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Supplementary Information

Gradient Core-shell Structure Enabling High Energy Storage Performances in PVDF-based Copolymers

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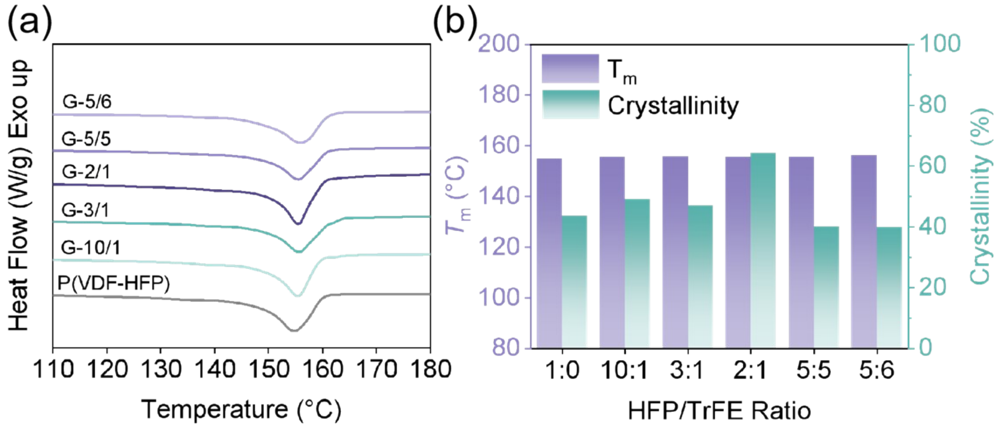

Figure S1. (a) DSC curves of gradient core-shell structured P(VDF-HFP)/P(VDF-TrFE) hybrid films with various HFP/TrFE monomer ratios. (b) Comparison on the melting temperature and crystallinity of the hybrid films with respect to different HFP/TrFE monomer ratios.

Finite Element Analysis: The simulation was carried out on COMSOL Multiphysics 5.3a using Electrostatics module. The size of 2D model is 2μm×2μm. Adjusting the grayscale of the P(VDF-HFP) and P(VDF-TrFE) based on the SEM images, and set the dielectric constants according to the grayscale of the images. The dielectric constants of P(VDF-HFP) and P(VDF-TrFE) for simulation are set as 11.6 and 17.8 based on previous reported data, respectively. To simulate the local electric field distribution, the voltage at top and bottom surfaces of the model is set to 1200 V and 0 V, respectively, while the other surfaces are defined to be insulating, resulting in an external field of 600 MV/m.

Molecular Dynamic Simulation: The molecular models of core-shell structured P(VDF-HFP)/P(VDF-TrFE) hybrid films were built by Materials Studio. In order to form a core-shell structure with different concentration gradients, corresponding to the actual experiment, the inner blend of one P(VDF-TrFE) chain and thirty P(VDF-HFP) chains were set to be surrounded by the outer blend of two P(VDF-TrFE) chains and 120 P(VDF-HFP) chains to form G-10/1 structure, as shown in Fig. S2a. Similarly, the inner blend of two P(VDF-TrFE) chains and six P(VDF-HFP) chains were set to be surrounded by the outer blend of one P(VDF-TrFE) chain and nine P(VDF-HFP) chains to form G-5/5 structure, as shown in Fig. S2b. The size of the simulation box was about 155 Å × 155 Å × 110 Å and 65 Å × 65 Å × 110 Å, respectively. The *forcite* module was used to add topology information and optimize the molecular structure in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). In the simulation of crystalline phases, all the molecular chains of P(VDF-TrFE) were artificially set as rigid bodies, and the topological relationship between each atom was fixed so that it existed in the system in crystalline form, while P(VDF-HFP) was not modified. The initial temperature of the system was set to 0.15 K. During the equilibration process, the P(VDF-TrFE)/P(VDF-HFP) copolymer system was firstly relaxed from 0.15 K to 293.15 K for 10 ps in the isothermal-isobaric (NPT) ensemble, and the pressure was set to be 1.0 atm. After that, the copolymer system was further equilibrated at 293.15 K and 1.0 atm for 100 ps in the isothermal-isobaric (NPT) ensemble with the constant number of particles, pressure, and thermostat temperature, which corresponded to the constant temperature and constant pressure experiments. Finally, the copolymer system was equilibrated at 293.15 K for another 100 ps in the canonical (NVT) ensemble, and the total energy of the copolymer system kept at a relatively constant level before the equilibration run was completed, which implies that the structure was equilibrated properly. The constant temperature and pressure were controlled by the Nosé–Hoover thermostat and barostat during the simulation. The intermolecular and intramolecular interactions of P(VDF-HFP) and P(VDF-TrFE) copolymer systems are described by the all-atom Consistent Valence Forcefield.

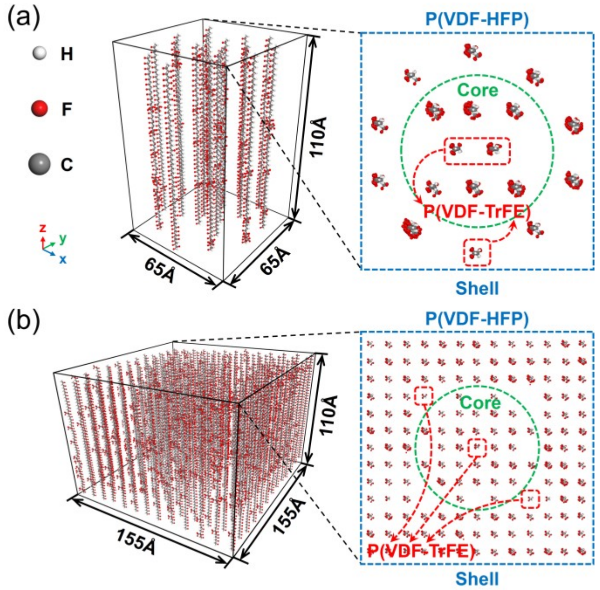

Figure S2. The molecular structures for molecular dynamic simulation. (a) G-5/5 and (b) G-10/1 films.

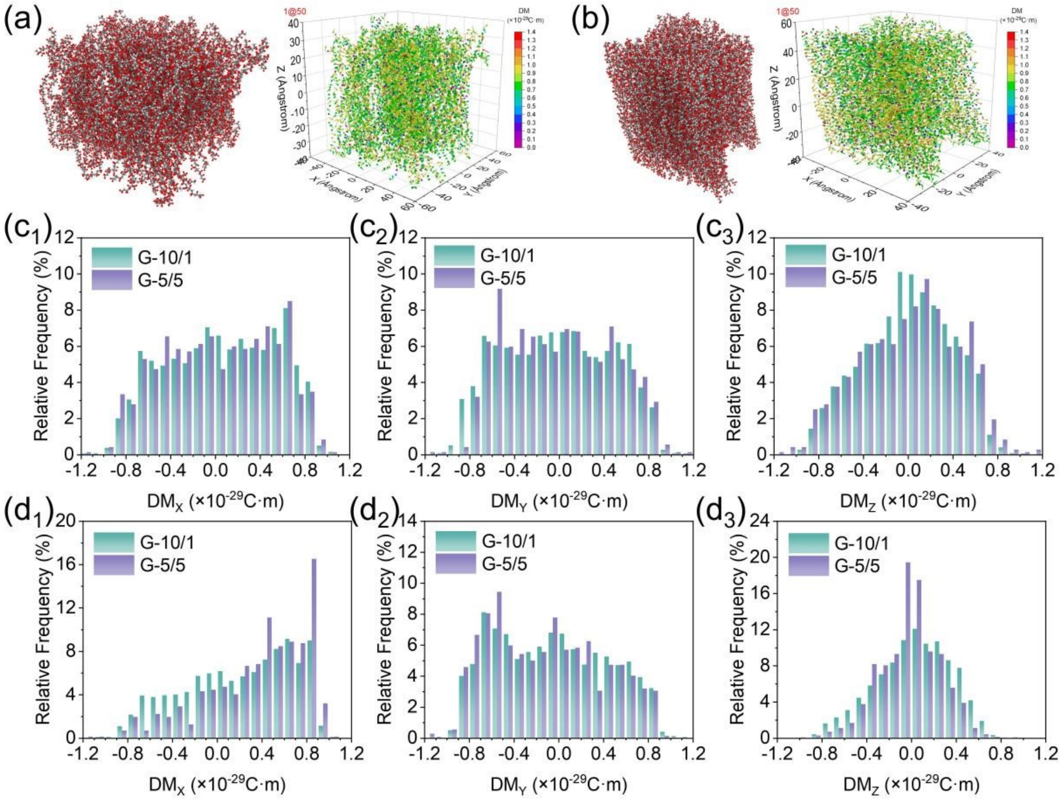

Figure S3. Molecular structure and corresponding 3D distribution of dipole moments of (a) amorphous and (b) crystalline G-10/1 film. Comparison on modulus distributions of dipole moments in three directions between G-10/1 and G-5/5 films in (c) amorphous and (d) crystalline state.

Table S1. Comparison on energy storage performances between recent reported studies and this work.

Materials	Structure	E_b (MV/m)	U_e (J/cm^3)	Cycling stability	Ref
PVDF+PMMA	Bilayer	767.1	19.1	/	[S1]
PET+P(VDF-HFP)+PET	Sandwich	583	8.2	/	[S2]
PMMA+PMMA/P(VDF-HFP) +P(VDF-HFP)	Sandwich	623	7.3	/	[S3]
PVTC+PEI+PVTC	Sandwich	500	11	/	[S4]
PEI+P(VDF-HFP)+BTO@PEI	Sandwich	530	8	/	[S5]
PEI+PEI/P(VDF-HFP) +P(VDF-HFP)	Sandwich	758	12.2	1.5×10^5	[S6]
PMMA/PVTC+DE/PVTC +PMMA/PVTC	Sandwich	790	20.1	10^5	[S7]
FPE+P(VDF-HFP)+FPE	Sandwich	563.6	11	/	[S8]
P(VDF-HFP)+P(VDF-HFP)/PMMA +P(VDF-HFP)	Sandwich	680	28.7	/	[S9]
PCBM@PMMA/PVDF	Organic Filler	685.7	21.9		[S10]
NBR@P(VDF-HFP)	Organic Filler	510	11.3	5×10^3	[S11]
CR-S@PVDF	Organic Filler	450	10.3	5×10^4	[S12]
MBS@P(VDF-HFP)	Organic Filler	515	12.3	/	[S13]
PVDF/f-PPTA	Blend Polymer	629	20.7	10^5	[S14]
PMMA/PVDF	Blend Polymer	640	20.7	/	[S15]
PVDF/PMMA-co-GMA	Blend Polymer	600	10.8	/	[S16]
PA513/PP	Blend Polymer	692.3	4.4	/	[S17]
epoxy/PTFE	Blend Polymer	555	3.6	/	[S18]
P(VDF-HFP)/P(VDF-TrFE)	Core-shell Blend	664.6	20.7	10^6	[S19]
P(VDF-HFP)/P(VDF-TrFE)	**Gradient Core-shell**	**694.8**	**23.6**	**10^7**	***This Work***

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