Supporting Information

Using novel rigid-fluoride polymer to control the interfacial thickness

of graphene and tailor the dielectric behavior of poly(vinylidene

fluoride-trifluoroethylene-chlorotrifluoroethylene) nanocomposites

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Synthesis of 2,5-bis[(4-trifluoromethoxyphenyl)oxycarbonyl]styrene (TFMS) monomer

2-vinylterephthalic acid (VTA) (2g, 10.4 mmol) was added into 250 mL round bottom flask with 100 mL dried dichlormethane, and then a drop of DMF was added. At the same time, oxalyl chloride (3.1g, 24.4 mmol) was mixed up with 30 mL dried dichlormethane added dropwise into the flask in a period of 1 h. The mixture was stirred at room temperature for 6 h, and then the yellow liquid was obtained by removing the dichlormethane. 4-(Trifluoromethoxy)phenol (3.8g, 21.3 mmol) and triethylamine (3 mL) were dissolved in 50 mL dried THF in a 250 mL round bottom flask. Under intense stirring at 0 °C, yellow liquid with 50 mL dried THF slowly added into the flask within 1 h. The mixture was further stirred for 8 h at room temperature, and then we distilled off the THF by evaporation under reduced pressure. The residue was dissolved in dried dichlormethane and the ammonium salt by extraction was removed with water, and again the dichlormethane was distilled off by

evaporation under reduced pressure. The crude product was purified by using column chromatography on silica gel with dichlomethane and mineral ether as eluant, and then the TFMS from distilling off the solvent by evaporation under reduced pressure was obtained.

Characterization

The morphology of the composites was performed by scanning electron microscopy (SEM, JSM-6390). Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 20 °C min⁻¹ in a nitrogen atmosphere. Fourier-transform infrared (FT-IR) spectroscopy was performed with a Nicolet 6700 instrument over the range of 4000-450 cm⁻¹ to determine the functionalization of the samples. Nuclear magnetic resonance (NMR) measurements were performed on a Bruker ARX400 MHz spectrometer using with CDCl₃ as solvent, tetramethylsilane (TMS) as the internal standard at room temperature. Raman spectroscopy was detected by LabRAM HR. The apparent number average molecular weight (M_n) and polydispersityindex (PDI, M_w/M_n) were measured on a Gel permeation chromatography (GPC) (WATERS 1515) instrument with a set of HT3, HT4 and HT5. The µ-styragel columns used THF as an eluent and the flow rate was 1.0 mL min⁻¹ at 38 °C. The GPC data were calibrated with polystyrene standards. The morphology and microstructure of the samples were observed by atomic force microscopy (AFM, NanoMan VS, USA). Liquid crystalline texture of the polymers was examined under POM (Leica DM-LM-P) equipped with a Mettler-Toledo hot stage (FP82HT). Powder one-dimensional wide-angle X-ray diffraction (1D WAXD) experiments were performed on a BRUKER AXS D8 Advance diffractometer with a 40 kV FL tubes as the X-ray source (Cu Ka) and the LYNXEYE XE detector. The sample stage was set horizontally. Two-dimensional wide-angle X-ray diffraction (2D WAXD) was carried out using a BRUKER AXS D8 Discover diffractometer, equipped with a 40 kV FL tube as the X-ray source (Cu Ka) and VANTEC 500 detector. The point-focused Xray beam was aligned either perpendicular or parallel to the mechanical shearing direction and background scattering was recorded and subtracted from the sample patterns. Transmission electron microscopy (TEM) images were obtained from a

JEOL JEM-2100 instrument operated at an accelerating voltage at 200 kV. The samples were prepared by dropping the sample solutions onto carbon-coated copper grids and air-drying before measurement. Frequency-dependent dielectric constant and dielectric loss were measured using an Agilent 4294A LCR meter with a frequency range from 1 kHz to 10 MHz. Electric displacement–electric field loops and leakage current were measured by a Precision Premier II ferroelectric polarization tester (Radiant, Inc.) at room temperature and 100 Hz.



Figure S1. ¹H NMR spectra of the monomer TFMS in CDCl₃.



Figure S2. TEM images of GO



Figure S3. Photographs of 0.46% rGO/P(VDF-TrFE-CTFE) and 0.46% rGO @PTFMS-1 rGO/P(VDF-TrFE-CTFE) nanocomposite film (a), enlarge images of 0.46% rGO/P(VDF-TrFE-CTFE) and 0.46% rGO@PTFMS-1 rGO/P(VDF-TrFE-CTFE) nanocomposite films by POM under natural light.



Figure S4. Frequency dependence of the conductivity of the rGO/P(VDF-TrFE-CTFE) (a), (b) rGO@PTFMS-1/ P(VDF-TrFE-CTFE), (c)rGO@PTFMS-2/ P(VDF-TrFE-CTFE).