Nonspherical chiral helical polymer particles with programmable morphology prepared by electrospraying

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Table S1. GPC test data.

Polymerization were performed under conditions: monomer concentration 0.05M; catalyst concentration 0.005M; the reaction solvent $CHCl_3$, 30 °C for 3 h.

Polymers	PA[c]	R-FA[c]	Mn	Mw/Mn
PPA	10	0	47000[a]	1.3
poly(R-FA$_2$-*co*-PA$_8$)	8	2	15479[b]	3.7
poly(R-FA$_5$-*co*-PA$_5$)	5	5	7045[b]	2.2
poly(R-FA$_8$-*co*-PA$_2$)	2	8	5125[b]	1.9
R-PFA	0	10	4930[b]	1.8

[a]Measured by GPC (polystyrene as standards; toluene as eluent)
[b]Measured by GPC (polystyrene as standards; THF as eluent)
[c]The molar ratio of the comonomer.

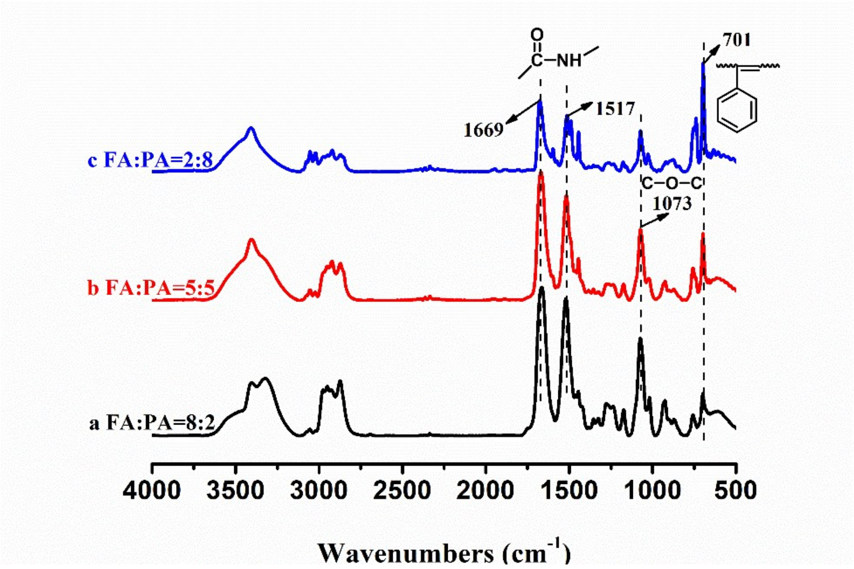

Figure S1. FT-IR spectra of poly(R-FA_8-*co*-PA_2) (a), poly(R-FA_5-*co*-PA_5) (b), and poly(R-FA_2-*co*-PA_8) (c). The spectra were recorded in KBr tablet.

Table S2. Solubility of PPA and PFA in common electrospray solvents (g/mL).

Solvent polymer	DMF	Toluene	$CHCl_3$	Dioxane	OX	THF
PPA	/	0.40	››0.50	0.007	0.50	0.01
PFA	›1.00	››1.00	››1.00	0.95	0.20	›1.00

"/": Almost insoluble

Table S3. Preparation of electrospraying solutions.

Polymers	PPA	PFA	Copolymers	R-PFA_8-*b*-PPA_2 (v/v)	R-PFA_5-*b*-PPA_5 (v/v)	R-PFA_2-*b*-PPA_8(v/v)
Solvents	OX	DMF	DMF	DMF:OX = 4:1	OX: DMF = 4:1	OX

Table S4. Electrospraying parameters

ES particles	Concentrations (wt %)	Positive Voltage (+ kV)	Negative Voltage (– kV)	Solidification distance (cm)	Spinning speed (mL/min)
PPA	17~26	7	2	16	0.004
PFA	20~38	9	2	16	0.004
Copolymers	17~44	11	2	16	0.004
Blends	23~28	7	2	16	0.004

Temperature 30 ℃, 35% RH, stainless steel needle (i.d.:0.4mm), plastic syringe (2.5 mL).

The polymer solutions were placed in a 2.5 ml syringe and was continuously pushed by the syringe pump at a flow rate of 0.004 ml/h to a stainless steel blunt nozzle with a stainless-steel needle (i.d.: 0.4 mm), which was connected to the high-voltage power supply. The high-voltage power supply was used to generate 5-12 kV potential difference between the nozzle and the grounded aluminum foil. A spraying distance of 16 cm between the nozzle and the collector was chosen for each set of experiments.

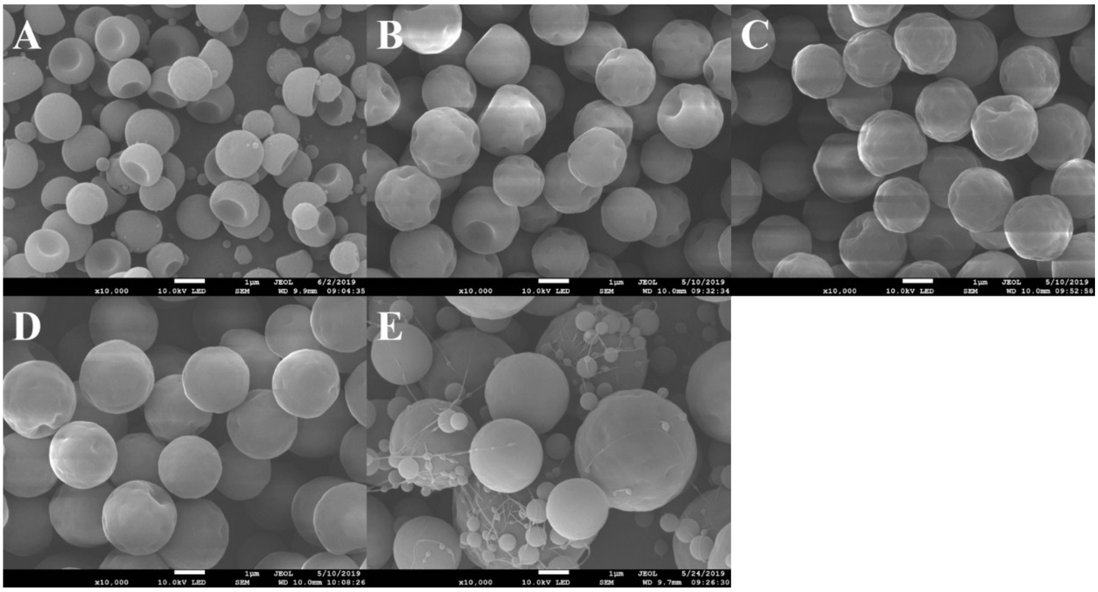

Figure S2. SEM images of the particles made of R-PFA (A, 20 wt%), (B, 26 wt%), (C, 28 wt%), (D, 30 wt%) and (E, 38 wt%) by electrospraying. DMF as solvent.

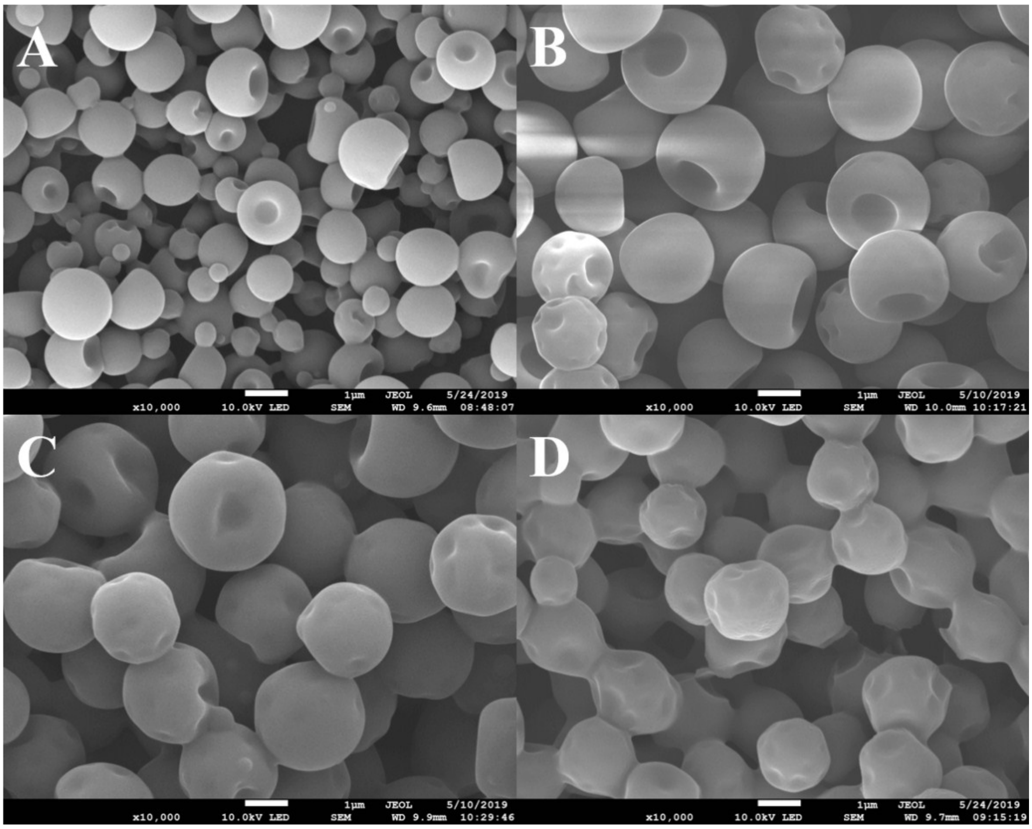

Figure S3. SEM images of the particles made of poly(R-FA_8-*co*-PA_2) (A, 26 wt%), (B, 28 wt%), (C, 31 wt%) and (D, 34 wt%) by electrospraying. DMF as solvent.

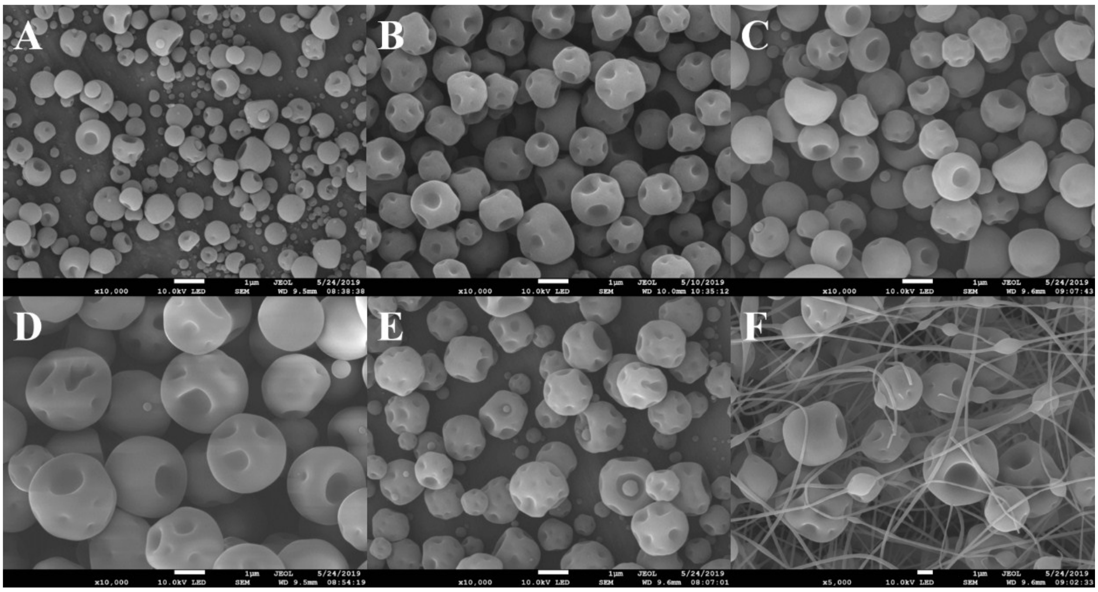

Figure S4. SEM images of the particles made of poly(R-FA$_5$-*co*-PA$_5$) (A, 17 wt%), (B, 23 wt%), (C, 28 wt%), (D, 38 wt%), (E, 41 wt%) and (F, 44 wt%) by electrospraying. DMF as solvent.

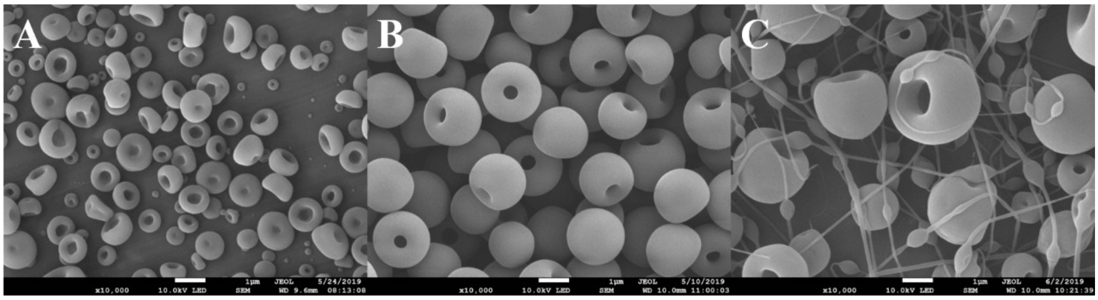

Figure S5. SEM images of the particles made of poly(R-FA$_2$-*co*-PA$_8$) (A, 17 wt%), (B, 28 wt%) and (C, 33 wt%) by electrospraying.

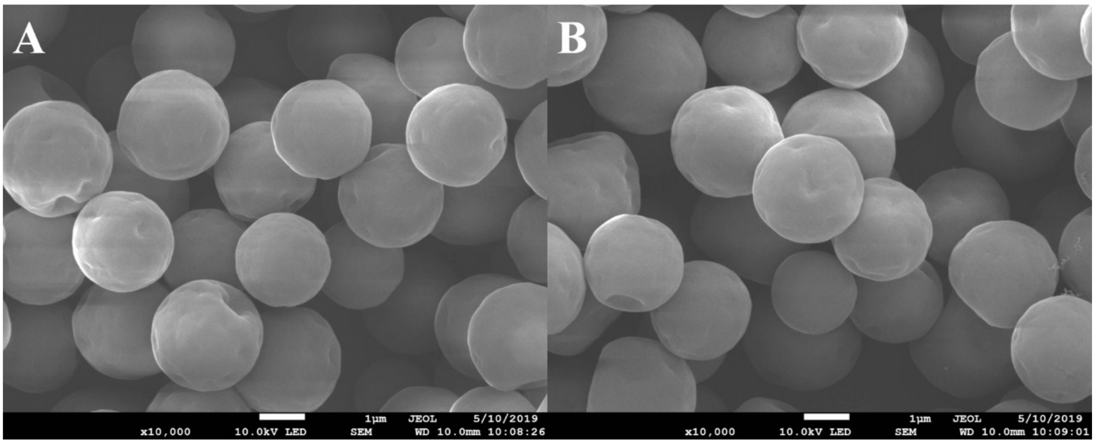

Figure S6. SEM images of the particles made of R-PFA (A, 30 wt%), and S-PFA (B, 30 wt%) by electrospraying.

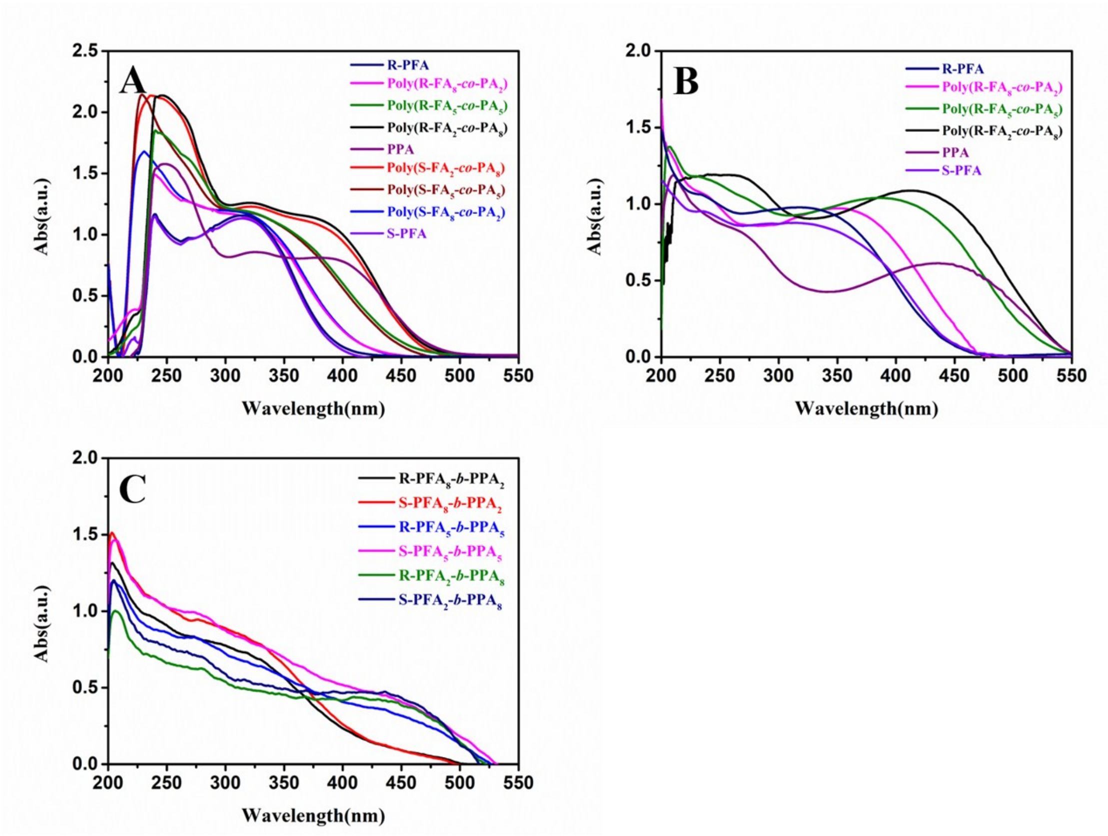

Figure S7. UV−vis absorption spectra recorded in electrosprayed particles made of PPA, R(S)-PFA and their copolymers and blends, corresponding to different test methods: solution CD test method (A) and solid potassium bromide tablet CD test method (B, C). The CD spectra were recorded at room temperature and using KBr tablets.

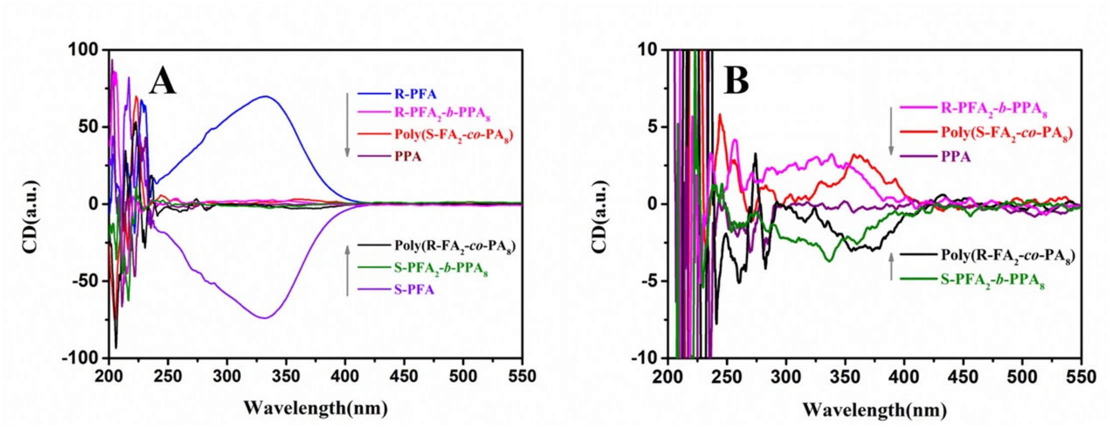

Figure S8. CD spectra of PPA, R(S)-PFA, poly(R(S)-FA$_2$-*co*-PA$_8$) and R(S)-PFA$_2$-*b*-PPA$_8$. The CD spectra were recorded by dissolving them in THF (A, B), B is the partially enlarged spectra. The CD spectra were recorded at room temperature.

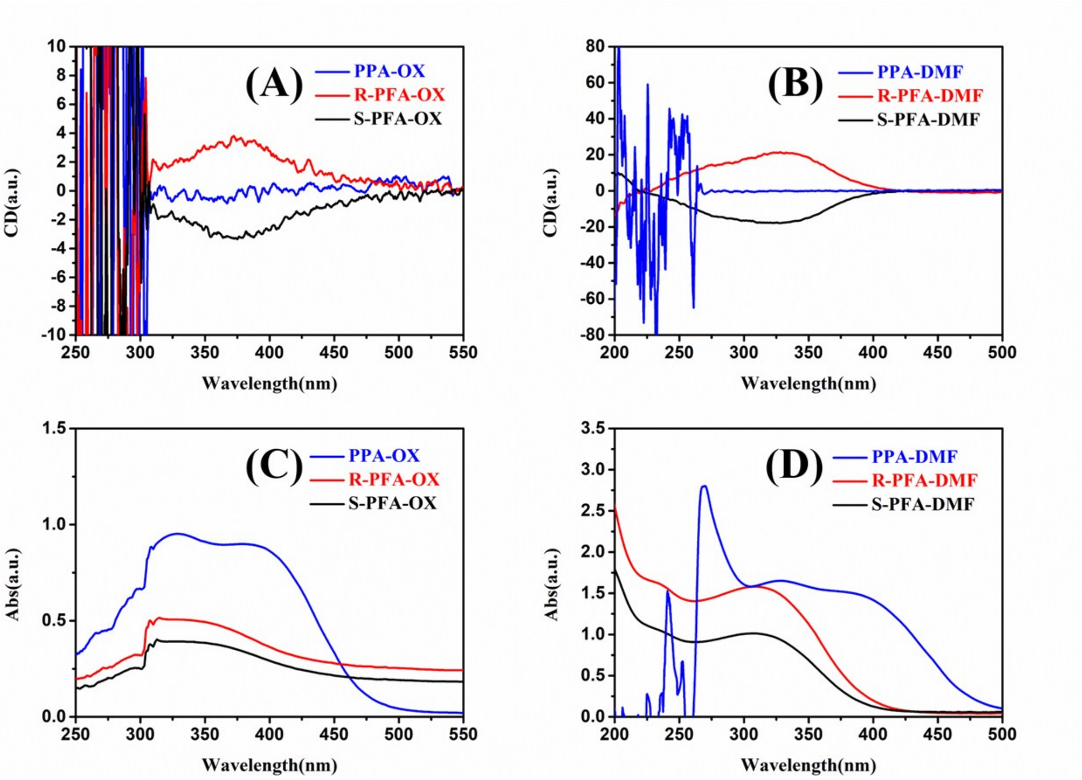

Figure S9. Typical CD & UV−vis absorption spectra of electrosprayed particles consisting of PPA, R(S)-PFA. The CD & UV−vis absorption spectra were recorded by dissolving them in OX (A, C), DMF (B, D). The CD spectra were recorded at room temperature.

Herein, we take electrosprayed particles made from R(S)-PFA and PPA as examples to investigate the chirality of particles in OX and DMF. The results show that CD peaks appeared mainly at 300-450 nm. The UV-vis absorption peaks appear in the corresponding position. This indicates that the solvent used in electrospraying does not affect the optical activity of the polymers. The difference of the CD effects (and UV-vis absorptions) should be due to the varied solubility of the same polymer in the solvents.

Experimental Section

Measurements

Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet NEXUS 670 spectrophotometer (KBr tablet). Circular dichroism (CD) and UV-vis absorption spectra were conducted on a Jasco-815 spectrometer. The morphology of samples was observed with a Hitachi S-7800 scanning electron microscope (SEM). Number-average molecular weight and molecular weight polydispersity were determined by GPC (polystyrene as standards; toluene and THF as eluent). Electrospraying was conducted in electrospinning machine (TEADFS-100).