Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

High-temperature dielectric polymer Poly(acrylonitrile butadiene styrene) with enhanced energy density and efficiency by the cyano group

Fei Wen,[ac†] Lin Zhang,[b†] Ping Wang,[a] Lili Li,[a*] Jianguo Chen,[d] Chao Chen,[c] Wei Wu,[a] Gaofeng Wang,[a] Shujun Zhang[c*]

[a]Engineering Research Center of Smart Microsensors and Microsystems, Ministry of Education, College of Electronics and Information, Hangzhou Dianzi University Hangzhou 310018, China

[b] Media Lab, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

[c] Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, NSW 2500, Australia

[d] School of Materials Science and Engineering, Shanghai University Shanghai, 200444, China

These authors (Fei Wen and Lin Zhang) contributed equally to this work

[*]Corresponding authors: Email: lilili@hdu.edu.cn (L. Li), shujun@uow.edu.au (S.J. Zhang)

Section S1: Experimental

Materials:

Polystyrene (PS, Polyrex®) and Poly(Acrylonitrile-Butadiene-Styrene) (ABS, Polylac®777e) are supplied by Chi Mei chemical Co. Ltd., BOPP is supplied by Maitefei films Co. Ltd.

The PS films preparation:

The PS was dispersed into ethyl acetate, and stirred vigorously for 2 h. Films with thickness of 15 μm were fabricated via solution casting process by casting the polymer solution (about 5 wt% in ethyl acetate) onto glass substrate and evaporating the solvent completely at 70 ^{o}C. The cast films were dried at 200 ^{o}C for 2 h to remove solvent residue, and subsequently peeled off from the substrate in DI water.

Dielectric Measurements:

The temperature dependencies of the dielectric properties of the polymer films were measured by an HP (Agilent-4990, USA) LCR meter over a temperature range of room temperature to high temperature (120-140 °C). The E_b was measured 20 times under a DC electric field at a ramping rate of 500 V/s and a limit current of 5 mA with an auto voltage withstanding tester (RK2674B) at different temperatures (Room temperature, 90, 120 °C). The value of E_b was analyzed by the Weibull distribution function.

Ferroelectric Measurements:

The polarization–electric field loops (*P-E* loop) were measured by using a TF 2000 analyzer (axi ACCT, Aachen, Germany) with a triangular waveform at frequency of 10 Hz, from room temperature to high temperature (90-120 °C). The fatigue test of chargedischarge was performed up to 10^5 cycles with pulse field amplitudes of 300 MV/m and frequency of 500 Hz.

Differential Scanning Calorimeter Measurements:

Thermal transition data of composites were obtained with a differential scanning calorimeter (DSC, TA Instruments Q100) from room temperature to 165 °C with a heating rate of 3 °C/min.

Thermo-gravimetric analyses Measurements

Thermo-gravimetric analyses (TGA) (NETZSCH STA449C) were carried out for studying the structure of PS and ABS polymer from room temperature to 600 °C with a heating rate of 5 °C/min.

^{1}HNMR Description

^{1}H NMR spectra were measured on a Bruker (Advance III) 400 MHz spectrometer with acetone-d6 as the solvent and tetramethylsilane as an internal standard.

Section 2 ^{1}HNMR results

The composition of the ABS was characterized by ^{1}HNMR as shown in **Fig. S1**. The proton assignment was as follows: 6.7 ppm to 7.7 ppm [m, 5H, $–C_6H_5$ phenyl from styrene]), 5.0 ppm to 5.8 ppm [m, 2H, $–CH_2CH=CHCH_2–$ from butadiene], 2.7 ppm to 3.2 ppm [m, 1H, $–CH(C_6H_5)–CH_2–$], 1.4 ppm to 2.2 ppm [m, 2H, $–CH_2–CH(C_6H_5)–$, m, 4H, $–CH_2CH=CHCH_2–$ and m, 2H, $–CH_2–CH(CN)–$], 2.5 ppm to 2.2 ppm [m, 1H, $–CH(CN)–$], 1.2 ppm to 1.4 ppm [m, 3H, $–CH(CN)–CH_3$], and 0.8 ppm to 1.0 ppm [m, 3H, $–CH(C_6H_5)–CH_3$]. The chemical composition of the copolymer was calculated from ^{1}HNMR based on the integral of peaks at 6.7 ppm to 7.7 ppm, 5.0 ppm to 5.8 ppm and 2.2 ppm to 2.5 ppm, leading to the result that the ABS copolymer contains 18 mol.% butadiene, 36 mol.% acrylonitrile and 46 mol.% styrene units.

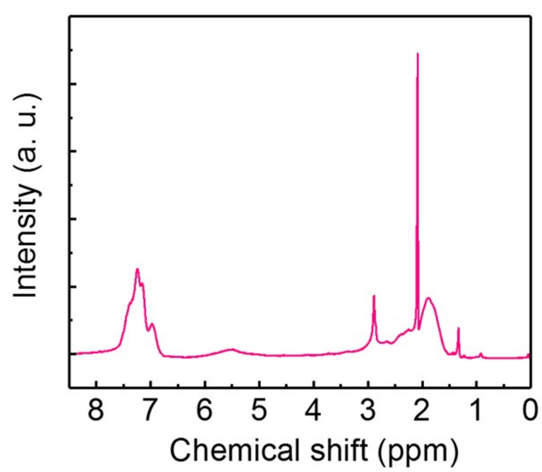

Fig. S1 The ^{1}HNMR spectrum of ABS.

Section 3 TGA results

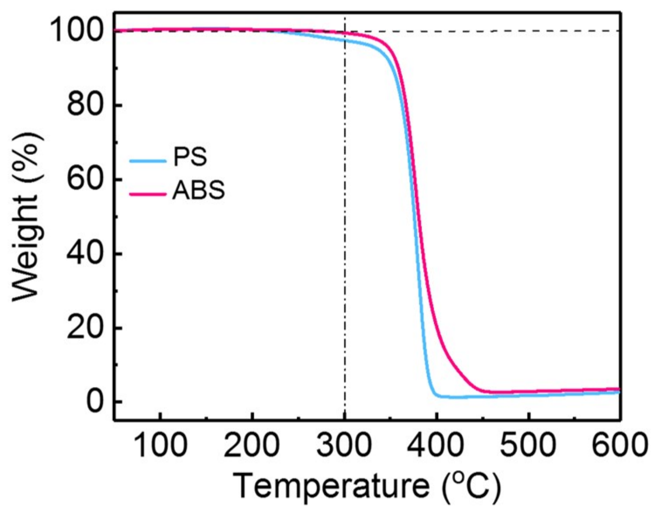

Fig. S2 The TGA of the PS and ABS film.

Section 4 Morphology and DSC results

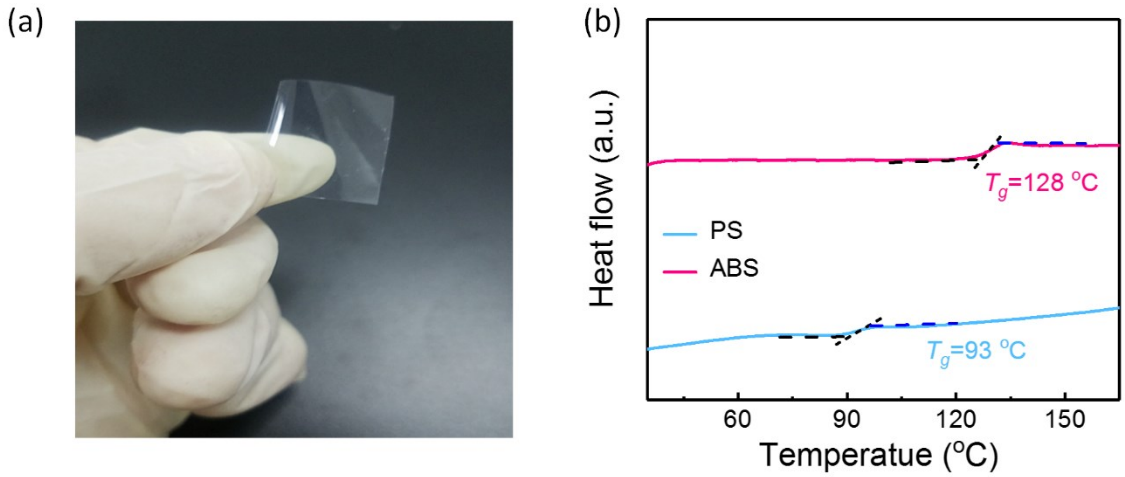

Fig. S3 (a) The morphology of ABS film and (b) heat flow of the PS and ABS film by DSC.

Section 5 Conductiviey and leakage current density

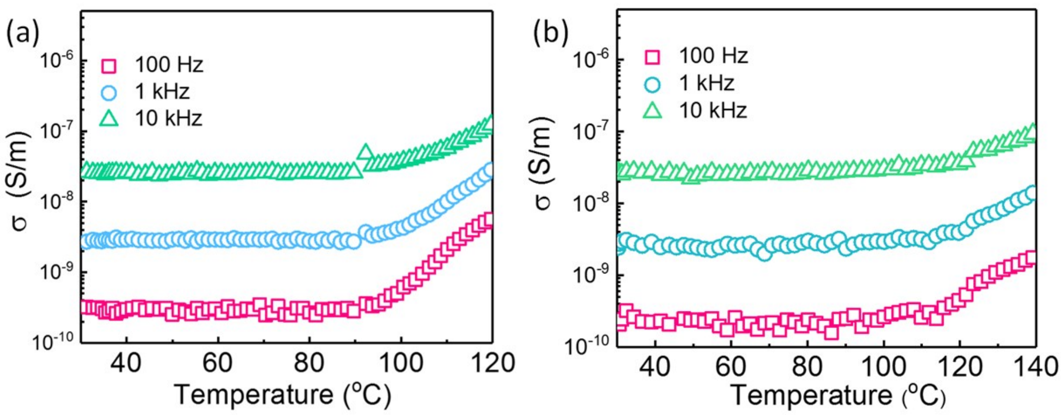

Fig. S4 AC conductivity as function of temperature at frequencies of 100 Hz, 1 kHz and 10 kHz for (a) PS and (b) ABS.

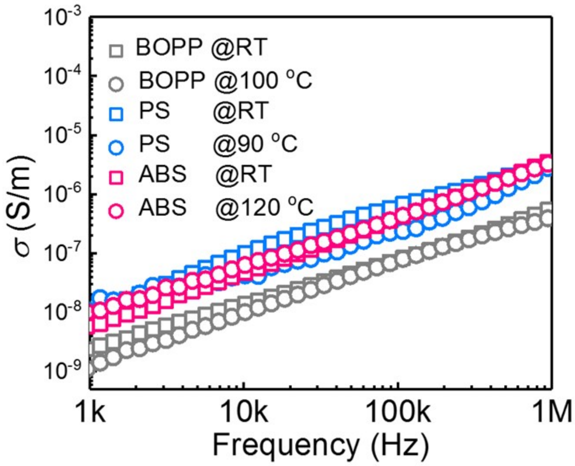

Fig. S5 AC conductivity as a function of frequencies (1 kHz-1 MHz) at room temperature (RT) and elevated temperature for BOPP, PS and ABS.

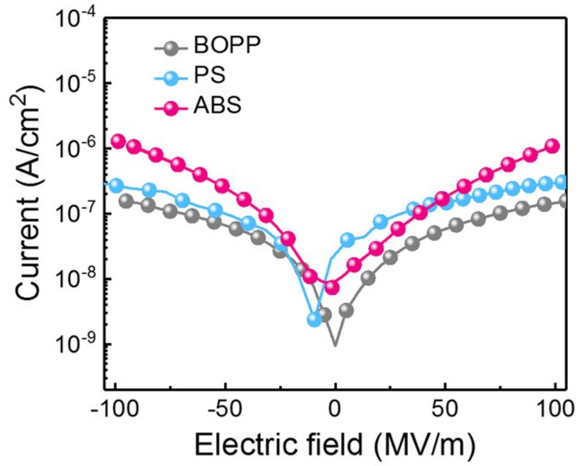

Fig. S6 The leakage current density vs. electric field at elevated temperature, BOPP (100 ^{o}C), PS (90 ^{o}C) and ABS (120 ^{o}C).

Section 6 P-E loop and energy storage

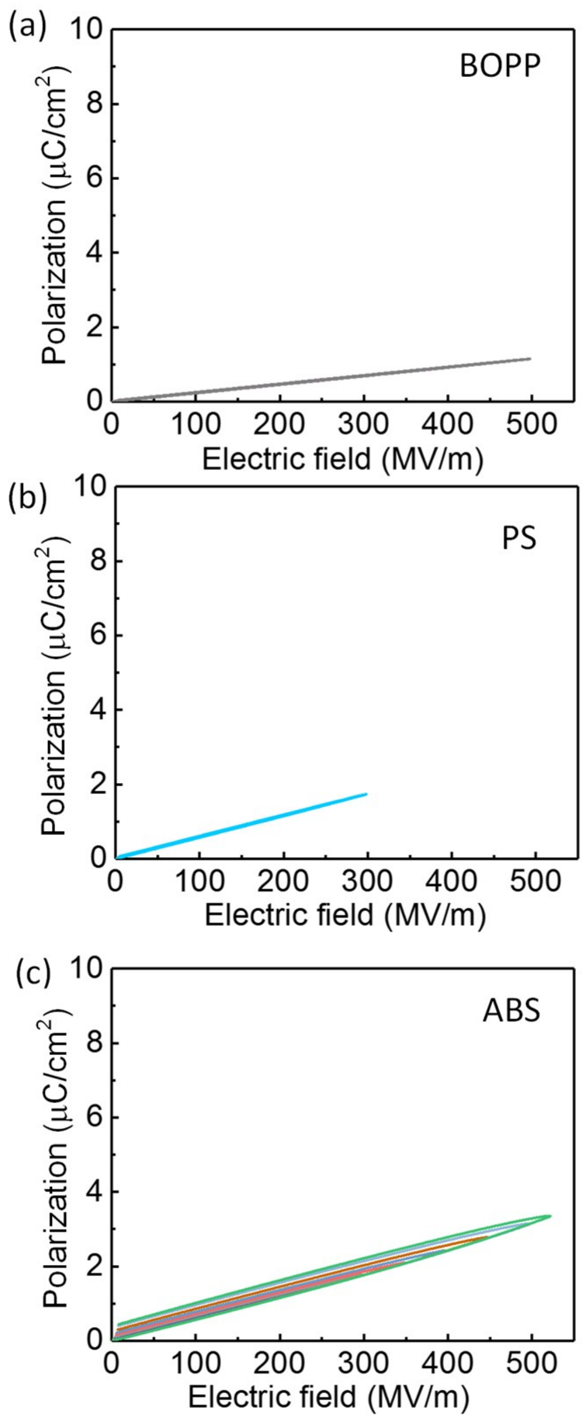

Fig. S7 The *P-E* loops as functions of electric field at room temperature at 10 Hz for (a) BOPP (b) PS and (c) ABS.

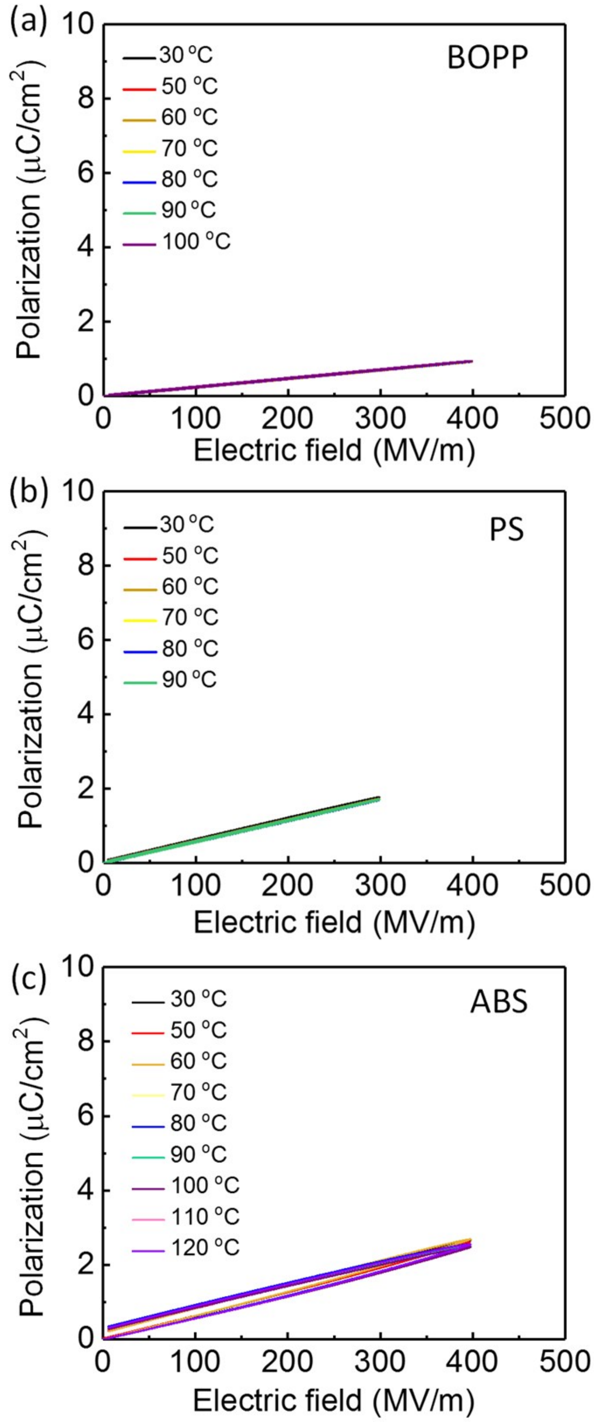

Fig. S8 (a) The *P*-*E* loops as functions of temperature under 400 MV/m at 10 Hz for BOPP. (b) The *P*-*E* loops as functions of temperature under 300 MV/m at 10 Hz for PS. (c) The *P*-*E* loops as a functions of temperature under 400 MV/m at 10 Hz for ABS.

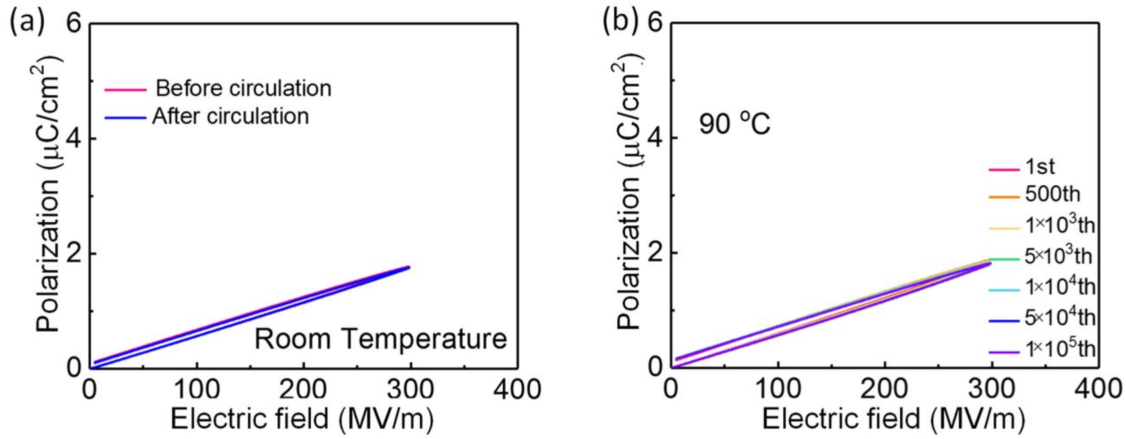

Fig. S9 (a) The before and after cycling *P-E* loops as functions of electric field at room temperature at 10 Hz for ABS. (b) The *P-E* loops of ABS with different cycling numbers at 10 Hz and 90 °C.

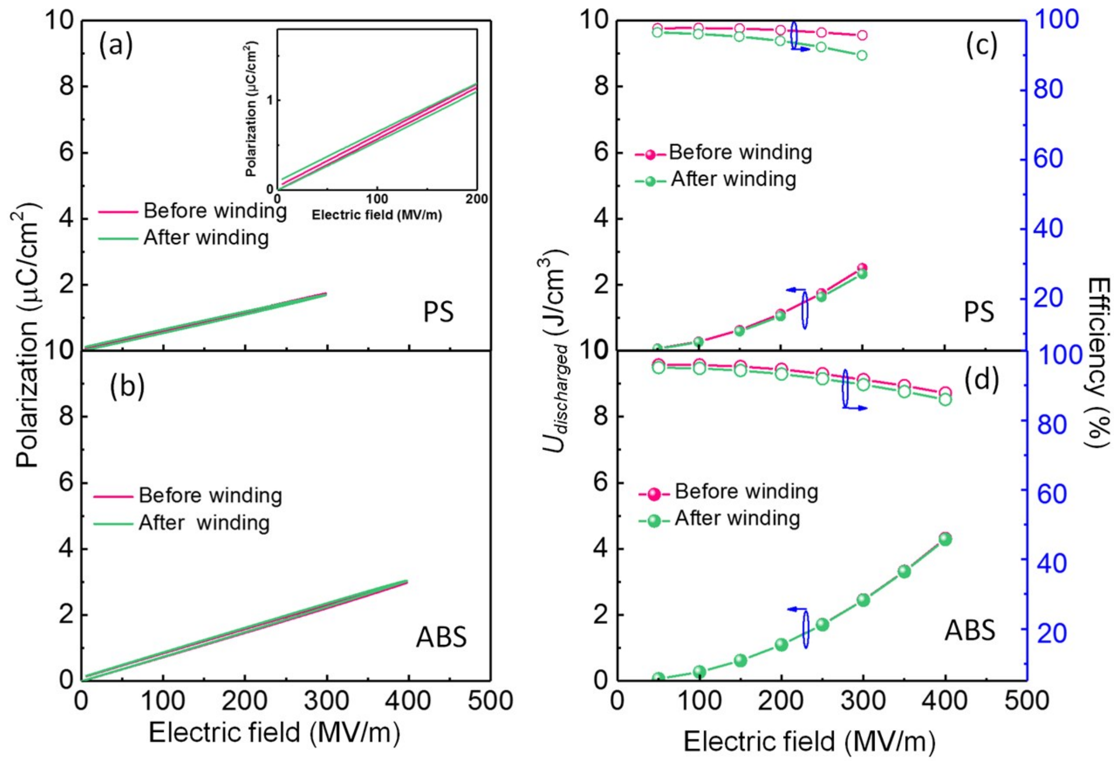

Fig. S10 (a) The *P-E* loops for PS before and after winding test under 300 MV/m at room temperature and 10 Hz, the inset figure is partially enlarged view. (b) The *P-E* loops for ABS before and after winding test under 400 MV/m at room temperature and 10 Hz. (c) The discharged energy density and efficiency as functions of electric field for PS before and after winding test. (d) The discharged energy density and efficiency as functions of electric field for ABS before and after winding test.