

Supporting Information

Enhanced permittivity in polymer blends via tailoring the orderliness of semiconductive liquid crystalline polymers and intermolecular interactions

Kun Qian^a, Rui Qiao^a, Sheng Chen^{*a}, Hang Luo^{*b} and Dou Zhang^b

^a Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, China

^b State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China

Table S1. Abbreviation and full name

| Abbreviation | Full name |
|---|---|
| MHT | 2-[3,6,7,10,11-pentakis(hexyloxy)-2-oxytriphenylene] ethyl methacrylate |
| M9F | 2-(perfluorobutyl) ethyl methacrylate |
| PHT | poly{2-[3,6,7,10,11-pentakis(hexyloxy)-2-oxytriphenylene] methacrylate} |
| P9F | poly [2-(perfluorobutyl) ethyl methacrylate] |
| RAFT | reversible-addition–fragmentation chain transfer |
| PVDF | poly(vinylidene fluoride) |
| THF | tetrahydrofuran |
| DMF | dimethylformamide |
| BaTiO ₃ | barium titanate |
| SrTiO ₃ | strontium titanate |
| CaCu ₃ Ti ₄ O ₁₂ | calcium copper titanate |
| PTTEMA | poly{2-(2, 2':5', 2'' -terthien-5-yl)ethyl methacrylate} |
| PCMS | poly(p-chloromethyl styrene) |
| PPy | polypyrrole |
| PANI | polyaniline |
| CuPc | copper phthalocyanine oligomer |
| PVDF-CTFE | poly(vinylidene fluoride-chlorotrifluoroethylene) |
| AIBN | azodiisobutyronitrile |
| CTA | 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid |
| M _w | weight-average molecular weight |
| M _n | number-average molecular weight |
| TMS | tetramethylsilane |
| NMR | nuclear magnetic resonance |
| GPC | gel permeation chromatography |
| DSC | differential scanning calorimetry |
| 1D WAXD | one-dimensional wide-angle X-ray diffraction |
| SAXS | small-angle X-ray scattering |
| FT-IR | fourier-transform infrared |
| TGA | thermogravimetric analysis |
| SEM | scanning electron microscopy |
| POM | polarized optical microscopy |
| PDI | polydispersity index |
| T _i | clearing point |
| T _d | thermal decomposition temperatures |
| X _c | crystallinity |
| ΔH _m | melting enthalpy |
| W _f | mass ratio |
| ε | dielectric constant |

Characterization

Nuclear magnetic resonance (NMR) measurements were performed on a Bruker ARX400 MHz spectrometer using with CDCl_3 as solvent, tetramethylsilane (TMS) as the internal standard at room temperature.

Gel permeation chromatography (GPC). The apparent number average molecular weight (M_n) and polydispersity index ($\text{PDI} = M_w/M_n$) were measured on a 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 at 38 °C. The GPC data were calibrated with polystyrene standards.

Differential scanning calorimetry (DSC). DSC traces of the polymer were obtained using a TA Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rates of 10 °C/min. The sample with a typical mass of about 5 mg was encapsulated in sealed aluminium pans.

Powder 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 a LYNXEYE_XE detector. The scanning speed of 1D WAXD was 2°/min.

Small-angle X-ray scattering (SAXS). SAXS were performed with a high-flux SAXS instrument (SAXSess, Anton Paar), equipped with Kratky block-collimation system and a Philips PW 3830 sealed-tube X-ray generator (Cu Ka).

Fourier-transform infrared (FT-IR) spectroscopy was performed with a Nicolet 6700 instrument over the range of 4000~600 cm^{-1} to determine the functionalization of the samples.

Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 20 °C/min in a nitrogen atmosphere.

The morphology of the composites was performed by scanning electron microscopy (SEM, JSM-6390).

Liquid crystalline texture of the polymers was examined under polarized optical microscopy (POM, Leica DM-LMP) equipped with a Mettler-Toledo hot stage (FP82HT).

Frequency-dependent dielectric constant, dielectric loss and conductivity were measured using an Agilent 4294A LCR meter with a frequency range from 100 Hz to 10 MHz.

Table S2. Physical properties of three kinds of polymer alloy films under different polymer content.

| Sample | T_m (K) ^a | ΔH_m (J/g) ^b | X_c (%) ^c |
|------------------------|------------------------|---------------------------------|------------------------|
| PVDF | 431.87 | 24.68 | 24.03 |
| 1%PHT/PVDF | 432.51 | 31.14 | 30.63 |
| 3%PHT/PVDF | 432.55 | 31.09 | 31.21 |
| 5%PHT/PVDF | 435.26 | 28.20 | 28.90 |
| 10%PHT/PVDF | 433.17 | 29.23 | 31.62 |
| 15%PHT/PVDF | 433.24 | 27.40 | 31.39 |
| 20%PHT/PVDF | 433.65 | 26.77 | 32.58 |
| 30%PHT/PVDF | 433.24 | 18.92 | 26.32 |
| 40%PHT/PVDF | 433.52 | 15.47 | 25.11 |
| PVDF | 431.87 | 24.68 | 24.03 |
| 5%PHT- <i>co</i> -P9F | 431.55 | 29.82 | 30.56 |
| 10%PHT- <i>co</i> -P9F | 431.64 | 27.21 | 29.44 |
| 15%PHT- <i>co</i> -P9F | 431.69 | 26.45 | 30.30 |
| 20%PHT- <i>co</i> -P9F | 432.27 | 23.92 | 29.11 |
| 30%PHT- <i>co</i> -P9F | 431.46 | 20.64 | 28.71 |
| 40%PHT- <i>co</i> -P9F | 431.45 | 17.42 | 28.27 |
| 50%PHT- <i>co</i> -P9F | 431.50 | 13.89 | 27.05 |
| PVDF | 431.87 | 24.68 | 24.03 |
| 5%PHT- <i>b</i> -P9F | 432.19 | 29.71 | 30.45 |
| 10%PHT- <i>b</i> -P9F | 432.13 | 29.03 | 31.41 |
| 15%PHT- <i>b</i> -P9F | 431.87 | 26.08 | 29.88 |
| 20%PHT- <i>b</i> -P9F | 432.01 | 24.74 | 30.11 |
| 30%PHT- <i>b</i> -P9F | 431.78 | 20.28 | 28.21 |
| 40%PHT- <i>b</i> -P9F | 431.51 | 18.63 | 30.23 |
| 50%PHT- <i>b</i> -P9F | 431.63 | 15.55 | 30.28 |

^a The melting temperatures (T_m) were measured by DSC at a heating rate of 10 °C/min under nitrogen atmosphere during the second heating process.

^b ΔH_m : the value of the melting enthalpy of the sample resulting from the second DSC heating process

^c X_c : the crystallinity.

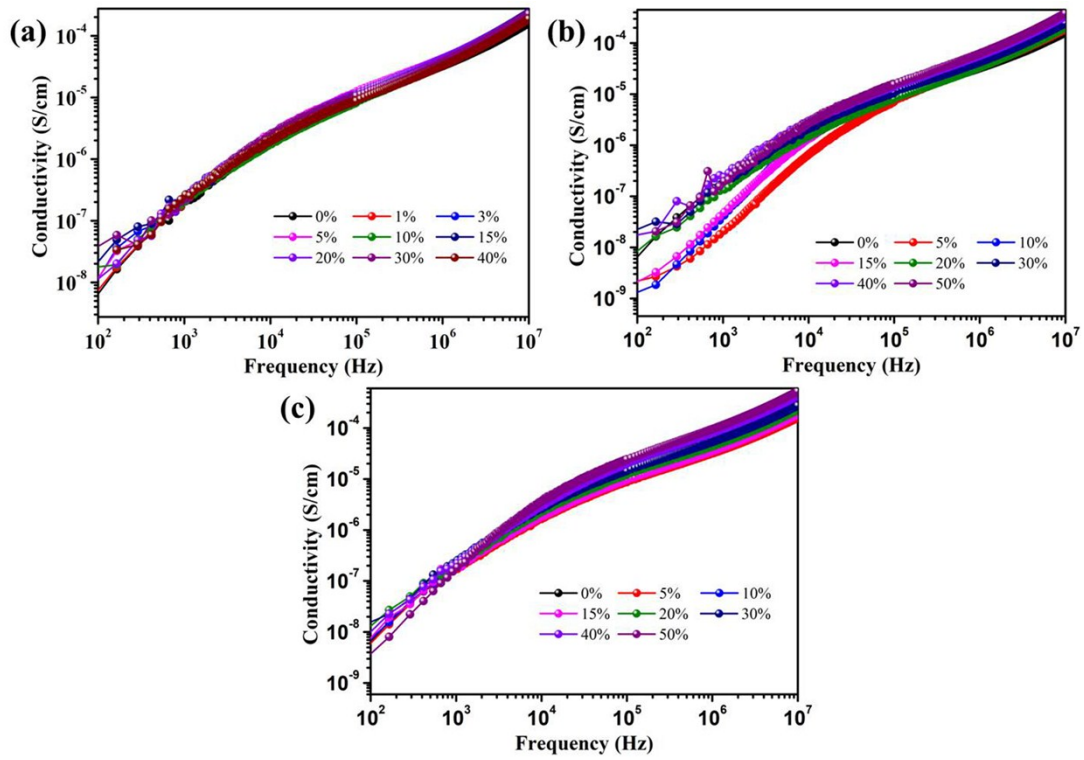


Figure S1. Frequency dependence of the conductivity of (a) PHT/PVDF; (b) PHT-*co*-P9F/PVDF and (c) PHT-*b*-P9F/PVDF polymer alloys at room temperature.