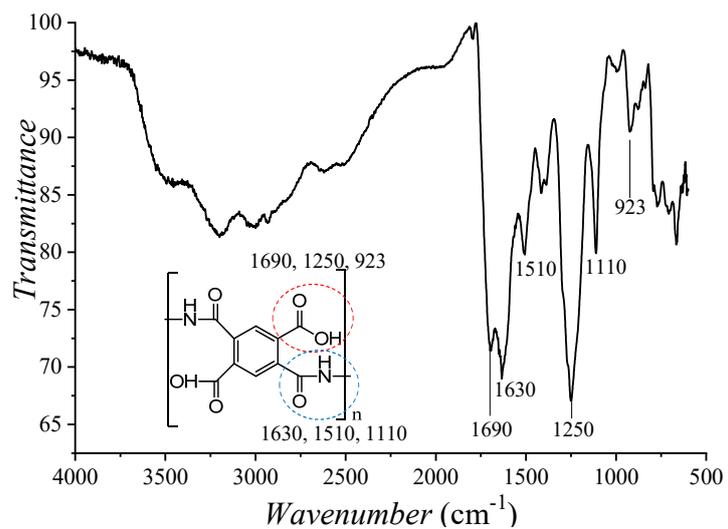


Figure S2. FTIR spectrum of PAA.

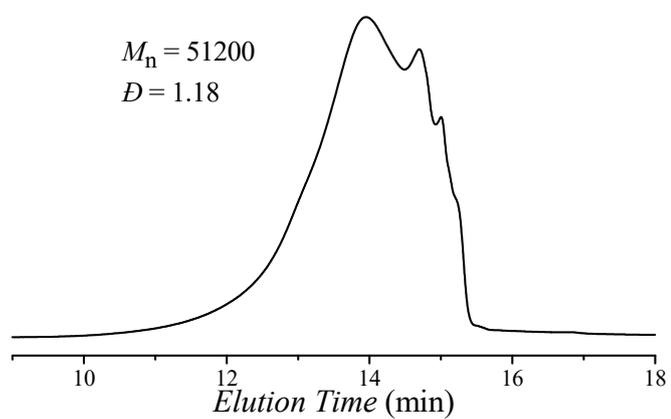


Figure S3. DMF GPC trace of PAA.

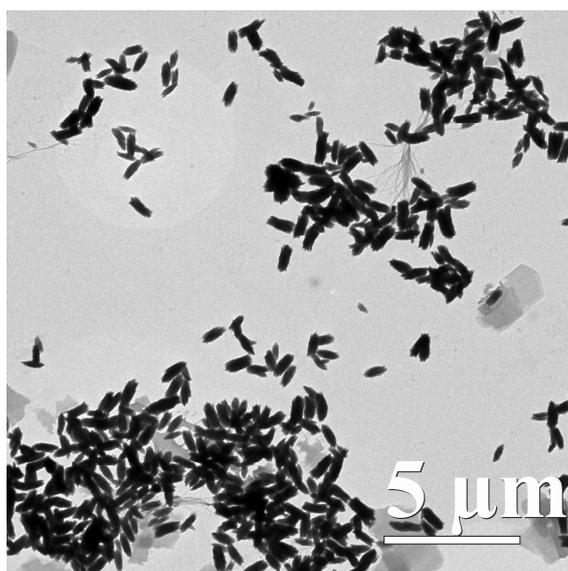


Figure S4. TEM image of nanobundles at low magnification.

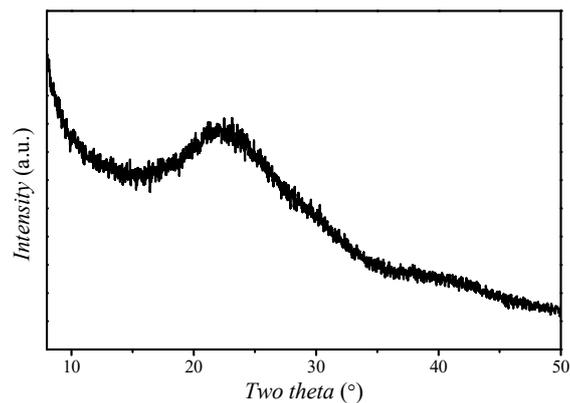


Figure S5. XRD pattern of PAA powder.

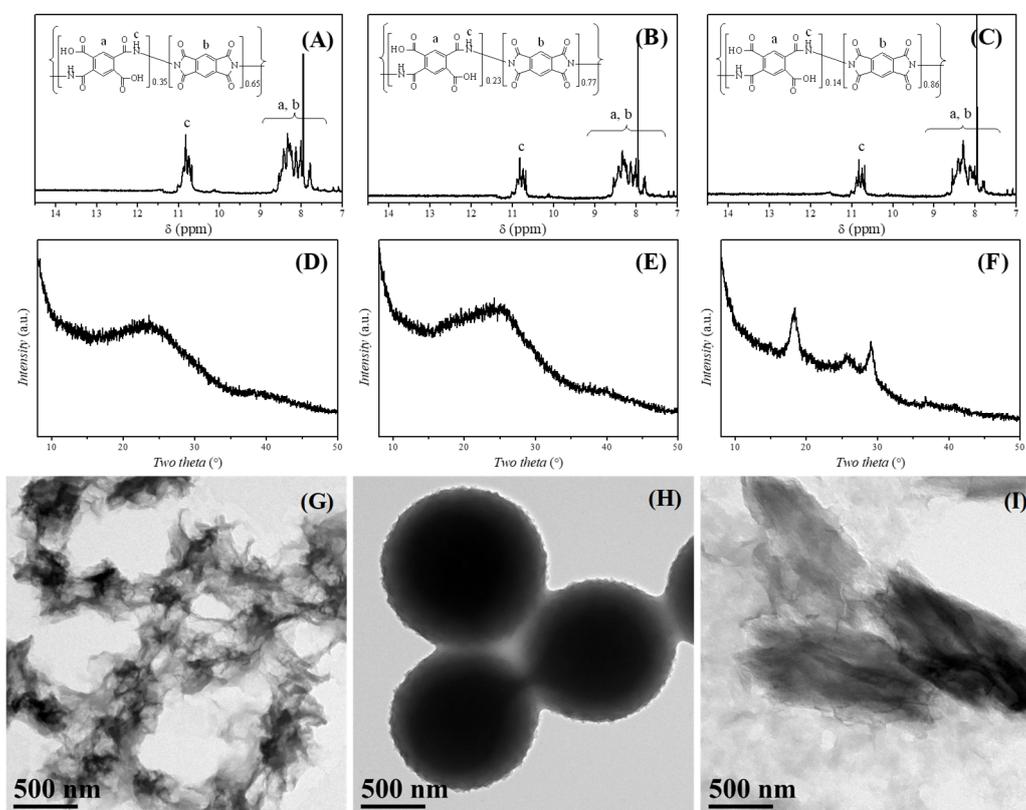


Figure S6. Self-assembly of P(AA-*stat*-I) with different degree of imidization by solvent switch method. (A, B, C) NMR spectra of P(AA-*stat*-I) with degrees of imidization of 65, 77 and 86%, noted as P(AA_{0.35}-*stat*-I_{0.65}), P(AA_{0.23}-*stat*-I_{0.77}) and P(AA_{0.14}-*stat*-I_{0.86}), as calculated by the ratio of integral intensities of peaks c, and a, b in (A, B, C); (D, E, F) and (G, H, I) are the corresponding XRD patterns and TEM images of the nanostructures self-assembled from P(AA_{0.35}-*stat*-I_{0.65}), P(AA_{0.23}-*stat*-I_{0.77}) and P(AA_{0.14}-*stat*-I_{0.86}) in DMF/water.

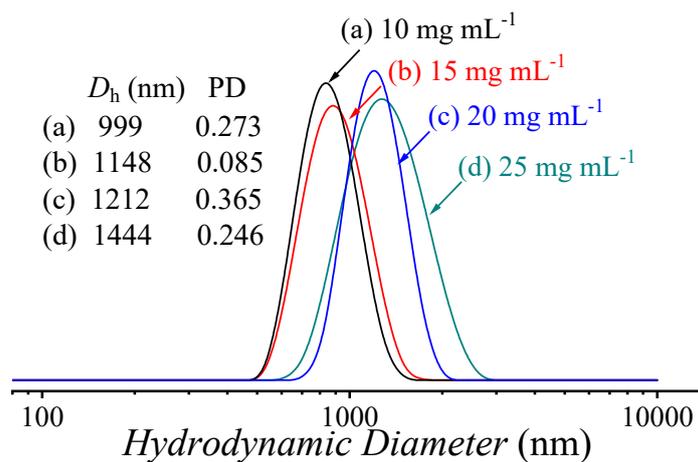


Figure S7. DLS results of the flower-shaped structures self-assembled in DMF/water at different concentrations.

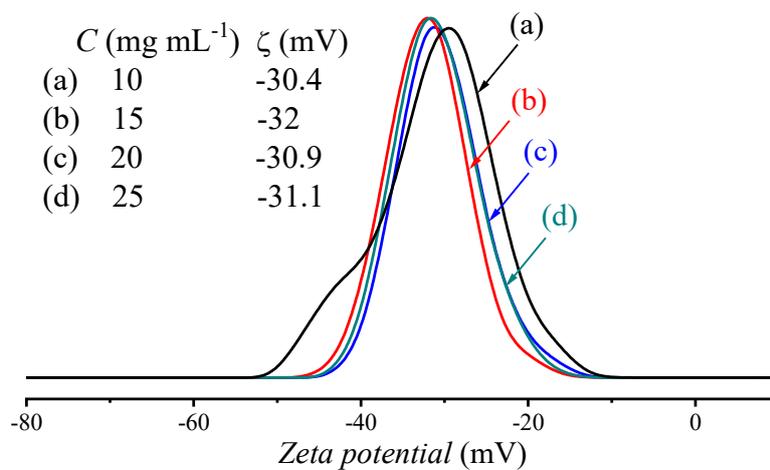


Figure S8. Zeta potentials of the flower-shaped structures self-assembled in DMF/water at different concentrations.

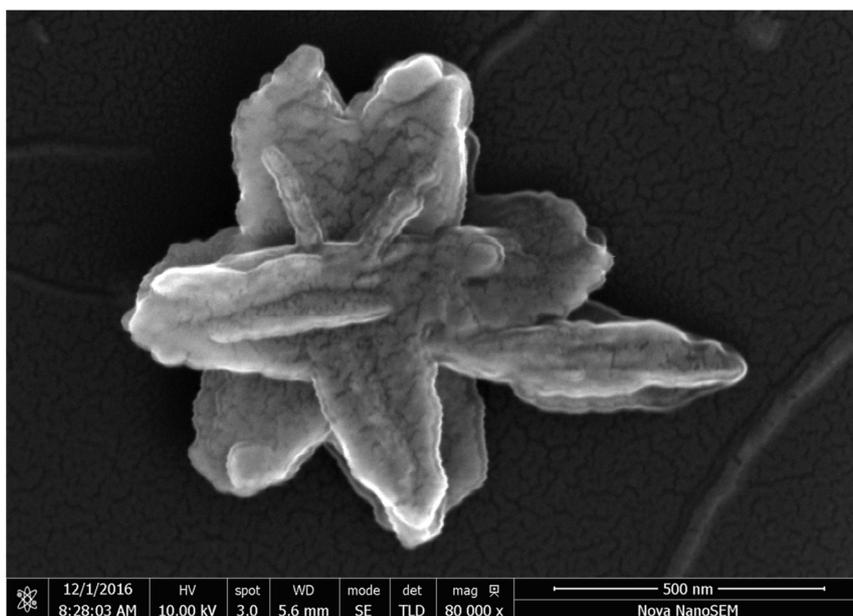


Figure S9. SEM image of the flower-shaped structure when the concentration of P(AA_{0.08}-*stat*-I_{0.92}) is 15 mg mL⁻¹.

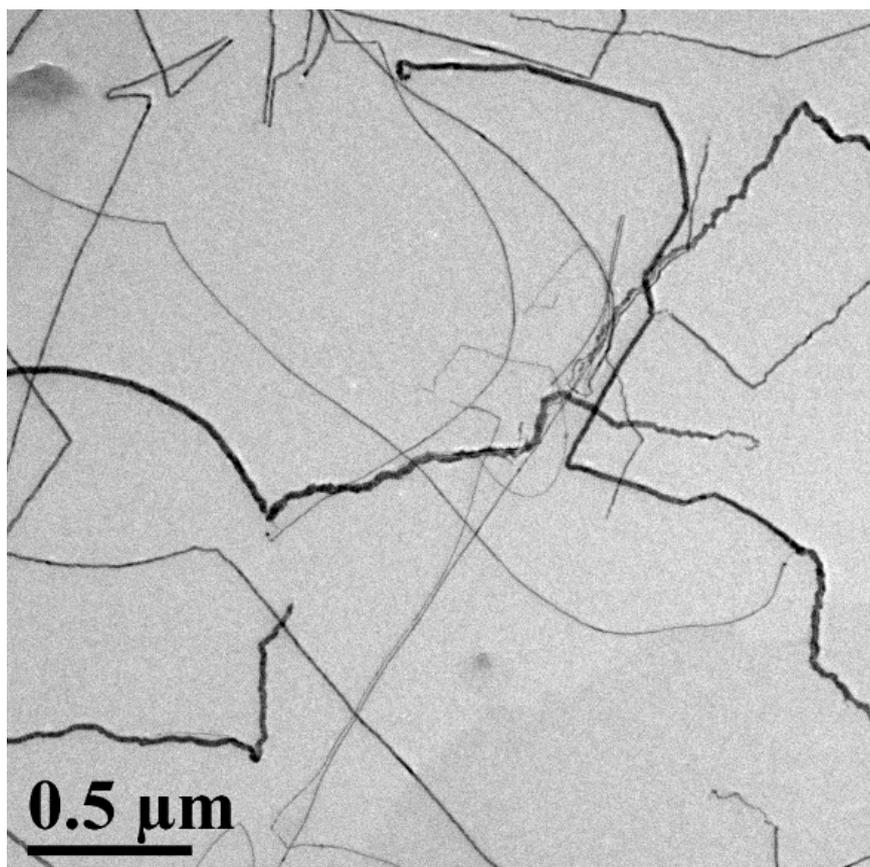


Figure S10. Nanofibers prepared by the ICI-CDSA of PAA in DMF at 40 mg mL⁻¹ and thermo-treated at 153 °C for 5 min.