Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Evidence for Complexation-Induced Micro-Extension of Poly(Vinyl Alcohol) Chains in Interphase and Amorphous Domains from Solid-State NMR

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1. Multi-peak fitting of different iodinated PVA samples.

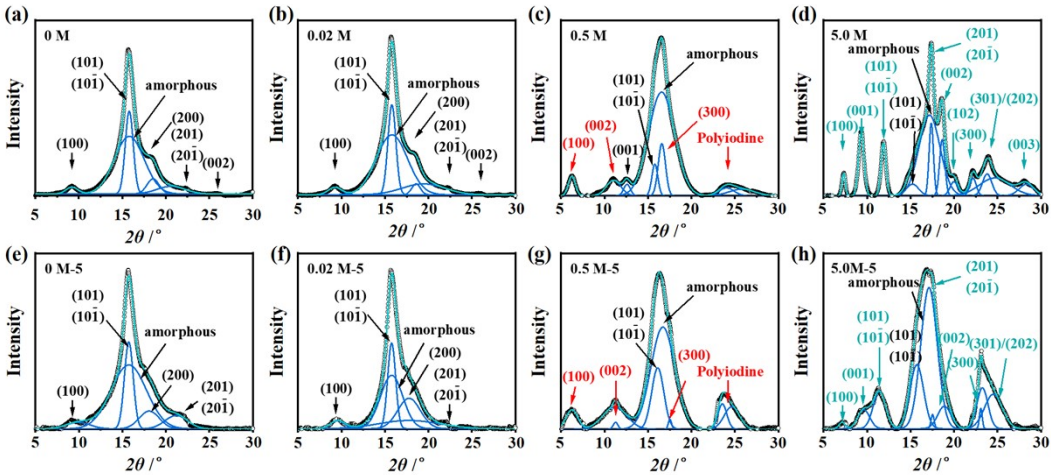

Fig. S1. Multi-peak fitting of One-dimensional integrated WAXS curves of the unoriented [(a)-(d)] and oriented [(e)-(h)] PVA films of 0 M, 0.02 M, 0.5 M and 5 M iodine concentrations. The crystal index of different crystals is labeled in various colors: black, red, and green for PVA crystal, PVA–I_3^- complex I, and PVA–I_3^- complex II, respectively.

2. Integrated results of CP/MAS spectra.

Table S1. Integrated chemical shift, full width at half-maximum (FWHM) of lines C(H)(I/II/III) for the CP/MAS spectra of the unoriented and oriented samples.

Sample		Chemical shift/ ppm			FWHM/ Hz		
		C(H)			C(H)		
		I	II	III	I	II	III
Unoriented	0 M	75.8	70.1	64.4	446	445	402
	0.02 M	75.8	70.1	64.3	454	444	402
	0.5 M	75.3	70.0	64.4	396	423	397
	5 M	75.3	70.4	65.0	422	377	398
Oriented	0 M	75.7	70.1	64.3	434	426	406
	0.02 M	75.7	70.1	64.3	475	429	412
	0.5 M	75.3	70.4	64.4	760	459	530
	5 M	73.3	70.4	65.1	1083	349	504

3. ^{13}C T_1 relaxation curves of unoriented samples (0.5 M and 5 M).

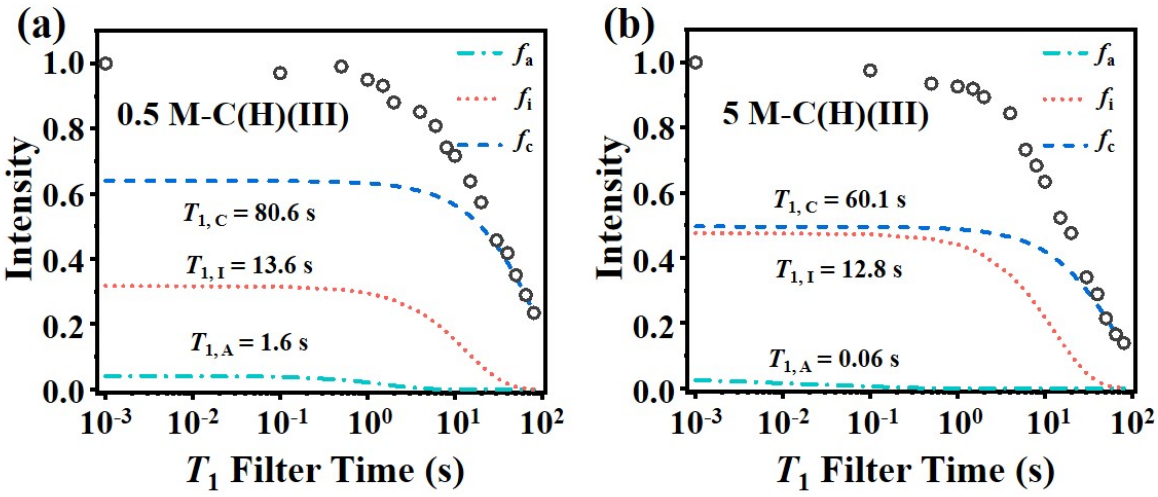

Fig. S2. Torchia ^{13}C T_1 relaxation curves of unoriented iodinated PVA films at (a) 0.5 M and (b) 5 M.

4. ^{13}C DP/MAS spectra of pure PVA film with different recycle delay times and NS.

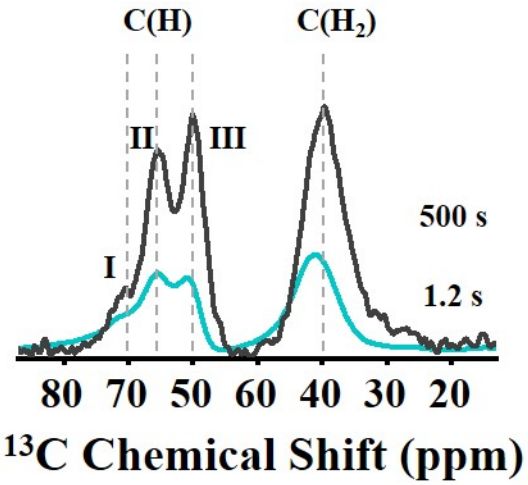

Fig. S3. ^{13}C DP/MAS spectra of pure PVA film (0 M) with different recycle delay times and NS: Black-500 s (128 scans) for sufficient fully signals, Green-1.2 s (30720 scans) for the amorphous signal. The signal of 500 s is scaled by 240 to compensate for the different NS [1,2].

5. Integrated results of the three-phase spectra.

Table S2. Integrated chemical shift, full width at half-maximum (FWHM) of lines C(H)(I/II/III) for the three-phase spectra of the unoriented and oriented samples.

Sample		Phase	Chemical shift/ ppm			FWHM/ Hz		
			C(H)			C(H)		
			I	II	III	I	II	III
Unoriented	0 M	C	76.3	70.4	64.3	609	441	418
		I	75.8	69.9	64.6	421	461	390
		A	73.7	69.8	65.1	946	426	390
	0.02 M	C	76.4	70.3	64.1	433	459	420
		I	75.5	69.9	64.5	395	462	416
		A	74.1	69.6	64.9	969	449	390
	0.5 M	C	75.7	70.2	64.3	359	418	377
		I	74.9	69.8	64.5	406	410	418
		A	73.7	69.8	65.1	924	390	389
	5 M	C	75.6	70.5	64.6	405	437	431
		I	75.1	70.4	65.2	455	368	428
		A	74.8	70.4	65.6	618	368	391
Oriented	0 M-5	C	76.2	70.3	64.1	483	420	430
		I	75.4	69.9	64.7	462	435	399
		A	74.9	69.8	65.0	734	426	391
	0.02 M-5	C	76.1	70.4	64.0	526	428	457
		I	75.5	69.9	64.4	419	442	401
		A	74.1	69.8	64.9	942	409	417
	0.5 M-5	C	-	-	-	-	-	-
		I	-	-	-	-	-	-
		A	74.2	70.0	64.8	1224	507	466
	5 M-5	C	-	-	-	-	-	-
		I	-	-	-	-	-	-
		A	73.6	70.6	65.4	1251	408	473

6. SUPER results of the pure PVA film.

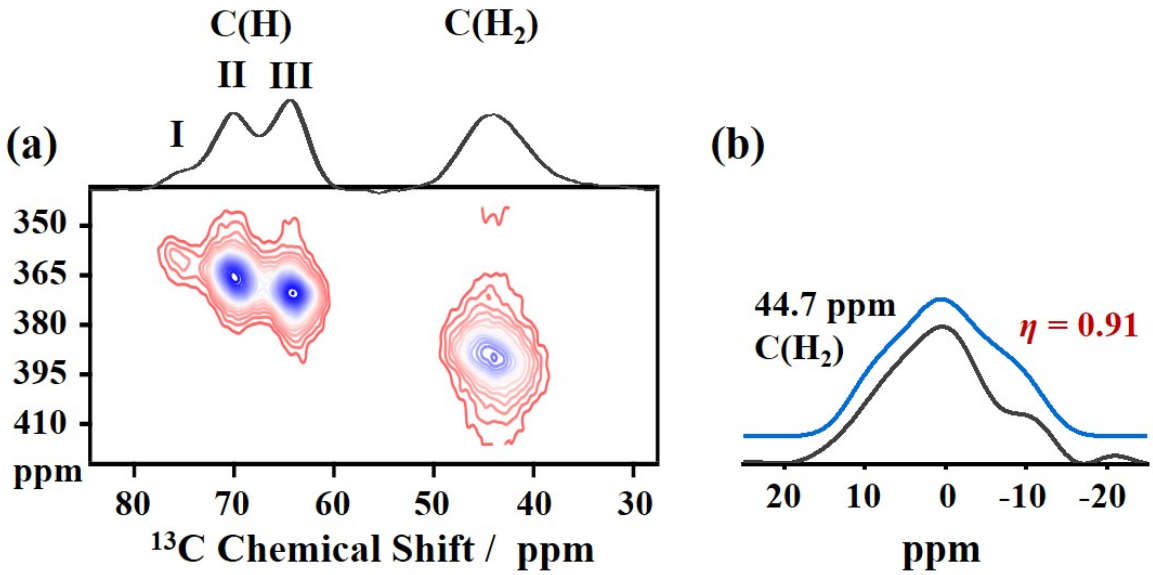

Fig. S4. (a) Unsheared 2D SUPER spectra of 0 M obtained at a MAS rate of 5 kHz. (b) Corresponding powder pattern extracted at the labeled ppm value (black line), it is obtained by shifting the isotropic chemical shift to δ = 0 ppm. The simulated CSA curve (blue line) was carried out by the NMR WEBLAB online software.[3] The line shape analysis of the chemical shift principal value (δ_{11}, δ_{22}, and δ_{33}) and an asymmetry parameter η can be obtained. $\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso})$, where $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ and assuming that $|\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}| \geq |\delta_{33} - \delta_{iso}|$, $0 \leq \eta \leq 1$.[4]

7. Simulation of the static ^{13}C CP spectra of $C(H_2)$

In this work, simulation of the static ^{13}C CP spectra of $C(H_2)$ was carried out by the NMR simulation software "SIMPSON". The crystal file used in" SIMPSON" was generated using the step method to simulate the line shape of the powder pattern. For the simulation of the oriented sample, based on the step method, MATLAB software was used to generate (α, β) pairs with α span over [0, 360] degrees and β covered an adjustable range as [a, b] between [0,180] degree. Finally, the weighting factor w was normalized to [0,1]. The step method was defined as follows:[5]

$$0 \leq \alpha < 2pi, 0 \leq \beta < \frac{pi}{2} \tag{1}$$

$$\alpha_i = \frac{2pi}{N_\alpha}, 0 \leq i \leq N_\alpha - 1 \tag{2}$$

$$\beta_j = \frac{pi}{4N_\beta}(2j+1), 0 \leq j \leq N_\beta - 1 \tag{3}$$

$$w_j = sin\beta_j \tag{4}$$

$$w_j = \frac{sin\beta_j}{\Sigma_j sin\beta_j} \quad \text{normalized} \tag{5}$$

α and β were azimuth and polar angle of magnetic field B_0 in the chemical shift principle axis system, respectively. N_α and N_β divided the range of integration for the α and β angles into evenly spaced segments, respectively, giving a total number of orientations $N_\alpha * N_\beta$.

This gives a hemisphere distribution set $S_{hemi} = \{\alpha_i, \beta_j, w_j\}$, where the weights depend only on the β angle. For the simulation of the crystalline domain (0°), β of 1°±1° was used in the simulation. β of 1°±1° and β of 35° ~ 50° were combined in the simulation of the interphase domain (0°) where 35° ~ 50° was determined

by the chemical shift position relative to 1°.

8. Torchia ^{13}C T_1 relaxation curves of oriented iodinated PVA films.

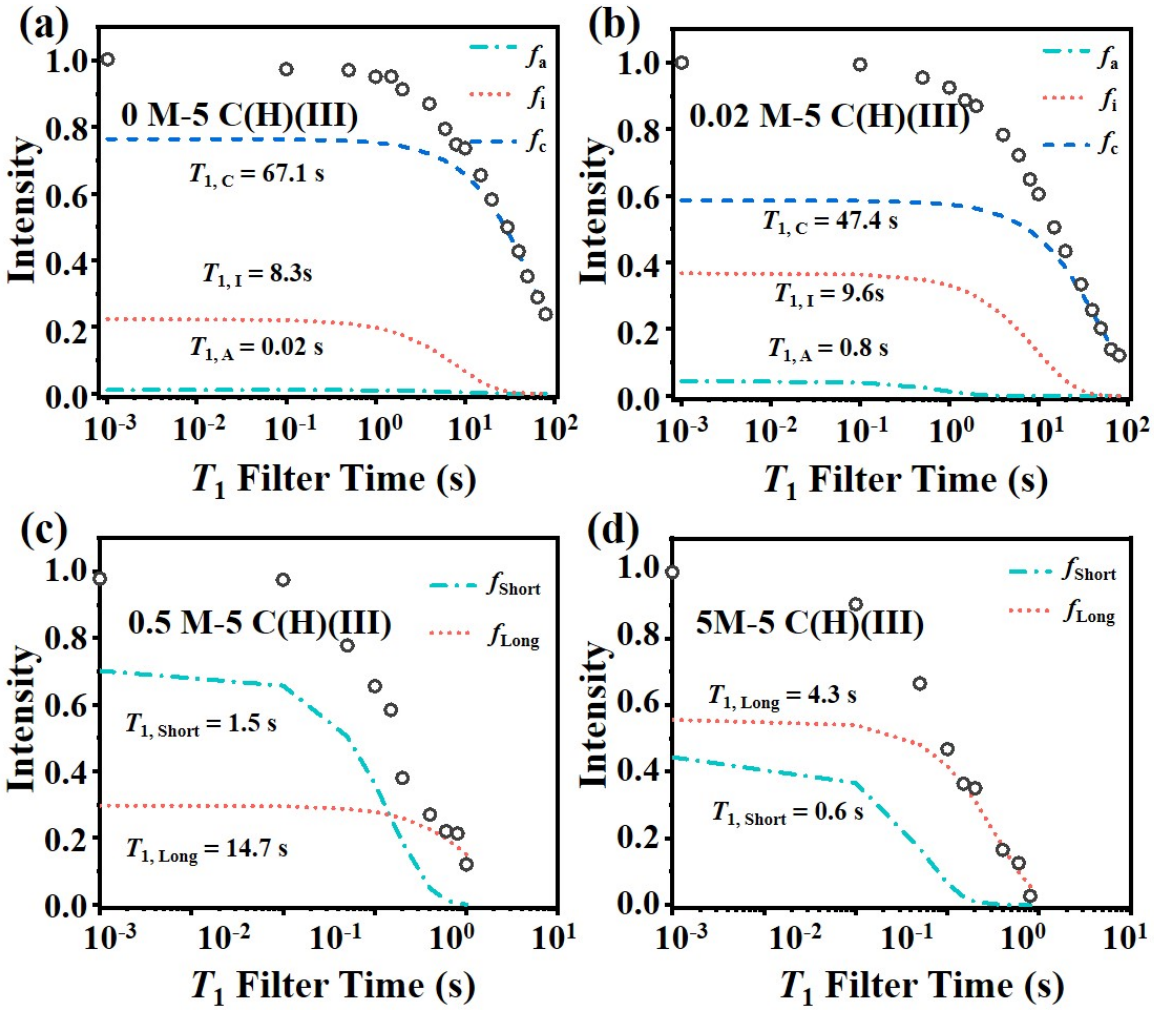

Fig. S5. Torchia ^{13}C T_1 relaxation curves of oriented iodinated PVA films at (a) 0 M, (b) 0.02 M, (c) 0.5 M and (d) 5 M.

9. Deconvoluted ^{13}C CP/MAS spectra of oriented iodinated PVA films.

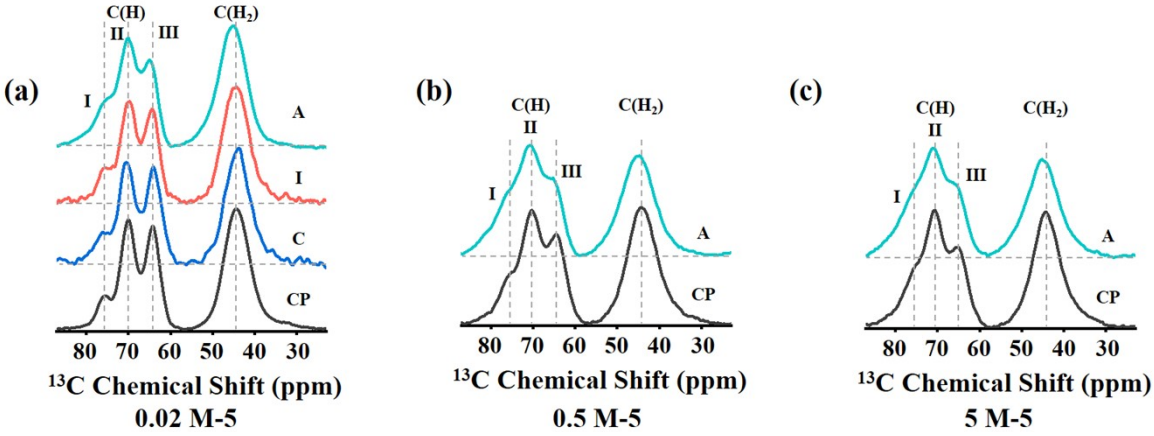

Fig. S6. Deconvoluted ^{13}C CP/MAS spectra of oriented iodinated PVA films at (a) 0.02 M, (b) 0.5 M and (c) 5 M.

References

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