



Double-stranded block copolymer with dual-polarized linker for improving dielectric and electrical energy storage performance



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ABSTRACT

The double-stranded block copolymers containing ionic conductive and strong polar segments were synthesized by ring-opening metathesis polymerization, and self-assembled into the hollow sphere nanostructure. These block copolymers displayed high dielectric constant of 25, low dielectric loss of 0.02, enhanced stored/released energy density of 2.60/2.38 J cm⁻³ at 245 MV m⁻¹, and good charge-discharge efficiency of 91.5%, which were much better than those of double-stranded block copolymers without the strong polar substituents on the aromatic linker. The excellent dielectric properties of copolymers were attributed to the combination of strong dipolar, ionic, and interfacial polarizations, as well as the well-defined nanostructure to effectively inhibit the leakage current of the conductive domains by the insulating blocks.

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1. Introduction

Polymer dielectrics with high dielectric constant, high breakdown voltage capability, high energy density, excellent charge-discharge efficiency, and low loss factor are of great interest and basic requirements as materials in energy storage, film capacitor, and pulsed power applications because they have some advantages of light weight, low cost, high breakdown strength, and so on [1–5]. The fluorinated polymers, such as poly(vinylidene fluoride) (PVDF) with a large dipole moment and relatively high dielectric constant [5–8], are the best candidate for a high dielectric property material and have been widely studied. However, the high dielectric loss of PVDF-based ferroelectric polymers can reduce the charge-discharge efficiency, cause dielectric heating, and limit the frequency response of the capacitors [5,9].

As all known, dipolar, ionic, and interfacial polarizations may affect the dielectric performance of polymers [5,9–11]. Mostly, dipolar polarization can obviously increase the dielectric constant of polymers because of the large dipole moment [9]. Typical examples including PVDF and random copolymers bearing strong polar groups of trifluoroethylene (TrFE) and tetrafluoroethylene (TFE) have high dielectric constants. However, the high hysteresis

loss coming from the ferroelectric domains in isomorphous crystals can greatly reduce the charge-discharge efficiency. Instead of using the polymers containing large ferroelectric domains, a dipolar glass polymer containing polar sulfone group in the side chain was synthesized, its dielectric constant increased to 12 as a direct consequence of the easy dipole rotation, and the dielectric loss maintains at a low value of 0.02 [9]. Besides, the dipolar glass polymer has a high energy density capability and charge-discharge efficiency at relatively high temperature of 75 °C. Ionic polarization [5,12–15], which is from the small relative displacements of ions under the applied electric field, can substantially increase the dielectric constant and enhance the capacitance of gate dielectrics for organic field effect transistors [5]. Ionic polymers have a larger polarizability volume than the small ionic monomers and the dipoles prefer parallel alignment to avoid the overlap of the volume, resulting in the high static dielectric constant of 30–100 [16], but the high dielectric loss of 10⁻¹ is not suitable for fast discharge film capacitors due to a serious leakage current from the transport of ions over a long distance. Nevertheless, the ionic block copolymers with a well-defined nanostructure can effectively decrease the dielectric loss to a reasonable low level of 0.04–0.03 in comparison to the corresponding ionic homopolymer (0.13–0.09), because the ions are isolated between the insulating blocks for inhibiting the transport of ions in conductive blocks, while dielectric constant is not significantly reduced [13]. Interfacial polarization refers to charge and ion carriers accumulated at interfaces in multicomponent polymer systems, and its basic idea is to utilize the high

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dielectric constant of fillers (BaTiO₃, graphene, metal particles, and so on) to enhance the apparent permittivity of dielectrics [5,17,18]. For example, the composite PVDF-TrFE-CFE containing graphene oxide has a dielectric constant of above 10000 and loss of below 2, which was one of the best-reported dielectric constant and loss value for this type of material [17]. However, the composite connected graphene oxide tends to form a conduction pathway along the percolated polymer/filler interface, and usually incurs a high dielectric loss and low breakdown voltage, which limits the application in energy storage materials. To avoid the fillers gathered in a polymer matrix, one way is to form the covalent-linkage between the conductive filler and insulating polymer matrix [19,20], another way is to synthesize the core-shell nanostructures [10,21], and the essence is also to isolate conductive fillers. Therefore, it is envisioned that combining multiple polarizations and constructing well-defined nanostructure should be practical ways to obtain the high performance dielectric materials.

Perylene bisimide (PBI) is known as a kind of low dielectric constant and poor solubility material [22], by introducing the small dipolar group, such as *m*-(trifluoromethyl)phenyl possessing a high dipole moment ($\mu \sim 4.3D$) [23], into the bay-positions of PBI moiety, it may effectively to increase the dipole moment and twist the planarity of PBI, so as to improve the dielectric properties and solubility. Moreover, the large electron delocalization of PBI with additional four *m*-(trifluoromethyl)phenyl groups in the bay-positions should further enhance the electronic polarization due to the narrower band gap at an electric field and promote the dielectric properties. In addition, PBI can be readily used as a rigid linker to construct the double-stranded polymer structures, which have greater resistance to irradiation as well as thermal and chemical degradation in comparison to their single-stranded counterparts [24–27]. Herein, the double-stranded block copolymers with an ionic-dipolar dual-polarized PBI linker were synthesized via ring-opening metathesis polymerization, for improving the dielectric properties of block copolymers by the contribution of multiple polarizations and self-assembled nanostructure.

2. Experimental

2.1. Materials

endo-N-(4-Hydroxyphenyl)-norbornene-dicarboximide (*endo*-NDI) [13], dicarboxyl-contained perylene bisimide (PBI-COOH) [25], *N*-3,5-bis(trifluoromethyl)biphenyl-norbornene pyrrolidine (TNP) [28], and [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][bis(3-bromopyridine)]benzylidene ruthenium dichloride (Ru-III) [29] were prepared according to the previous procedures. Potassium carbonate (K₂CO₃), bis(trifluoromethyl)phenyl boronic acid, tetrakis(triphenylphosphine)palladium(0) (Pd(P(C₆H₅)₃)₄), 4-dimethylaminopyridine (DMAP), acryloyl chloride, ethyl acetate (EtOAc), petroleum ether, magnesium sulfate (MgSO₄), glacial acid (HAc), and propionic acid were purchased from Shanghai Chemical Reagents Co, and used as received without purification. Solvents were distilled over drying agents under nitrogen prior to use: dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃) from calcium hydride; tetrahydrofuran (THF) from sodium/benzophenone. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI·HCl), 4-dimethylaminopyridine (DMAP), 2-aminoethanol, and 2-ethylhexylamine were purchased from Energy Chemical. All reactions were carried out under dry nitrogen atmosphere using standard Schlenk-line technique.

2.2. Characterization

¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were recorded

using tetramethylsilane as an internal standard on a Bruker DPX spectrometer. UV-vis absorption spectra were measured on a UV-1800 spectrometer with the concentration of 1.0×10^{-3} mg mL⁻¹. IR spectra were recorded on a Perkin Elmer Spectrum using KBr pellets. Gel permeation chromatography (GPC) was used to calculate relative molecular weight and molecular weight distribution equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 mm bead size; 10³, 10⁴, and 10⁵ Å pore size). GPC measurements were carried out at 40 °C using 0.05 mol L⁻¹ of bis(trifluoromethane)sulfonimide lithium salt-contained THF as the eluent with a flow rate of 1.0 mL min⁻¹. Thermal gravimetric analysis (TGA) was performed using an SDTA851e/SF/1100 TGA instrument under nitrogen flow at a heating rate of 10 °C min⁻¹ from 25 to 800 °C. Differential scanning calorimeter (DSC) was performed on a Netzsch 204F1 in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from 40 to 250 °C and held at this temperature for 3 min to eliminate the thermal history, and then, they were cooled to room temperature and heated again from 40 to 250 °C at a heating or cooling rate of 10 °C min⁻¹. The system was calibrated with polystyrene standard. Transmission electron microscopy (TEM) images were recorded on the JEOL2100F microscopes operating at 120 kV. Samples for TEM measurement were prepared by depositing a drop of THF solution with different concentration on the copper grids coated with carbon, followed by air-drying. Additionally, the samples were not stained before measurement because the electron density difference between the two blocks provided sufficient contrast for TEM imaging. The hydrodynamic diameter was determined by means of dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW). The Nano ZS instrument incorporates noninvasive backscattering (NIBS) optics with a detection angle of 173°. The *z*-average diameter of the sample was automatically provided by the instrument using cumulate analysis. Dielectric measurements were carried out by a Novocontrol BDS40 dielectric spectrum analyzer over the frequency range of 100 Hz to 1 MHz at room temperature, and a contacting electrode method was used. The edge side (*d*) of the guarded electrode is 0.3 mm. The capacitance (*C_p*) and the dissipation factor (dielectric loss, or tanδ) of the tested films were recorded. The dielectric constant (ϵ_r) can be calculated by equation (1):

$$\epsilon_r = C_p l / \epsilon_0 A \quad (1)$$

Where *l* is the thickness of the film and ϵ_0 , the permittivity of the free space, is 8.85×10^{-12} F m⁻¹, *A* is the guarded electrode area, $A = \pi d^2$. The conductivity (σ) is calculated according to the following equation (2):

$$\sigma = G \cdot A / l \quad (2)$$

Where *G* is the conductance.

Preparation of film sample: polymer was dissolved in a selected solvent to a solution concentration of 20 wt%, and then, the mixture was stirred for 12 h at room temperature. After that, the solution was added into a mold, and dried in air overnight, followed by continuous heat treatment in vacuum for another 12 h to evaporate all the solvents. At last, the film was obtained by heat pressing. The typical thickness of polymer film was about 40–50 μm. The electric displacement (*D*)-electric field (*E*) hysteresis loops were recorded for applied voltages up to 10000 V with a cycle frequency of 1000 Hz.

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