Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Centimeter-scale giant spherulites in mixtures of polar polymers and crystallizable diluent: Morphology, structure, formation and application

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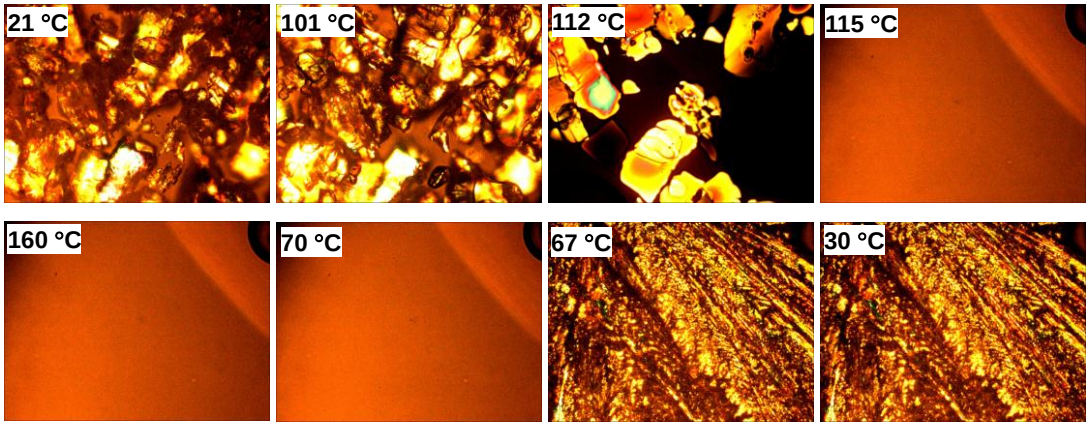

Fig. S1 POM images for phase transition of DMSO2 crystals which were heated on a hot stage (CSS450, Linkam, UK) from 21 °C to 160 °C for 1 min, and then cooled to 30 °C at a rate of 10 °C/min with a temperature controller (Linksys32, Linkam, UK). During the temperature region of 21~101 °C, isolated DMSO2 crystals present subtle change. The crystals melt completely when they were heated around 115 °C. As the melt was cooled to 67 °C, needle crystals nearly come out in a moment, meaning the fast crystallization. However, no spherulites can be formed for DMSO2 itself.

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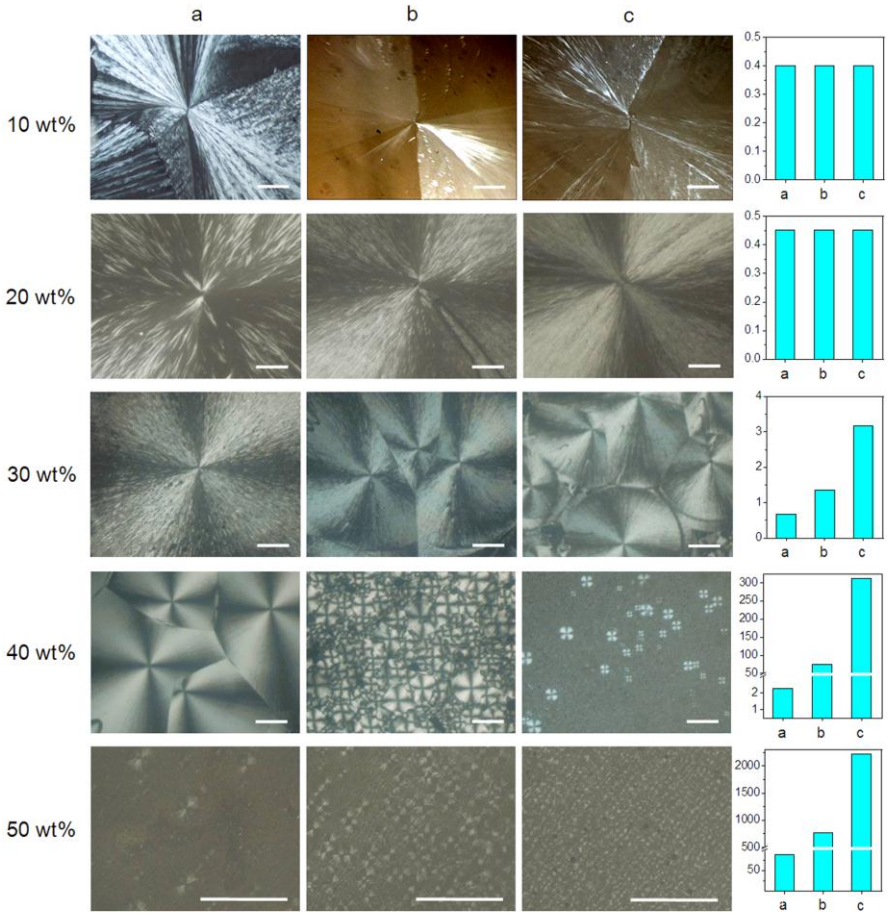

Fig. S2 POM images of PAN/DMSO2 films with different PAN percentages quenched in cooling baths of (a) air at 30 °C, (b) water at 4 °C, and (c) liquid nitrogen. Insets are nucleation density of spherulites (y-axis, 1/mm^2) varies with cooling baths (x-axis).

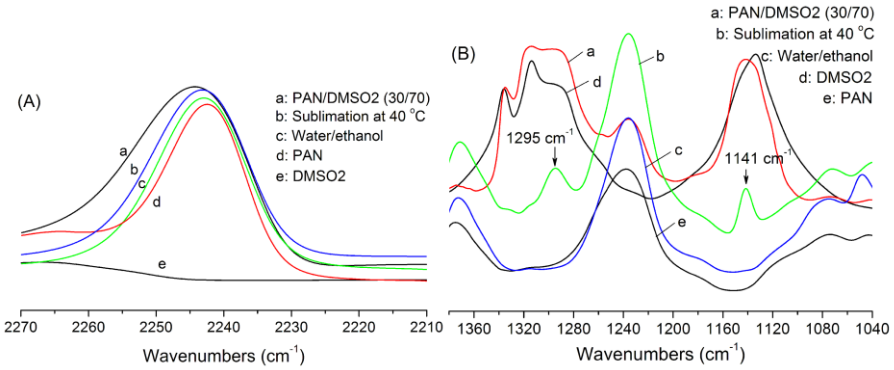

Fig. S3 FTIR spectra recorded at room temperature: (a) CN stretching band in the range of 2210–2270 cm^{-1}; (b) symmetric OSO stretching band in the range of 1040–1200 cm^{-1}. Dash: PAN/DMSO2 film containing 30 wt% PAN; dash dot: PAN/DMSO2 film pretreated by sublimating at 40 °C for 10 days; short dash: PAN/DMSO2 film washed by DI water and ethanol for 5 days in turn.

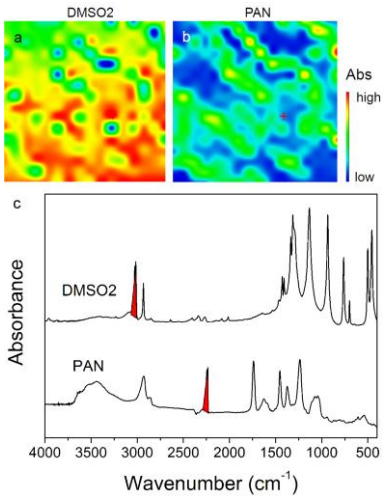

Fig. S4 FTIR images (1500 × 1500 μm^2) showing the distribution of (a) DMSO2 based on the CH_3 stretching band and (b) PAN based on the CN stretching band. (c) Absorption spectra of DMSO2 and PAN. Vibration bands at 3015 and 2242 cm^{-1} were selected to characterize DMSO2 and PAN, respectively, because these two vibrations are isolated bands without any overlapping and have high signal-to-noise ratio. It is obvious that PAN and DMSO2 distribute in alternating regions of the spherulites, suggesting they undergo phase separation in the film prepared by slowly cooling. FTIR images were recorded using a Bruker imaging system consisting of a Bruker Vertex 70 infrared spectrometer (Brucker Optics, Switzerland).

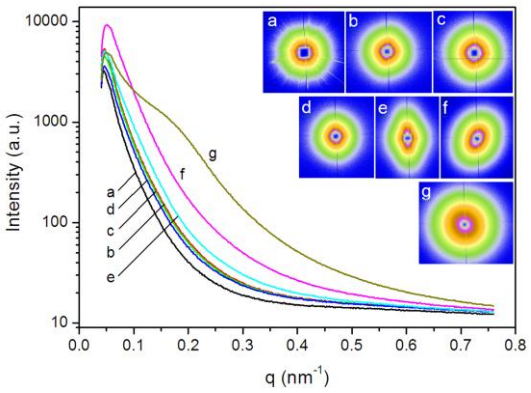

Fig. S5 SAXS profiles and images (insets) of pure DMSO2 (a) and PAN/DMSO2 films with PAN percentage of (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 40 wt%, (f) 50 wt%, and (g) 60 wt%. Films were prepared by cooling at 0.5 °C/min.

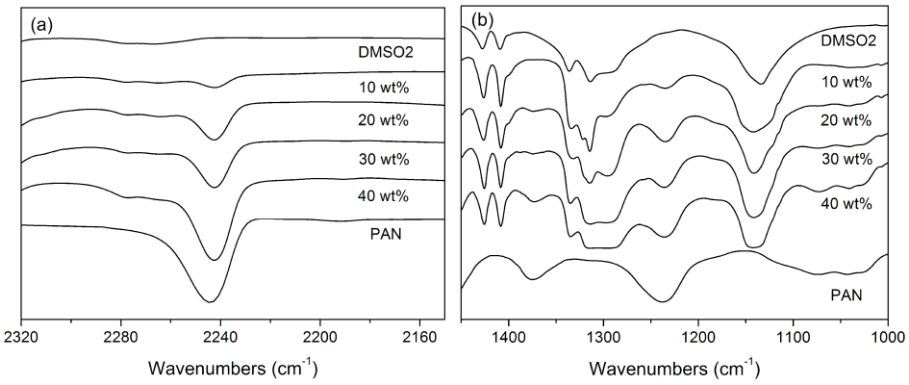

Fig. S6 FTIR spectra of PAN/DMSO2 films in the ranges of 2320–2150 cm^{-1} and 1450–1000 cm^{-1}. FTIR spectra were measured with a Brucker Vector 22 spectrometer (Brucker Optics, Switzerland). Thirty two scans were taken for each spectrum at a nominal resolution of 2 cm^{-1}.

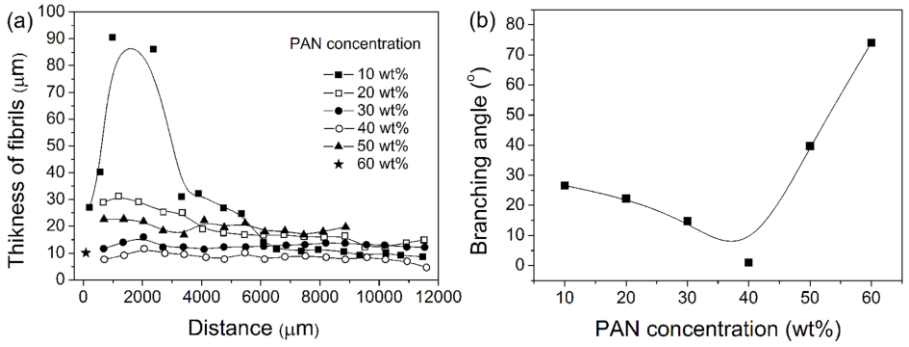

Fig. S7 (a) Distance-dependent thickness of fibrils in giant spherulites with different PAN concentrations. (b) PAN concentration-dependent branching angles of fibrils at 3 mm far from the centre of a giant spherulite.

Table S1 *d* spacing, Miller indices (*h*,*k*,*l*), and relative intensity (I/I_1) of diffraction peak of DMSO2 crystals for pure DMSO2 and PAN/DMSO2 films.

PAN percentage (wt%)	(110)		(111)		(200)		(021)		(112)		(022)	
	d (Å)	I/I_1	*d* (Å)	I/I_1	*d* (Å)	I/I_1	*d* (Å)	I/I_1	*d* (Å)	I/I_1	*d* (Å)	I/I_1
0	5.39	100.0	4.34	53.7	3.66	37.6	3.51	15.9	3.04	10.5	2.70	30.7
10	5.43	4.0			3.68	100.0					2.71	1.0
20	5.42	7.1			3.67	100.0					2.71	1.9
30	5.43	100.0	4.37	27.5	3.67	99.9	3.53	7.3	3.04	1.6	2.71	17.0
40	5.43	100.0	4.37	33.3	3.67	35.3	3.53	18.5			2.71	22.7
50	5.44	79.3	4.38	100.0	3.68	40.0	3.54	30.8	3.05	13.6	2.72	21.9

The *d* spacing calculated from corresponding peaks slightly increases with PAN percentage, and is larger than that of pure DMSO2 crystals. This is indicative of the enlarged interplane distance between crystal planes. Moreover, the preferential crystal plane of DMSO2 is different in each pattern according to the highest diffraction peak (I/I_1 = 110). In detail, a preferential crystal plane of (200) is exposed in the cases with 10–30 wt% PAN, whereas (110) plane is for those with 30–40 wt% PAN and (111) plane is for the one with 50 wt% PAN.