Gradient Copolymerization towards High-performance Monocomponent Polymers for Energy and Charge Storages

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Article

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Abstract

Polymers with excellent dielectric and electret capabilities are crucial for energy storage films, organic electronics and environmental filtrations. Nanocomposites is an emerging effective method, but the characteristics of complicated preparation, poor uniformity and high cost restrict its massive and practical applications. Here, we propose a gradient copolymerization strategy with controllable micro-phase interfaces for dielectric capability modulation, and gradient ethylene-styrene copolymer (PESt) exhibits extraordinarily enhanced dielectric, electrical insulating and electret properties against polyethylene and polystyrene. PESt exhibits a dielectric energy density towards $23 \text{ J}\cdot\text{cm}^{-3}$, far exceeding commercially applied polymers and is comparable to nano-composites. By applying PESt as electret layer in organic field-effect transistors, largely enhanced memory window, optimized stability and field-effect mobility over $27 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ are achieved. Finally, PESt electret is employed in environmental filtrations with 20% enhancement in filtration efficiency. The simplicity and processability of gradient copolymerization against nano-composite, further suggest its potential in designing high-performance dielectric/electret polymers.

Introduction

Dielectric polymers of superb energy and charge storage properties are widely applied in power equipment,^{1–4} electronic devices^{5,6} and environmental/medical filtration.^{7–9} For example, in electrical industry, polymer based power capacitors are of massive applications in large-scale electricity storage and power converters in pulse power systems as well as electric vehicles.^{10–12} In field of organic electronics, charges in polymeric electret provide built-in electrostatic fields in optimizing the performance of organic field-effect transistors (OFETs),^{13,14} which is also regarded as the basis of nonvolatile flash memories.^{15,16} Additionally, in field of environmental and medical filtrations, electrostatic attraction between polymer electret and dusts as well as suspended organisms in air is widely employed in masks,^{17,18} while the electret-induced adsorption plays an important role in sustaining long-term filtration efficiency.¹⁹

Monocomponent linear polymers such as biaxially oriented polypropylene (BOPP), polycarbonate (PC), poly(phenylene sulfide) (PPS), poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) are widely applied in power energy storages owing to their high power density and charge-discharge efficiency ($>90\%$).²⁰ However, the energy density of these linear polymers is comparatively low ($< 5 \text{ J}\cdot\text{cm}^{-3}$), which thus requires large-area films to warrant sufficient dielectric energy.¹ Multicomponent dielectrics, such as nano-composite, multi-layered dielectric polymers and polymer blends emerge recently with notable enhancement in energy density.² However, these methods exhibit the characteristics of complicated preparation, poor uniformity and high cost, which restrict their application potentials in rapid manufacturing and practical engineering. Consequently, soluble monocomponent polymer with high energy density and high charge-discharge efficiency is of great demands both scientifically and commercially.

In aspect of molecular and condensed matter structures, commercial polymers for dielectric energy storage and electrets are usually (semi)crystalline, as higher stereo-regularity contributes to higher structural stability and thus better electrical/electronic stability.²¹ In fact, the dielectric polarization with permanent molecular dipole represents a dielectric ordering, which thus requires ordering of polymer chains, consequently certain crystallinity is necessary to stabilize such dielectric dipoles. On the other hand, crystallization of polymer chains into microdomains usually decreases the energy of localized electronic states to immobilize electret charges.^{22,23} Therefore, as compared with amorphous insulating polymers, semicrystalline insulating polymers would be more favorable for electrical insulator and electret applications due to their superior rheological and mechanical properties²⁴ as well as better dipole and charge stabilizing capability.²⁵ However, traditional nonpolar semicrystalline polymers such as linear polyethylene (PE) and syndiotactic polystyrene (s-PS) are typically not soluble in any organic solvent at room temperature, leading to the poor film-forming ability and quality which limit their applications in large-scale manufacturing and micro/nano-scale devices. Consequently, the community is continuously looking for polymers simultaneously with good solubility and appropriate crystallinity for energy and charge storages.

In this work, we propose a gradient copolymerization strategy with controllable micro-phase interfacial region for dielectric capability improvement, and a class of solution processible semicrystalline gradient copolymers composed of syndiotactic polystyrene and polyethylene sequences, namely gradient ethylene/styrene copolymer (PESt) is introduced.

Results

Structure and characteristics of PESt

Semicrystalline polymer is composed of crystalline domains, amorphous domains and domain boundaries. The energetic disorder of localized electronic states in domain boundaries should be much broader than those in completely crystalline or amorphous domains, as the microscopic structures of diverse boundaries are widely dispersed, leading to the multi-dispersed density-of-states (DOS) of electronic sites (Fig. 1a). The tail of the wide DOS profile represents the low energy states, which could maximally stabilize charge carriers, contributing to good charge storage property. Similarly, the energy diversity of dielectric dipoles in crystalline domains, amorphous domains and domain boundaries contributes to a widely-dispersed energy distribution profile. Moreover, the morphological diversity of domain boundaries leads to the fact that some states at the boundary could stabilize the dielectric dipoles, contributing to enhanced dielectric constant and energy storage property. Therefore, solution-processible polycrystalline films with nanoscale crystallites and huge-area boundaries are attracting wide interests for dielectric and electret applications.

Since PE and s-PS are not soluble in any organic solvent at room temperature, copolymerization provides an effective strategy in improving the solubility, while conventional PE-PS block copolymers based on such nonpolar chains still suffer from poor solubility and aggregation in solution. On the contrary,

completely random PE-PS copolymers do not crystallize, although they are soluble. From this viewpoint, gradient copolymers with suitable chemical structures, could simultaneously provide good solubility and sufficient crystallinity.

Taking above consideration into account, in this work, we propose a gradient copolymer of ethylene and styrene, PEST, afforded by coordination polymerization, which is quickly dissolvable in *o*-dichlorobenzene, toluene, chloroform, even in tetrahydrofuran at room temperature (the dissolving could be accelerated at 80 °C). More importantly, once the copolymer is dissolved, the solution is stable at room temperature, without aggregation in solution.

Hence, three PESTs with gradually increased styrene content (PESt15: 14.7 mol%, PEST37: 36.7 mol%, PEST59: 59.2 mol%) were synthesized through increasing the initial styrene concentration (Table S1). Fig. S1 and S2 are the ^1H and ^{13}C NMR spectra of PEST correspondingly. In the ^{13}C NMR spectrum of PEST, the resonances at 43.8, 40.5 and 29.5 ppm suggest the copolymer contains syndiotactic polystyrene and polyethylene sequences.²⁶ The thermal behavior of PEST was characterized by differential scanning calorimetry (DSC) (Fig. 1b). PEST15 has a melting point at 111 °C which should be derived from polyethylene sequences as obvious 110 and 200 orientation peaks of PE are observed in its X-ray diffraction (XRD) spectrum (Fig. 1c). The T_m value attributed to PE sequences is lower than that of neat PE, suggesting that the PE sequence length is not too long.²⁷ With the styrene content increasing to 36.7 mol%, the length of PE sequences decreases, confirmed by the results that the melting point of PEST37 appears at 104 °C and the diffraction intensities of peaks at 21° and 24° from PE crystalline become weak, while the length of s-PS sequence increases since an endothermic peak appears at 225 °C in the DSC signal and the diffraction peaks at 10° and 18° assigned to s-PS become more obvious. When the styrene content increases to 59.2 mol%, the PE sequence length further decreases, leading to the disappearance of endothermic peak in the DSC curve and the diffraction peaks in the XRD spectrum derive from PE sequence. In contrast, the length of s-PS sequence becomes longer. Thus, the melting point of PEST59 shifts to 233 °C and the diffraction intensities of peaks at 10° and 18° increase. In combination of kinetic study result (Table S2) that with the polymerization prolonging, the styrene content within PEST decreases, the gradient distribution of ethylene and styrene units within PEST is proposed. The thermal decomposition temperature of PEST was determined by thermogravimetric analysis (TGA) (Fig. 1d). The onset temperature at 5% loss ($T_{\text{onset}}^{5\%}$) of PEST15 is 316 °C. With the styrene content increasing from 14.7 mol% to 36.7 mol%, $T_{\text{onset}}^{5\%}$ dramatically increases by 47 °C, to 363 °C (copolymer PEST37). Further increasing the styrene content from 36.7 mol% to 59.2 mol%, $T_{\text{onset}}^{5\%}$ is only improved from 363 °C to 387 °C. As elevated temperatures over room temperature occur in electrical equipment and electronic devices, the gradually enhanced tolerance to temperature variations from PEST15 to PEST59 contributes to better thermal stability and high temperature operation performance.

The morphology of PEST films were characterized by atomic force microscopy (AFM, Fig. 1e). The film surface of PEST59 is smoother as compared with those of PEST15 and PEST37, showing a height difference within ± 1 nm. Besides, transmission electron microscopy (TEM) image of PEST59 in Fig. 1f shows a high-quality film with staggered arrangement of crystalline and amorphous regions.

The optical absorbance of PEST was determined by a UV-Vis light absorption spectrometer (Fig. 1g). The absorption peaks of PEST15, PEST37 and PEST59 are all at 196 nm, showing light absorption signal of PS. The absorbance of the three PESTs is smaller than 1%, indicating excellent optical transparency which is applicable in organic transparent optoelectronics.

Dielectric characterization of PEST

As indicated in TEM image, in contrary to the sharp phase boundary in block copolymers, gradient copolymers show broad nano-scale interfacial region,²⁸ which is acknowledged contributing in modulation of dielectric and electrical insulating performance of polymeric materials. Here, the dielectric and charge trapping characteristics of PEST are analyzed by frequency domain dielectric spectrum (FDS), isothermal surface potential decay (ISPD), and thermally stimulated current (TSC) experiments, and compared with PE and s-PS.

For PEST15 with styrene content of 14.7 mol% in Fig. 2a, dielectric constant is 2.5 and is stable in frequency range from 10^{-1} Hz to 10^6 Hz at temperatures below 120 °C. At elevated temperatures, dielectric constant rapidly increases at low frequencies, but keeps barely changed at higher frequencies. At the highest temperature of 140 °C, the dielectric constant reaches above 20, indicating broad dielectric relaxations. The dielectric constant of PEST37 is 2.6 in Fig. 2b, showing 0.1 increase as compared with PEST15. At elevated temperatures, the dielectric constant increases to 7.8 at 140 °C, 10^{-1} Hz while it decreases to 2.3 at higher frequencies. The dielectric constant of PEST59 in Fig. 2c is 3.3 at low frequencies, and shows slight decrease with the increased frequency towards 10^6 Hz. In frequency range of $10^{-1} \sim 10^1$ Hz, obvious increase in dielectric constant is observed at 120 °C and 140 °C. Comparison in FDS spectra of PEST15, PEST37 and PEST59 at 140 °C demonstrates that the increase in dielectric constant of PEST59 is the smallest at elevated temperatures, indicating the enhanced thermal stability.

In Fig. 2d, the dielectric constant and dielectric loss of PEST15, PEST37 and PEST59 are compared with PE and s-PS. ϵ_r of PEST15 ($\epsilon_r = 2.5$) is larger than PE of 2.3, but 0.05 smaller than s-PS of 2.55 (as demonstrated in Fig. S3). As there is only 14.7 mol% styrene in PEST15, the relatively stronger polarization is contributed by both the branched benzene ring and the broad nano-scale interfaces between PE macro-phase and PS macro-phase. The dielectric constant of PEST increases with the enlarged styrene content, the dielectric constants of PEST37 and PEST59 are both extraordinarily larger than s-PS. Especially for PEST59 ($\epsilon_r = 3.2$), the peculiar large dielectric constant benefits the application in energy and charge storage.

In aspect of dielectric loss, $\tan\delta$ of PE is comparatively large in typical insulating polymers, which is 0.012 at 50 Hz, 20 °C in Fig. 2d, otherwise the dielectric losses of PEST15, PEST37, PEST59 and s-PS are all at 10^{-3} level. Notably, PEST37 ($\tan\delta = 0.0018$) and PEST59 ($\tan\delta = 0.0025$) show smaller dielectric loss than s-PS ($\tan\delta = 0.0028$). Thus, PEST with higher styrene ratio exhibits extraordinarily good dielectric performance as larger dielectric constant and smaller dielectric loss are simultaneously achieved, compared to PE and s-PS.

ISPD is further conducted to investigate charge storage characteristics of PEST, as demonstrated in Fig. 2e. PE experiences the quickest decay, followed by PEST15, s-PS, PEST37, and PEST59 with gradually slowed down decay rate, indicating the formation of deep traps. In aspect of initial surface potential, PEST59 exhibits the highest value of 3015 V. Thus, it could expect larger trap density in gradient copolymers compared with corresponding monomers.

The detailed distributions of trap depth (i.e. trap energy) and trap density are obtained by analyzing the ISPD results with Simmon's equation,²⁹ the results are demonstrated in Fig. 2f. As the ISPD results are fitted by a double-exponential equation, two peak values are most ordinarily observed in trap depth distributions.³⁰ A shallow trap with activation energy of 0.91 eV and a deep trap with activation energy of 0.985 eV are observed in PE. As for PEST, the trap depth is increasing with increased styrene content. The trap depth of s-PS is 1.02 eV, which is larger than that of PEST15 (0.99 eV), but smaller than that of PEST37 (1.08 eV) and PEST59 (1.09 eV). Therefore, the gradient molecular structure contributes to the formation of deep traps in ethylene-styrene copolymerization system.

In Fig. 2g, TSC of PE shows T_{peak} at 56.5 °C, followed by PEST15 of 88.5 °C, PS of 119.5 °C, PEST37 of 128.0 °C, and PEST59 of 138.5 °C in ascending order. As the peak temperature is proportional to trap depth, TSC result shows perfect consistency with ISPD. Theoretically, TSC is expressed as,³¹

$$I_{\text{TSC}}(T) = \frac{p}{\tau} \exp\left[-\frac{E_T}{kT} - \frac{1}{\beta\tau} \int_{T_0}^T \exp\left(-\frac{E_T}{kT'}\right) dT'\right] \quad (1)$$

where I_{TSC} is the TSC in A; T is the test temperature in K; p is the polarization intensity in C/m²; τ is the relaxation time in s; E_T is the activation energy (trap depth) in eV; k is the Boltzmann constant; b is the temperature ramping rate in K/s.

The trap depth and trap density are thus calculated based on a Matlab fitting, and the results are shown in Fig. 2h. Based on TSC calculation, PE owns the smallest trap depth of 0.8 eV, and PEST59 exhibits the largest trap depth of 1.6 eV. The trap depths of PEST15, PEST37 and PS are between those of PE and PEST59, which are PEST15 of 0.9 eV, PS of 1.2 eV and PEST37 of 1.3 eV, respectively. The comparison in trap depth obtained from ISPD and TSC perfectly matches, indicating a more stable dielectric electret with increased trap depth in gradient copolymers, both on surface and in bulk of the film.

More importantly, the gradient molecular structure contributes in building up deeper traps with activation energy far beyond corresponding amorphous dielectric polymers. The related mechanism is physically similar with that of nano-filler reinforced dielectric, as the broad nano-scale interface exhibits strong charge immobilization characteristics which acts as trapping centers to capture free charges. With the increased styrene content towards 50% in PEST, the interfacial region is maximally broadened, which increases the deep trap content, leading to increase in average trap depth as demonstrated in Fig. 2f.

In aspect of trap amount, as TSC expresses more information of bulk traps than ISPD, and is obtained with the pre-treatment of long-term high temperature polarization, it could expect a comprehensive trap fulfillment and detrapping process. Thus, the integral area of TSC curve represents intrinsic bulk trap density in dielectric polymers. In Fig. 2h, it is observed that the trap density of PEST is around $7 \times 10^{-9} \text{ A} \cdot ^\circ\text{C}$, which is larger than simply PE ($4.8 \times 10^{-9} \text{ A} \cdot ^\circ\text{C}$) or s-PS ($5.6 \times 10^{-9} \text{ A} \cdot ^\circ\text{C}$). Thus, the extended interfacial region generates 20~40% more deep traps by contributions of gradient structure.

In mechanism, the conjugated p bond in benzene ring forms strong charge withdrawing ability compared with unsaturated C-C bond on the backbone of polyethylene and polystyrene, which physically absorbs free charges. As styrene content is gradually increased from PEST15 to PEST59, the charge trapping ability is enlarged by contributions of increased benzene density. However, with the solitary contribution of benzene, the charge trap density of PEST could never reach that of polystyrene. Thus, it should be expected that the large amount of deep traps is generated by the broad nano-scale interfaces, formed by the gradient structure.

The enlarged deep trap density modulates charge transfer and accumulation characteristics within the polymer film, leading to enhanced dielectric and electret performance. With the characteristic of solution processability, PEST is further applied as energy storage film in power capacitors, dielectric layer in OFET memories and stable electret in porous filter materials.

Application in power energy storage

In order to investigate the energy storage performance of PEST, room temperature DC breakdown test was first conducted, the results are demonstrated in Weibull distributions in Fig. 3a. PE exhibits the smallest breakdown strength of 327.2 kV/mm, while that of s-PS is 377.1 kV/mm. The breakdown strengths of PEST15, PEST37 and PEST59 are 360.8 kV/mm, 441.7 kV/mm and 521.8 kV/mm, respectively, which are increasing with increased styrene ratio. To be noticed that PEST37 and PEST59 exhibit extraordinary breakdown strengths, showing 22.4% and 44.6% increase as compared with s-PS.

Another key parameter in characterizing electrical insulating performance of a dielectric is volume resistivity, as shown in Fig. 3b. PE exhibits the smallest volume resistivity of $2.71 \times 10^{15} \text{ W} \cdot \text{cm}$, while PEST59 exhibits the highest resistivity of $3.86 \times 10^{16} \text{ W} \cdot \text{cm}$. The result of volume resistivity shows strong correlation with breakdown strength in Fig. 3a, indicating contributions of nano-scale interfacial traps in determining electrical insulating performance.

The charge transfer and accumulation characteristics dominate the insulating performance of dielectric film at the mechanism level, and charge mobility is expressed as $m = L^2/t_T V_0$, where L is sample thickness, t_T is transit time and V_0 is initial voltage of ISPD. The obtained charge mobility under high electric field is shown in Fig. 3b. PE exhibits the largest charge mobility of $2.78 \times 10^{-14} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, and PEST59 exhibits the smallest charge mobility of $7.91 \times 10^{-16} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. Negative correlation exists between charge mobility and breakdown strength, as higher mobility leads to smaller breakdown strength.³⁰ The electrical insulating performance is modulated by manipulating deep traps, controlled by interfacial structure. The generated deep traps suppress charge migration to nearly 1/35 of PE in mobility, which suppress charge acceleration under extreme voltages, leading to the greatly enhanced dielectric and electrical insulating capability of PEST, especially PEST37 and PEST59.

Generally, the dielectric strength of an organic polymer is dependent on its molecular and condensed matter structures. Normally following the same sample preparation procedure, the resistivity and breakdown strength of a copolymer are between its polymeric monomers. However, PEST shows abnormally enhanced breakdown performance. The large area two-phase nano-scale interfacial region in PEST is morphologically like that in nano-doped polymers.^{20,32-34} Typically, nano $\text{SiO}_2/\text{TiO}_2$ is added into dielectric polymers, introducing deep traps at interactive area around the nano particles, and consequently results in 10-20% increase in breakdown strength.³⁵⁻³⁸ Based on the experimental results in Fig. 2, it is confirmed that large amount of interfacial deep traps is formed in gradient structure of PEST, showing the nano-enhanced effect of insulating performance. Thus, it could expect gradient polymerization as an advanced effective technique with the potential in replacing nano-doping in enhancing the dielectric performance, as it exhibits the advantages of solution processing and larger insulating performance enhancement towards 50%.

As the dielectric constant and breakdown strength of PEST are synchronously enlarged compared to either PE or s-PS, the energy storage characteristics are further investigated, and compared with typical commercially applied dielectric films, as demonstrated in Fig. 3d-f.

For linear polymers, the energy density is expressed as, $U_e = 0.5 \epsilon_0 \epsilon_r E_b^2$, where ϵ_0 is the vacuum dielectric constant, ϵ_r is the dielectric constant of polymer, E_b is the electrical breakdown strength. Based on equation above, the energy densities of PEST15, PEST37 and PEST59 are calculated. For thickness of 150 μm samples, due to the enhanced dielectric constant and breakdown strength, energy density of PEST59 is reaching $7.7 \text{ J} \cdot \text{cm}^{-3}$, which is far larger than other dielectric polymers at room temperature, including the polymeric monomers of PE ($2.1 \text{ J} \cdot \text{cm}^{-3}$) and s-PS ($3.1 \text{ J} \cdot \text{cm}^{-3}$).

Power capacitor usually works in elevated temperatures as a result of severe heating during operation. In universal standard, the maximum working temperature of the dielectric film in power capacitors is 70 °C, however during extreme conditions, the temperature could reach 100 °C.^{39,40} Here, electrical breakdown and energy density of the polymers are investigated at elevated temperatures of 40 °C, 70 °C and 100 °C, as demonstrated in Fig. 3c and Fig. 3d, the detailed breakdown strengths in Weibull distributions are

demonstrated in Fig. S4. The breakdown strengths of PEST are linearly decreasing with increased temperature, while PE and s-PS show rapid exponential decrease at 40 °C and 70 °C correspondingly. PEST shows stronger anti-thermal performance as both of PEST37 and PEST59 maintain high breakdown strengths at extreme temperature of 100 °C. In Fig. 3d, the energy densities of all five polymers are decreasing with raised temperature due to the decreased breakdown strength. However, PEST59 keeps high energy storage performance above 5 J·cm⁻³ at 70 °C and 100 °C, which is comparatively larger than the widely applied BOPP of < 2 J·cm⁻³ at thickness of 150 μm.⁴¹⁻⁴³

To further investigate the energy storage property of PEST, PEST59 of the best performance is taken as an example and compared with typical linear polymers applied in power capacitors. To be noticed that the breakdown strength of a dielectric is strongly dependent on film thickness. Thinner film exhibits larger breakdown strength as a result of limited space charge accumulation and thus suppressed inner electric field distortion.²⁹ Therefore, the thickness dependent electrical breakdown of PEST59 is experimentally investigated before calculating the energy density, as demonstrated in Fig. 3e. As the statistical data of linear polymers in Fig. 3f are all in thickness of 2~10 μm, PEST59 is controlled to 5 μm in thickness, measured by step profilers, and its dielectric strength is increased to 890.1 kV/mm, leading to the energy density of 22.9 J·cm⁻³. In Fig. 3f, it is clearly demonstrated that PEST59 exhibits a tremendous improvement as compared to the typical polymeric materials applied in power capacitor such as BOPP, PET and PC. Moreover, PEST59 is solution processable, which is favorable for large-area rapid manufacturing, showing advantages in both film processing and energy storage density.

Application in field-effect transistors and memories

Insulating polymers with varied dielectric performances lead to regulated OFET performance. Here, PEST was applied as gate dielectric and p-channel semiconductor 2,7-di dodecyl [1]benzothieno[3,2-b][1]benzothiophene (C12-BTBT) was served as the charge transfer layer to fabricate bottom-gate top-contact OFET, of which the structure is demonstrated in Fig. 4a. The transfer characteristics of C12-BTBT/PEST transistors are first investigated, as shown in Fig. 4b. The on current of C12-BTBT/PEST15 transistor is 1.43·10⁻⁴ A, while those of C12-BTBT/PEST37 and C12-BTBT/PEST59 transistors are 2.77·10⁻⁴ A and 6.73·10⁻⁴ A respectively. As the off-state currents of these 3 types of OFETs are nearly the same at 10⁻¹⁰ A level, the on/off ratios are 2.1·10⁵, 4.1·10⁵ and 1.0·10⁶, and the threshold voltages are -34 V, -32 V and -24 V, respectively, in orders of PEST15, PEST37 and PEST59 devices. Thus, C12-BTBT/PEST59 transistor exhibits the best OFET performance, as the largest on-state current, highest on/off ratio and smallest threshold voltage are synergistically achieved. The field-effect mobility of OFET is expressed as,⁴⁴

$$I_d = \frac{W}{2L} \mu_{sat} C_i (V_g - V_{th})^2 \quad (2)$$

where I_d is the drain current, W is the channel width, L is the channel length, C_i is the capacitance of the dielectric layer, V_g is the source-gate voltage, and V_{th} is the threshold voltage. By applying Equation 2, the

field-effect mobility is obtained, and is demonstrated in Fig. 4c. m_{sat} of OFET is dependent with V_g in index-like profile. C12-BTBT/PESt59 OFETs exhibit the highest mobility reaching $14.2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in saturation region, while those of C12-BTBT/PESt15 and C12-BTBT/PESt37 OFETs are $9.8 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and $5.7 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ respectively. As compared to the widely applied PS gate dielectric, C12-BTBT/PESt59 OFETs show competitive intrinsic performance, with slight difference in on/off ratio, but larger $m_{average}$ based on statistical data of 10 devices, as demonstrated in Table S3 in Supplementary information.

The output characteristics of OFETs with PESt15, PESt37 and PESt59 gate dielectrics are shown in Fig. S5. All three output characteristics are typical without nonlinearity in small source-drain voltage (V_d) region, indicating the contact resistance is well suppressed. The maximum on-state current in Fig. S5 is in accordance with transfer characteristics in Fig. 4b for each device, indicating stable operation of these OFETs.

Positive gate stress promotes electron injection into the polymeric dielectric in OFET, which induces strong hole transport in p-type semiconductors, and results in increased mobility. In this work, $\pm 80 \text{ V}$ gate voltages are applied with $V_d = 0 \text{ V}$ before operation, the field-effect mobility of OFETs is demonstrated in Fig. 4c. Different from the proportional relations in as-prepared OFETs, gate voltage dependent field-effect mobility of floating-gate OFETs experiences a linear increase at small V_g , followed by a quasi-platform at elevated voltages. Thus, OFETs can work with enhanced mobility at smaller voltages towards $V_g = 0 \text{ V}$. However, for PESt15 and PESt37 OFETs, the field-effect mobility is smaller when compared to the as-prepared devices in saturation region ($V_g = -60 \text{ V}$). Uncommonly, due to the large trap density as shown in Fig. 2h, PESt59 OFET exhibits a continuous increase in mobility after a short quasi-platform, and reaches $27.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at elevated V_g , which is 2 times of the as-prepared devices.

The dielectric characterization in Fig. 2 has already discussed molecular dependent charge trapping capability of PESt15, PESt37 and PESt59, and they are further analyzed in non-volatile OFET memory applications in Fig. 4d-f. After $+80 \text{ V}$ gate-stress, the on-state current of C12-BTBT/PESt15 device increases to $3.11 \cdot 10^{-4} \text{ A}$ in Fig. 4d, with off-state current slightly dropping, leading to the enlarged on/off ratio. The threshold voltage decreases to -19 V and the subthreshold swing (SS) characteristic is significantly improved. On the contrary, the threshold voltage enlarges to -43 V as the transfer curve shifts towards the direction of negative V_g after -80 V pre-treatment. As memory window is defined as the discrepancy of V_{th} between programmed and erased states, it is $\Delta V_{th} = 24 \text{ V}$ for C12-BTBT/PESt15 OFETs.

In C12-BTBT/PESt37 OFETs in Fig. 4e, the shift in transfer characteristics is rather obvious compared to C12-BTBT/PESt15 device. After positive programming, V_{th} shifts to -12 V from -32 V , while -80 V gate stress triggers negative shift towards $V_{th} = -46 \text{ V}$, resulting in a memory window of 34 V . Compared with that of PESt15 of 24 V , the memory window is enlarged by 50% with the replacement of gate dielectric polymer. As following the same treatment on C12-BTBT/PESt15 and C12-BTBT/PESt37 OFETs, the memory window of C12-BTBT/PESt59 device is 47 V in Fig. 4f, showing the best memory characteristics

among the three PEST devices. This enlargement of $D V_{th}$ is contributed by better shift performance after both positive programming (19 V) and negative erasing (28 V). Previous investigations on model gate dielectric PS show $D V_{th} = 33$ V in C12-BTBT/PS OFET with the statistical data of 10 devices.¹³ Thus, PEST37 shows comparable memory performance against PS based OFETs, and PEST59 shows 42% enhancement in memory window.

Mechanistically, memory window is controlled by space charge accumulation in gate dielectric, which is modulated by charge trap characteristics as analyzed in Fig. 2h. Trap density defines the capability of immobilized charges, which determines the electret intensity. Larger electret intensity leads to stronger compensation electric field that modulates charge transport of semiconducting layer, which eventually results in larger shifts of transfer characteristics as demonstrated in Fig. 4f. As the broad nano-scale interface in PEST contributes to the enriched charge traps compared with simply PE and s-PS, and PEST59 exhibits the largest trap density among the three copolymers (Fig. 2h). Consequently, it results in enlarged memory window in OFET memories.

The trap depth modulates the average immobilized duration of trapped charges, which determines stability of a polymer electret. Here, in order to systematically investigate the long-term operation of PEST based OFET memories, retention characteristic is obtained with a time interval of 104 s in ambient conditions at 45% relative humidity. As demonstrated in Fig. 4g, the initial programmed current largely varies with polymer dielectric, and PEST59 OFET exhibits the largest programmed current of 1.2×10^{-3} A, while that of PEST15 OFET is only 2.7×10^{-5} A, showing 2 orders decrease. The initial erased currents of the three OFETs are nearly the same, all at 10^{-10} A level. Thus, PEST59 OFET realizes the best initial performance with largest on-state current and on/off ratio.

In case of decay rate, PEST59 OFET shows superb memory characteristics with less than 1 order decay in programmed current and 2 orders decay in erased current at the end of 10^4 s. Comparatively, PEST15 and PEST37 OFETs exhibit observable quicker decay in both programmed and erased states. To be noticed that for all the three devices, the decay in erased current is more violent, which indicates that electrons are more firmly trapped than holes in PEST.

Distinctive retention of OFET memory is dependent on long-term stability of polymeric electret, which is closely related to relaxation time, controlled by trap depth. For PEST59 with trap depth of 1.6 eV (calculated from TSC results, shown in Fig. 2h), the trapped charges are more difficult to detrap, leading to the stable memory effect for both programmed and erased states. As PEST59 exhibits larger and deeper traps than s-PS, and s-PS typically owns larger trap density than the widely applied atactic polystyrene (a-PS) due to the enriched crystal-amorphous region, PEST59 is considered as an advanced gate dielectric for OFET memories.

In digital circuit applications, an inverter is realized based on two transistors (Fig. 4h). In order to achieve high performance inverter, the SS of T_{drive} should be small. As demonstrated in Fig. 4f, PEST59 OFET exhibits an enhanced SS performance after a positive gate stress treatment, leading to a gain

($|dV_{out}/dV_{in}|$) towards 15, as demonstrated in Fig. 4i. Comparatively, PS based OFETs show only a gain of 7 with the same $V_{DD} = -40$ V, as demonstrated in Fig. S6. Notably, controlled by the threshold voltage of OFET, PEST59 based inverter can operate with smaller $V_{in} = -10$ V, while the smallest operation voltage of PS based inverter is -20 V.

Application in environmental filtrations

In field of environmental filtrations, corona charging is commonly applied to form electret in enhancing filtration efficiency of polymeric mask.^{18,19} Here, with the strong charge trapping ability and excellent electret performance, PEST is coated on the surface of nylon fiber membrane to explore its application in enhancing filtration efficiency. The sample preparation is detailed in Methods, and corona charging and surface potential measurement were performed before filtration efficiency test, as indicated in Fig. 5a. The surface morphology and pore size of nylon fiber membrane were characterized by SEM, showing a smooth morphology of the original nylon fibers as demonstrated in Fig. 5b. After PEST solution treatment, a layer of dense micropores is formed on nylon fiber surface and the pore size distribution is wide in range from 1 μm to 6 μm (Fig. 5c). The formation of micropores can be attributed to the deposition and self-assembly of PEST during chloroform evaporation. After corona charging, one layer of PEST treated nylon fiber membrane was placed on inlet of a purifier in polluted environment for 3 days, and the SEM image in Fig. 5d clearly demonstrates the adsorbed and deposited dust on surface of the nylon fibers, showing excellent filtration performance.

The filtration characteristics of PEST treated nylon fiber are further quantitatively characterized by surface potential and particulate filtration efficiency (PFE) tests. In Fig. 5e, the untreated nylon fiber shows an initial surface potential of -2627 V after 5 kV corona charging. Comparatively, the initial surface potential of PEST treated nylon fiber is -3912 V, showing 50% increase against untreated samples. As discussed in Fig. 2g and 2h, the larger deep trap density in PEST contributes to the increased surface potential, which leads to stronger electrostatic potential to adsorb particles. For as long as 4 weeks, the surface potential of PEST coated nylon fiber membrane exhibits comparatively small attenuation as compared to untreated nylon, guaranteeing the long-term stable filtration when applied as facial mask materials.

PFE test was conducted with NaCl monodisperse aerosol with the diameter range in 0.3-5 μm , the results are demonstrated in Fig. 5f. PFEs of as-prepared nylon fiber and that with PEST treatment (without charging) are nearly the same, showing ~20 % PFE for 0.3 μm particles. The PFE increases with particle size, reaching ~72 % for 5 μm particles. By conducting corona charging, the PFE of nylon fiber membrane increases dramatically, and for PEST treated fiber membrane, the increase is more significant as compared with neat nylon fibers without PEST. The nylon fibers with PEST treatment show a PFE of 47.1 % for 0.3 μm particles, and 93.1 % for 5 μm particles. In particle size range from 0.3~5 μm , corona charged PEST-coated nylon shows ~25 % increase in PFE, while that of corona charged as-prepared sample is only ~12%. PEST introduces large amount of deep traps, which eventually leads to enhanced electrostatic field in filtrating particles for medical protection.

To be noticed that PFE is strongly related to corona charging voltage, as demonstrated in Fig. S7. The larger charging voltage enhances electron emission, which modulates electrostatic potential on surface of the sample. In this investigation, 10 kV is selected as the optimized charging voltage since further increasing charging voltage contributes little in enhancing surface potential and PFE.

Conclusions

In this work, a gradient copolymerization strategy is introduced for dielectric performance optimization of monocomponent polymers, and soluble semi-crystalline gradient ethylene-styrene copolymer (PESt) is designed. PESt exhibits excellent dielectric, electrical insulating and electret performances, which extraordinarily exceed those of neat PE and s-PS as a result of deep charge trapping centres introduced at the nano-scale macro-phase interfaces. In power storage applications, with the synergistically increased dielectric constant and breakdown strength, the energy density of PESt film reaches $22.9 \text{ J}\cdot\text{cm}^{-3}$, far exceeding that of massive applied polymers in power capacitors. In field of organic electronics, by applying PESt as the floating-gate and p-type C12-BTBT as semiconductor, OFET memory shows mobility up to $27 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, large memory window of 47 V and improved memory stability. In environmental filtrations, PESt electret induced by corona charging contributes to more than 20 % improved filter efficiency for air haze dusts. Consequently, gradient copolymerization serving as an emerging alternative strategy against nano-composite, shows a bright future in designing polymers for high performance energy/charge storage applications.

Methods

Material synthesis. PS with $M_w = 2000 \text{ kDa}$, PDI = 1.2 was purchased from the Sigma-Aldrich, and was used as purchased. PESt (PESt15, PESt37, PESt59) and semiconductor (C12-BTBT) were laboratory synthesized. The synthesis process of PESt was as follows. In the glove box, a reactor containing a magnetic stirring bar was charged with 70 mL toluene and styrene. The reactor was equipped with an ampoule bottle filled with 5 mL toluene solution of the complex 1 (9.4 mg, 20 μmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (17.4 mg, 20 μmol). The reactor was taken out of the glove box, connected to the Schlenk line, and set in the thermo stated oil bath (40 °C). The solution was degassed and then saturated with ethylene (1 atm) for three times under vigorous stirring. Then the solution of catalyst system was quickly transferred to the polymerization bottle to initiate the polymerization. The ethylene was consecutively fed during the whole polymerization process. The polymerization was quenched after a set amount of time by addition of acidified ethanol (50 mL). The precipitated polymer was filtered and washed with ethanol, and then dried under vacuum at 40°C until the weight had no change. The afforded copolymer was placed in a cellulose thimble and extracted successively with 50 mL boiling methyl ethyl ketone (MEK). After 6 hours, the MEK soluble fraction was dried under vacuum, and no extracts (atactic polystyrene) were found. Then the residue copolymer was extracted with boiling tetrahydrofuran (THF) for another 10 hours, and the copolymer was completely dissolved in boiling THF, neither insoluble PE or s-PS homopolymer was isolated.

Material characterization. The DSC was performed with DSC 822^e-700 (Mettler Toledo, Switzerland) at temperatures from 0 to 300 °C with a ramping rate of ± 10 °C/min. The TGA was performed with TGA/SDTA 851 (Mettler Toledo, Switzerland) at temperature ramping rate of 10 °C/min. DC breakdown was performed with a $\varphi = 25$ mm copper sphere-plate electrode stressed by a continuously increased voltage with the ramping rate of 1 kV/s. The volume resistivity was tested by a Keithley 6517B resistance meter with 250 V polarity reversal voltage. The trap information was obtained through ISPD experiment with needle voltage of -10 kV, grid electrode voltage of -3 kV, charging duration of 300 s, and testing duration of 21600 s. The TSC was conducted with Novo control concept 80 system with a polarization voltage of 250 V for 1 h at 130 °C. Then, the sample was rapidly cooled down to -100 °C with a ramping rate of -30 °C/min, and kept at -100 °C for 3 min to conduct depolarization. After that, TSC was obtained with a ramping rate of 5 °C/min to 150 °C. The dielectric spectrum was obtained by a Novo control concept 80 system with 1 V AC voltage in temperature range of -100 ~ 140 °C, frequency range of $10^{-1} \sim 10^6$ Hz. The AFM image was obtained by Asylum Research Cypher. The SEM image was obtained by VE-9800S (Keyence, Japan), with accelerating voltage of 0.5 kV. The TEM image was obtained by HT7700 (Hitachi, Japan). XRD was performed with SmartLab (Rigaku Corporation, Japan).

OFET fabrication and measurements. Bottom-gate top-contact OFET was fabricated on n-doped Si wafer with 300 nm thermally grown SiO₂. The channel length was 300 μ m and the channel width was 3 mm. The Si/SiO₂ substrate was cleaned with deionized water, acetone, and isopropanol respectively. PEST15, PEST37 and PEST59 were separately dissolved in *o*-dichlorobenzene with the concentration of 5 mg/mL. The dielectric film was first spin coated at 3000 rpm on 70 °C heated substrate. Then, thickness of 50 nm C12-BTBT, and 50 nm gold source-drain electrode were thermally evaporated onto the dielectric layer in turn at 0.5 Å/s. The OFET performance was tested with an Agilent Keysight B2900A Quick IV system in ambient at room temperature. Dielectric electret was generated with ± 80 V gate voltage for 1 s.

PESt for environmental filtrations. 100 mg PEST was dissolved in 10 mL CHCl₃ and stirred for 4 h at room temperature. Then, the nylon fiber membrane (12 · 12 cm²) was immersed into the as-prepared solution for 1 h at room temperature, taken out and allowed to dry in ambient environment. After drying, the microporous nylon fiber membrane modified with PEST was obtained by SEM. Corona charging was performed with the voltages of 0, 3, 5, 10 kV for 5 min. PFE was tested with SX-L1053C filter material tester by NaCl monodisperse aerosol with particle size from 0.3 ~ 5 μ m under the standards of ANSI/ASHRAE 52.1–1992 (USA) and EN779: 2002 (EU).

Data Availability

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding authors upon request.

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Declarations

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Author contributions Y. Z., B. L., S. L. and G. L. conceived and coordinated the work. Y. Z. designed the experiments and wrote the manuscript. W. L., N. Q. and H. C. fabricated and tested the transistors. S. Z. and Y. J. carried out the XRD and UV-Vis tests. Z. H. carried out the filtration test. B. L. synthesized the

materials. Y. N. and G. L. conducted the FDS measurement. S. Z. analyzed and contributed to discuss the results. All the authors commented and contributed to the editing of the manuscript.

Additional information

Supplementary information accompanies this paper at

Competing interests: The authors declare no competing interests.

Figures

Figure 1

Structure and characteristics of PEST. a) Schematic of microphase structure and density of states (DOS) distributions of PEST. Gradient copolymers PEST are composed of alternative polyethylene and polystyrene sequences, however the sequence length gradually varies along the polymer chain. b) DSC of

PESt15, PESt37 and PESt59. The arrows show the temperature scanning direction. c) XRD profiles of PESt15, PESt37 and PESt59. d) TGA profiles of PESt15, PESt37 and PESt59. e) AFM height image of PESt59 film. The scanning region is $5 \times 5 \mu\text{m}^2$. f) TEM image of PESt59 film. g) UV-Vis light absorption spectra of PESt15, PESt37 and PESt59.

Figure 2

Dielectric characteristics of PESt. a) FDS of PESt15. b) FDS of PESt37. c) FDS of PESt59. d) Comparisons of dielectric constant and 50 Hz dielectric loss of PE, PESt15, PESt37, PESt59 and s-PS at room temperature (20 °C). e) ISPD of PE, PESt15, PESt37, PESt59 and s-PS. f) Relations of trap depth with trap density of PE, PESt15, PESt37, PESt59 and s-PS, obtained from ISPD results. g) TSC spectra of PE, PESt15, PESt37, PESt59 and s-PS. h) Comparisons of trap depth and trap amount (TSC integral) of PE, PESt15, PESt37, PESt59 and s-PS.

Figure 3

Electrical insulation and energy storage characteristics of PEST. a) Weibull distributions of DC breakdown strength of PE, PEST15, PEST37, PEST59 and s-PS at 15 °C, obtained from 15 samples. b) Volume resistivity and high field charge mobility of PE, PEST15, PEST37, PEST59 and s-PS. c) Profiles of DC breakdown strength of PE, PEST15, PEST37, PEST59 and s-PS under temperatures of 15 °C, 40 °C, 70 °C and 100 °C. d) Energy density of PE, PEST15, PEST37, PEST59 and s-PS at room temperature. The film thickness is 150 μm . e) Thickness dependent DC breakdown strength of PEST59 at room temperature. f) Energy density comparison between PEST59 and commonly applied linear polymers in power capacitors.

Figure 4

OFET and memory performance based on PEST gate dielectrics. a) Scheme of OFET structure with polymer electret. b) Transfer characteristics of C12-BTBT/PESt OFETs with PEST as dielectric layer. c) Gate voltage dependent field-effect mobility of as-prepared and positive gate-stressed OFETs. "pos. str." represents positive stressed gate voltage. d-f) Memory characteristics of OFETs after ± 80 V programming and erasing treatments on d) PEST15, e) PEST37 and f) PEST59 gate dielectric OFETs. g) Retention characteristics of C12-BTBT/PESt OFETs. h) Schematic of CMOS-like inverter based on OFETs. Two OFETs with different characteristics tuned by PEST electret are used as loader and driver transistors, respectively. i) Output characteristics of the C12-BTBT/PESt59 inverter.

Figure 5

Environmental filtration performance of PEST electrets. a) Schematic of the coating process of PEST on filtration fiber membrane, corona charging, and haze filtration. Hereby, corona charging is used to inject charges into PEST to form electret. b) SEM image of untreated nylon fiber, showing a smooth surface. c) SEM image of PEST treated nylon fiber, showing porous PEST thin layer on nylon surface. d) SEM image of PEST treated nylon fiber after exposure to haze-polluted atmosphere. Inset is a zoomed SEM image, showing adsorbed dust on surface of the PEST layer. e) Changes of surface potential of nylon fiber membrane with and without PEST treatment after 5 kV corona charging for up to 28 days. f) PFE of nylon fiber membrane with and without PEST treatment, with and without 10 kV corona charging.

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