Supporting Information for

Excellent dielectric energy storage performance achieved by synergistically increasing permittivity and breakdown strength in poly(vinylidene chloride-vinyl chloride) with stabilized conformation

Yijin He[a#], Guanxiang Zhang[b#], Ba Qin[a], Wenxuan Li[a], Guansong He[c], Bofeng Zhu[b], Xiao Zhang[b], Shaobo Tan[a], Zhicheng Zhang[a*]*

[a]*National Innovation Platform (Center) for Industry-Education Integration of Energy Storage Technology, Xi'an Key Laboratory of Sustainable Energy Material Chemistry, School of Chemistry, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, P. R. China*

[b]*National Key Laboratory of Science and Technology on Vessel Integrated Power System, Naval University of Engineering, Wuhan 430034, P. R. China.*

[c]*Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, P. R. China*

*Corresponding Author:

Zhicheng Zhang: zhichengzhang@mail.xjtu.edu.cn

Shaobo Tan: shaobotan.1987@xjtu.edu.cn

Instruments and Characterization

ADVANCE III HD 600 MHz spectrometer was used to record the ^{1}H and ^{13}C NMR spectra with THF-d_8 as the solvent and tetramethyl silane as the internal standard. On a Tensor 27 (Bruker) made in Germany, Fourier transform infrared (FT-IR) spectra in transmittance mode were acquired. X-ray photoelectron spectroscopy (XPS) was employed using a Thermo Fisher Scientific instrument (Escalab Xi, USA) with dual anode Al/Mg targets at 400 W. On a METTLER DSC 3, differential scanning calorimetry (DSC) was carried out in a nitrogen environment at a heating rate of 10°C/min. The tensile test was performed using an electronic stretching machine (CMT6503, MTS) fitted with a 50 N weighing sensor and a 5 mm/min stretching rate. Sample in the shape of a dumbbell (12 mm × 2.0 mm × 0.5 mm). The automated fine coater (JEOL JFC-1600) was used to spray gold on both sides of polymer films to fabricate electrodes with an 80 nm thickness before testing the dielectric performance of the samples. Broadband dielectric spectroscopy (BDS) was obtained using a concept 80 broadband dielectric spectrometer with a temperature control function manufactured by the Novocontrol company in Germany, where the voltage is fixed at 1 V, the sweep frequency range is 10^{0}-10^{6} Hz, and the temperature range is -30 - 120°C. Beijing Beiguangjingyi Instrument Equipment Corporation, which provides an electric strength rate of 1 kV/min, produced breakdown voltage testing equipment. The 10 mm-diameter electrodes of the gadget are cylindrical. The breakdown voltage can be obtained when the leakage current reaches 10 mA. With a ferroelectric tester (Radiant Technologies, Premiere II), the displacement-electric field (*D*-*E*) loops and leakage current density of polymer film can be examined. At a frequency of 10 Hz, the DC electric field was applied to polymer films. With a load resistor resistance of 100 kΩ, PolyK Technologies (PKCPR1502) was used for charge-discharge testing, and the charge-discharge cycle was controlled by the LabVIEW program.

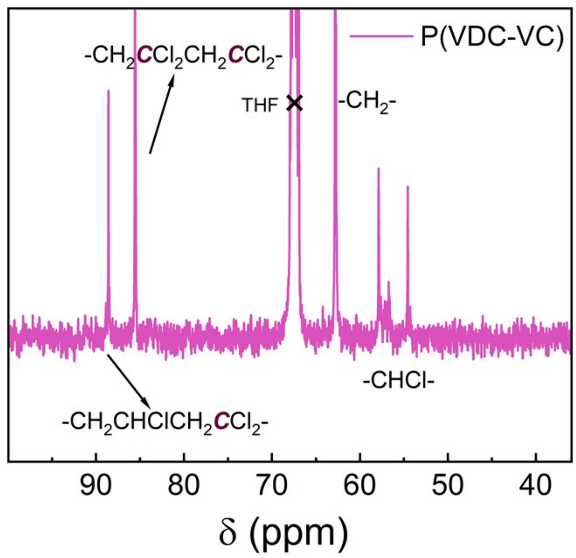

Figure S1. ^{13}C-NMR spectrum of P(VDC-VC).

Table S1. Sequence assignments in ^{1}H-NMR spectrum of P(VDC-VC)

Chemical shift (ppm)	Sequence	Assignment
1.2-1.6	$-CH_2CH_2CH_2-$	CH_2
2.0-2.6	$-CH_2CCl_2CH_2CCl_2-$	CH_2
2.8-3.4	$-CH_2CHClCH_2CCl_2-$	CHCl
3.7-4.2	$-CH_2CHClCH_2CHCl-$	CHCl
4.4-5.2	-CHCl-	CHCl

Table S2. Sequence composition in ^{13}C-NMR spectrum of P(VDC-VC)

Chemical shift (ppm)	Sequence	Assignment
54.5	BAB	$CHCl+CH_2$
56.6	AB	$CHCl+CH_2$
57.9	AAA+AB	$CHCl+CH_2$
62.8	BB	CH_2
85.5	BBB	CCl_2
88.5	ABB	CCl_2

The symbol A represents vinyl chloride (VC), whereas symbol B denotes vinylidene chloride (VDC)

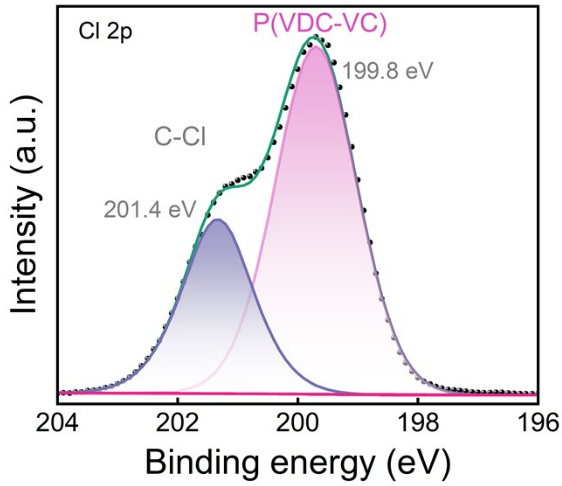

Figure S2. XPS spectrum of P(VDC-VC).

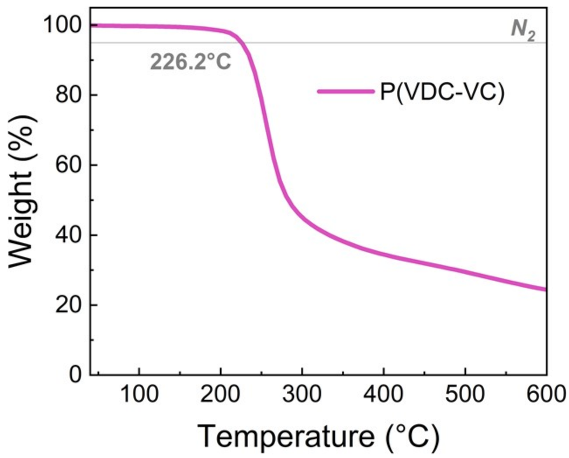

Figure S3. TGA thermogram of P(VDC-VC).

Table S3. Grain size and crystal planes of P(VDC-VC) and PVDF

	Crystal form	2θ (°)	Crystal plane (hkl)	Crystalline phase	Grain size (nm)
P(VDC-VC)	Monoclinic	15.7	100	α	8.3
		33.1	020	α	6.2
PVDF	Monoclinic	18.4	020	α	5.5
		20.2	110	α	7.1
		26.5	021	α	2.2
		36.1	200	α	3.7
		39.0	002	α	3.2

Due to the high electronegativity and strong polarity of fluorine atoms, PVDF exhibits strong intermolecular interactions, resulting in a higher Young's modulus compared to P(VDC-VC). Using Gaussian software, density functional theory (DFT), and reduced density gradient (RDG) scatter plots, the interactions of VDC-VC and VDF-VDF units were analyzed. The RDG scatter plots show sharp peaks near zero, confirming the presence of interactions. Furthermore, the interactions were visualized using the interaction region indicator (IRI) function. As illustrated in **Figures S4e and 4f**, the green regions represent the interaction isosurfaces of VDC-VC and VDF-VDF units, indicating stronger dipole-dipole interactions in VDF-VDF.

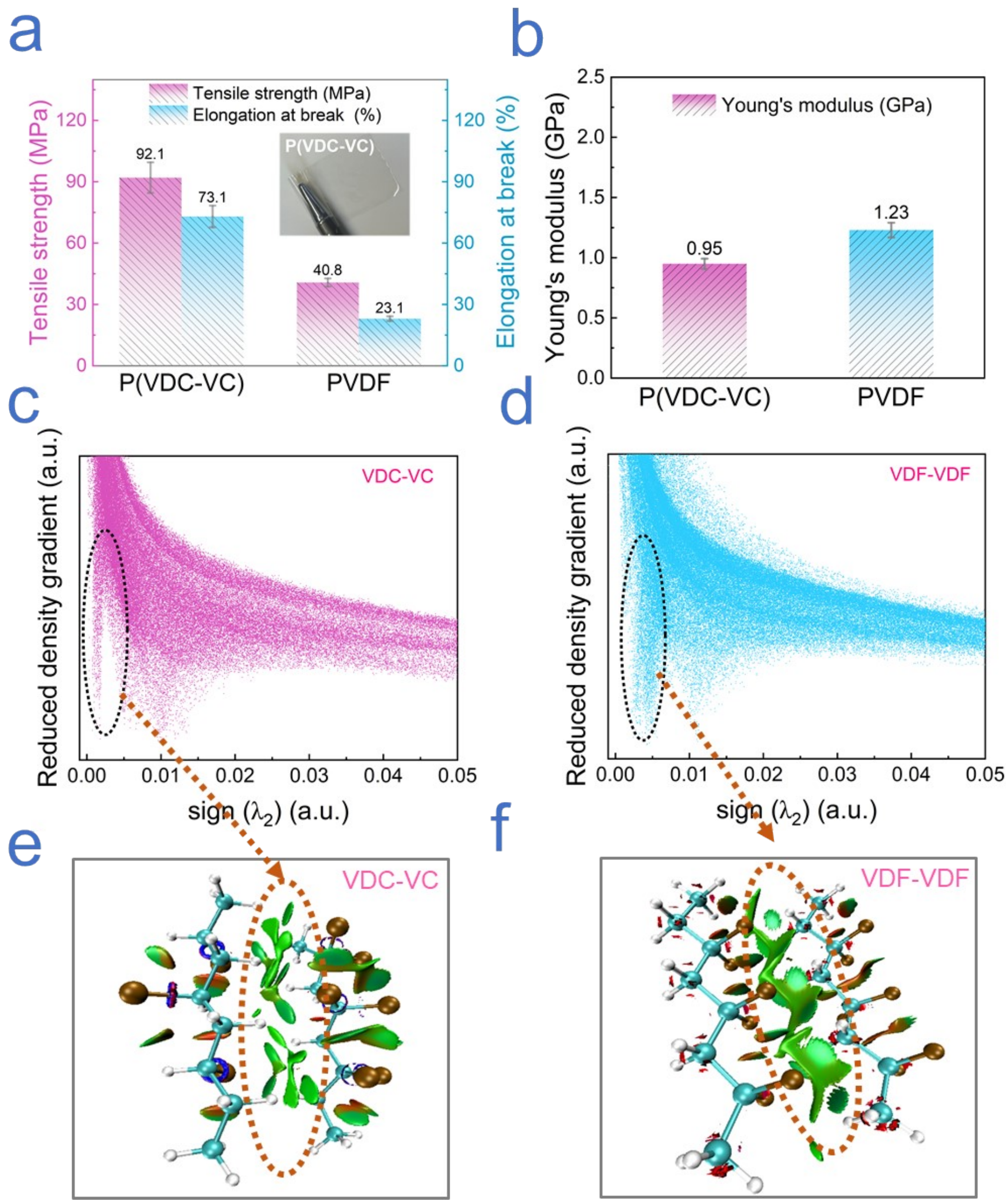

Figure S4. (a) Tensile strength and elongation at break of P(VDC-VC) and PVDF films; (b) Young's modulus for P(VDC-VC) and PVDF; (c-d) RDG scatter plot of VDC-VC units and VDF-VDF units, and (e-f) IRI analysis diagrams. The inset in a exhibits the image of P(VDF-VC) film.

As shown in **Figure S5**, P(VDC-VC) exhibits a high storage modulus of 8000 MPa in its frozen state at low temperatures. As the temperature increases, P(VDC-VC) transitions from a glassy state to a rubbery state, accompanied by a decrease in storage modulus. A peak in the loss modulus is observed within the room temperature range, which is associated with the glass transition temperature of (VDC-VC).

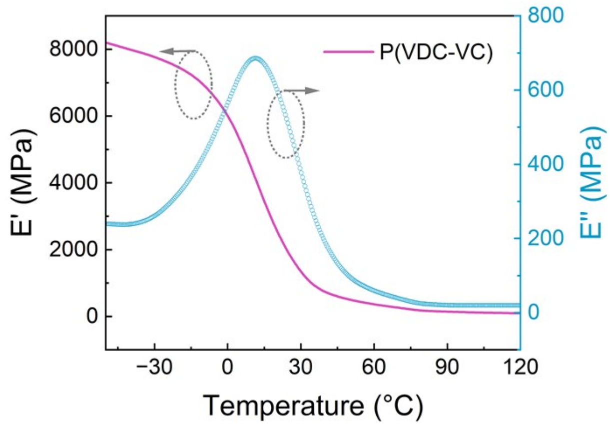

Figure S5. DMA results of P(VDC-VC) film.

As shown in **Figure S6**, P(VDC-VC) exhibits excellent conformational stability, low dielectric loss, and low P_r under high electric fields, maintaining stable quasi-linear dielectric polarization behavior. In contrast, PVDF experiences a sharp increase in P_r under high electric field, accompanied by a phase transition from non-polar α-phase to polar γ and β phases.

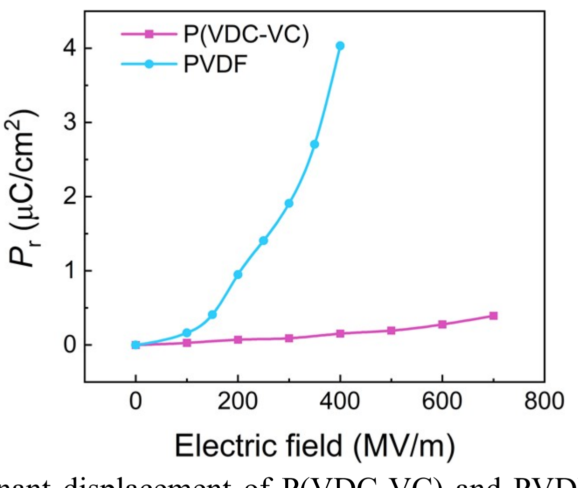

Figure S6. The remnant displacement of P(VDC-VC) and PVDF under the applied electric field.

As shown in the **Figure S7**, P(VDC-VC) maintains a breakdown strength of up to 600 MV/m at 80°C, with an energy storage density of 9.5 J/cm³ at 600 MV/m. Additionally, the discharge efficiency remains above 80% at an electric field of 450 MV/m.

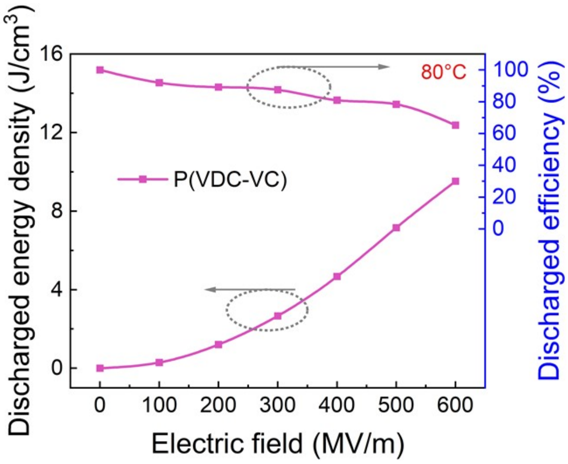

Figure S7. Discharged energy density and efficiency of P(VDC-VC) at 80°C.

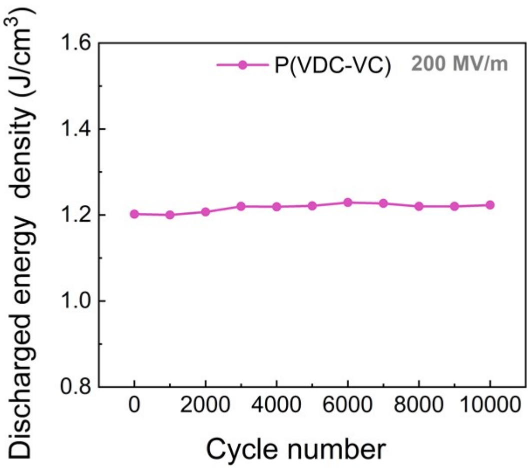

Figure S8. Charge-discharge cycling stability for P(VDC-VC) at 200 MV/m.