Bimodal Polymer Brush Core–Shell Barium Titanate Nanoparticles: A Strategy for High-Permittivity Polymer Nanocomposites

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Supporting Information

ABSTRACT: This paper presents a novel strategy to modify the surface chemistry of barium titanate (BaTiO₃, BT) with a bimodal population of oligothiophene polymer brushes using step-by-step reversible addition–fragmentation chain transfer (RAFT) polymerization. Compared with a previous strategy based on monomodal surface-tethered brushes, these hybrid nanoparticles, BaTiO₃ coated with bimodal oligothiophene polymer brushes, demonstrate extremely good dispersion behaviors as dielectric nanofillers in a matrix of oligothiophene polymers. These nanodielectric composites exhibit greatly improved dielectric performance and maintain linear displacement–polarization (D–E) profiles under high applied electric fields. This promising bimodal strategy could be generalized to a variety of nanoparticles for the development of novel dielectric nanocomposite systems.

INTRODUCTION

Polymer nanocomposites prepared by incorporation of inorganic nanoparticles into polymer matrices, offering a compromise of the best properties of ceramic and polymer dielectrics, represents one of the most promising approaches to achieving high-performance dielectrics.1–4 Although a myriad of polymer nanocomposites have been developed to date, there are still some challenging issues, such as homogeneous nanoparticle dispersion, reinforcement of polymer–particle interface adhesion, and minimization of dielectric loss. Accordingly, many strategies have been employed to address these issues by tailoring the nanoparticle/polymer interface5,6 via modification of nanoparticles with organic molecules, including coupling agents,6 surfactants,7,8 phosphoric acids,9,10 and others.11–13 However, these methods still have limitations because the surface modifiers do not contribute directly to achieving the goal of superior dielectric performance. Recently, significant efforts have been devoted to the development of core–shell nanoparticles,4 in which nanoparticles are modified with polymer shells using different synthetic techniques (e.g., grafting to,14–16 grafting from,17,18 etc.). Figure 1 shows the typical architectures of core–shell nanoparticles, including (a) single-layer structures composed of only polymers (e.g., homopolymers,8 block copolymers,19 etc.) and (b) double-layer structures containing both polymers and organic electroactive molecules. Most modified nanoparticles can be used to prepare single- or multiple-component nanocomposite systems.

Recently, we introduced novel polymers with conjugated oligothiophene side chains as nanodielectric materials.24,25 These polymers exhibit high dielectric permittivity (ε, ca. 9–11), which is much higher than most other polymers (e.g., 2–5 for polypropylene, polystyrene, etc.) and comparable with poly(vinylidene fluoride) (PVDF). Notably, our polymers also display low dielectric loss (<0.02) with striking consistency over a wide range of frequencies from 100 Hz up to several MHz. This performance is attributed to highly polarizable and fast-relaxing nanodipoles associated with nanoscale crystalline domains (<2 nm) composed of oligothiophene side groups. Shortly thereafter, we combined oligothiophene-containing polymers with barium titanate (BaTiO₃, BT) nanoparticles to develop core–shell nanoparticles with a single-layer structure for use in dielectric polymer nanocomposites.26 The oligothiophene-containing polymer was grafted from BT nanoparticles via in situ surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization. Compared with a previous strategy based on monomodal surface-tethered brushes, these hybrid nanoparticles, BaTiO₃ coated with bimodal oligothiophene polymer brushes, demonstrate extremely good dispersion behaviors as dielectric nanofillers in a matrix of oligothiophene polymers. These nanodielectric composites exhibit greatly improved dielectric performance and maintain linear displacement–polarization (D–E) profiles under high applied electric fields. This promising bimodal strategy could be generalized to a variety of nanoparticles for the development of novel dielectric nanocomposite systems.
fragmentation chain transfer (RAFT) polymerization in a controlled/living fashion. The robust surface control of shell chemistry and composition offers a facile approach to compatibilizing dielectric nanofillers in a matrix of oligothiophene polymers, leading to the formation of nanodielectric composites that exhibit enhanced dielectric permittivity (~20) with relatively low dielectric loss (<0.02) over a wide range of frequencies.

Based on this earlier work, herein we report the design and synthesis of BT based core−shell nanoparticles with a novel bimodal surface-grafted polymer architecture (Figure 1c) that differs from the commonly used architectures mentioned above. This approach was particularly inspired by recent work from the Benicewicz group27−30 and the Zhao group,31−33 Benicewicz et al. discovered27−29 that grafting bimodal polymer brushes on nanoparticles can significantly improve the miscibility of nanoparticle fillers and matrix polymers. In direct comparison, nanoparticles coated with monomodal polymer brushes are found to aggregate into a range of isotropic and anisotropic morphologies due to a delicate balance between enthalpic and entropic interfacial interactions. The balance between enthalpy and entropy leaves only a small window of grafting densities and molecular weights that can be used to achieve randomly dispersed filler morphologies. Benicewicz et al. showed that this limitation could be overcome using a bimodal architecture (Figure 1c) containing a low density of long polymer chains to offer sufficient entanglement with matrix polymer chains plus a high density of short brushes that imposes steric repulsion and screens particle/particle attraction. This architecture helps decouple interfacial enthalpic and entropic interactions and promotes uniform nanoparticle distribution in a polymer matrix.

In the current work, we employ this bimodal strategy to design and prepare novel hybrid BT nanoparticles that are surface-modified with oligothiophene-containing polymer brushes having a bimodal distribution of molecular weight. These bimodal-graft-functionalized BT nanoparticles were mixed with similar oligothiophene-containing polymers to prepare nanocomposites. Dielectric properties of these nanocomposites were compared to those of nanocomposites containing monomodal-graft-functionalized BT nanoparticles. In this manner, we demonstrate that this “bimodal” surface engineering strategy produces nanodielectric polymer composites with superior particle dispersion and remarkably enhances dielectric properties. Moreover, the bimodal strategy should be applicable to a variety of nanoparticles with other polarizable polymer shells.

**EXPERIMENTAL SECTION**

**Materials.** All reagents were purchased from Alfa Aesar or Sigma-Aldrich and used as received unless otherwise noted. 1,4-Dioxane was distilled over sodium and benzoquinone before use. Use of 2-(2,5′,2′-terthienyl-5-yl)ethyl methacrylate (TTEMA) monomer and grafting of TTEMA homopolymer (PTTEMA) from BaTiO3 nanoparticles with grafted chain transfer agent (4-cyanopentanoic acid dihydroxobenzene, CPDB) were carried out according to the methods reported in our previous work.4,20 The product particles are denoted as PTTEMA@BT.

**Cleavage of RAFT Agent Chain Ends from PTTEMA@BT Nanoparticles.** A tetrahydrofuran (THF) solution (30 mL) of the PTTEMA@BT nanoparticles (1.25 g) was sonicated for 15 min, purged with nitrogen for another 15 min, and followed by addition of 90 mg of azobisisobutyronitrile (AIBN) to the flask under a N2 atmosphere. The mixture was refluxed at 75 °C for 1 h and then cooled to room temperature. The particles were recovered by centrifugation at 8000 rpm for 7 min and then resuspended in 50 mL of THF; this was repeated three times. The resulting particles were dried at room temperature to obtain 1.2 g of PTTEMA@BT nanoparticles with RAFT agent chain ends cleaved.

**Second Amino-Functionalization of PTTEMA@BT Nanoparticles.** A dried toluene solution (30 mL) of the RAFT agent cleaved BT nanoparticles (1.15 g) was sonicated for 30 min and then purged with N2 gas for 15 min. Next, 0.128 g (0.58 mmol) of [3-(aminopropyl)tetrahydroxysilane was added under a N2 atmosphere. The reaction mixture was heated to 80 °C and maintained at these conditions overnight. After the flask was cooled to room temperature, the particles were recovered by centrifugation at 8000 rpm for 7 min. The particles were then resuspended in 50 mL of THF; this was repeated three times. The resulting particles were dried at room temperature to obtain 1.08 g of PTTEMA@BT nanoparticles with second amino-functionalization (PTTEMA@BT-NH2).

**Second CPDB Modification of PTTEMA@BT Nanoparticles.** A tetrahydrofuran (THF) solution (30 mL) of the amino-functionalized BaTiO3 nanoparticles (PTTEMA@BT-NH2, 1.03 g) was sonicated for 30 min in darkness, and then a THF solution of activated CPDB (2.8 mL, 0.2 g mL−1) was added dropwise to the suspension at 0 °C in an ice bath. After complete addition, the suspension was allowed to warm to room temperature and stirred overnight. The reaction mixture was then poured into a large amount of THF (100 mL). The particles were recovered by centrifugation at 8000 rpm for 10 min. The particles were then resuspended in 50 mL of THF and centrifuged; this was repeated several times until the supernatant layer after centrifugation was colorless. The product was dried at room temperature to obtain PTTEMA@BT particles with second functionalization of CPDB (PTTEMA@BT-CPDBNH2, 1.0 g).

**Grafting of 2-(2,5′,2′-terthienyl-5-yl)ethyl Methacrylate (TTEMA) Polymer Brush from PTTEMA@BT-CPDBNH2.** Homopolymer-modified BaTiO3 nanoparticles (PTTEMA@BT-CPDBNH2, 0.45 g), TTEMA (3.6 g, 10 mmol), AIBN (0.2 mg, 1.32 mmol), and 7.8 mL of dry 1,4-dioxane were added to a 25 mL Schlenk flask and degassed by five cycles of freeze−pump−thaw. The flask was then submerged into a 90 °C preheated oil bath and maintained in this state for 12 h. The reaction flask was immediately cooled in an ice bath, and the mixture was diluted with THF. The particles were recovered by centrifugation at 8000 rpm for 7 min, resuspended in 50 mL of THF, and then recentrifuged; this was repeated several times until the supernatant layer after centrifugation was colorless. The product was dried at room temperature to obtain 0.5 g of PTTEMA@BT particles with second functionalization by grafted PTTEMA polymer. The bimodal-polymer-grafted particles are denoted as B-PTTEMA@BT.

**Cleavage of Graft Polymer Brush from B-PTTEMA@BT Nanoparticles.** In a typical experiment, 50 mg of B-PTTEMA@BT nanoparticles was dissolved in 2 mL of THF. Aqueous HF (49%, 0.1 mL) was added, and the suspension was allowed to stir at room temperature overnight. The suspension was centrifuged, and the clear supernatant-layer polymer solution with light yellow color was collected, concentrated, and precipitated in cold hexane. The recovered PTTEMA polymer brush was then characterized by GPC analysis. Graft polymer brush from B-PTTEMA@BT (GPC): M1 = 17 000 g mol−1, D = 1.20; M2 = 154 000 g mol−1, D = 1.25.4,12

**Preparation of 2-(2,5′,2′-terthienyl-5-yl)ethyl Methacrylate (TTEMA) Homopolymer with High Molecular Weight via Free Radical Polymerization.** TTEMA (2.08 g, 5.77 mol), AIBN (5 mg, 0.03 mmol), and 4 mL of dry 1,4-dioxane were added to a 25 mL Schlenk flask and degassed by five cycles of freeze−pump−thaw. The flask was then submerged into a 90 °C preheated oil bath and maintained for 12 h of polymerization. Afterward, the reaction flask was immediately cooled in an ice bath, and the mixture was diluted with THF. The thermothiophene-containing polymer was purified by precipitation into cold hexane three times to remove any unreacted monomers and then vacuum-dried at room temperature, resulting in a light yellow powder. Yield: 1.45 g (70%). GPC: M1 = 67 000 g mol−1, D = 1.71

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Physical Characterization. \(^1\)H NMR (300 MHz) spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. FT-IR spectra were recorded using a BioRad Excalibur FTS3000. Gel permeation chromatography (GPC) was performed using a Waters GPC system equipped with a 515 HPLC pump, a 2410 refractive index detector, and three Styragel columns (HR1, HR3, and HR4 in the effective molecular weight range of 100–5000, 500–30000, and 5000–500000 g mol\(^{-1}\), respectively) with HPLC grade tetrahydrofuran (THF) as the eluent at 30 °C and a flow rate of 1.0 mL min\(^{-1}\). THF and polymer solutions were filtered through microfilters with a pore size of 0.2 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). The columns were calibrated against polystyrene standards.

Thermal transitions of the polymers were recorded by using differential scanning calorimetry (DSC) on a TA Instruments Q2000 in a temperature range from 0 to 200 °C at heating and cooling rates of 10 °C min\(^{-1}\) under constant N\(_2\) gas flow (50 mL min\(^{-1}\)). Samples (between 3 and 5 mg) were added to aluminum hermetic pans and sealed. The data were collected during the second heating and cooling cycle. Thermogravimetric analysis (TGA) was conducted on a TA Instruments Q5000 using a heating rate of 10 °C min\(^{-1}\) from room temperature to 1000 °C under constant N\(_2\) gas flow. Wide-angle X-ray diffraction (WAXD) measurements were conducted on a Rigaku D/MAX 2100 powder X-ray diffractometer (Cu K\(\alpha\) radiation) instrument. Transmission electron microscopy (TEM) images of particles were acquired using a Hitachi 8000 TEM operated with an accelerating voltage of 200 kV. TEM samples were prepared by dropping solution on carbon-supported copper grids and drying before observation. Images of nanocomposite films were acquired using a field-emission scanning electron microscope (FE-SEM, Zeiss UltraPlus, operated at 6 kV accelerating voltage).

Dielectric Property Characterization. Composite films for dielectric property characterization were prepared by solution blendig using tetrahydrofuran (THF). PTTEMA was dissolved in THF (50 mg mL\(^{-1}\)), and PTTEMA@BT or B-PTTEMA@BT particles were suspended in THF with 1–2 h sonication. The solutions were blended, sonicated for an additional 2 h, and then poured into heavy-gauge aluminum pans. The THF was removed by evaporation at 44 °C.
under reduced pressure (635 mmHg absolute) for about 2 h without any post-treatment (like thermal annealing). This resulted in films with uniform thickness and free of bubbles, cracks, or other defects (vide infra). Film thicknesses were measured at multiple positions with a micrometer and found to be in the 5–15 μm range. Strips of aluminum pan bearing polymer or composite films were cut using scissors. The aluminum pan served as the bottom electrode for dielectric measurements. Gold was sputter-coated under an argon atmosphere through a shadow mask to deposit circular gold electrodes (area 0.282 cm²) on the films’ top surfaces.

The complex impedance of polymer and composite film samples was measured using an impedance analyzer (Agilent model 4192A LF). Measurements were carried out at a fixed applied voltage (20 mV) and varying frequency (typically 10² to 1.2 × 10⁷ Hz). Impedance spectra were collected for 3–5 specimens of each sample to ensure reproducibility; average values are reported. The real and complex parts of the impedance, expressed as impedance magnitude and phase angle, were analyzed using a parallel RC circuit model describing a “leaky” capacitor, yielding values of relative permittivity (εᵣ) and loss tangent (tan δ) as functions of frequency.

Polarization measurements at higher applied voltages employed a Precision Multiferroic polarization tester (Radiant, Inc.). Polarization data (D vs E) were obtained with a cycle frequency of 1 kHz. The maximum applied field strength depended on the sample film thickness and breakdown strength. Stored energy density (D) was determined by numerical integration of E, according to W = \int E dD, from D = 0 to the maximum value of D (D_max) achieved in the hysteresis loop. Recovered energy density (\bar{W}) was determined by numerically integrating E from D_max to the value of D where E = 0. Percentage energy loss is computed as 100 × (\bar{W} - \bar{W}_r)/\bar{W}_r.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of B-PTTEMA@BT

By adopting a “grafting from” approach, we synthesized bimodal terthiophene-containing polymer brush-grafted BT nanoparticles (namely B-PTTEMA@BT) via step-by-step controlled radical polymerization (RAFT polymerization) (Scheme 1) using a surface-anchored chain transfer agent (CTA), 4-cyanopentanoic acid dithiobenzoate (CPDB). The RAFT polymerization of terthiophene-containing monomer 2-(2',5'-terthien-5-yl)ethyl methacrylate (TTEMA) for the first PTTEMA brush population on BT nanoparticles (PTTEMA@BT) followed a procedure reported earlier. TTEMA was first polymerized from CPDB anchored on the surface of BT nanoparticles (BT-CPDB) to yield PTTEMA brush-anchored PTTEMA@BT using AIBN as the initiator.

Prior to attachment of chain transfer agent for the second round of graft polymerization, it was necessary to cleave the CPDB from the first graft polymerization, which remained as an end group on the first PTTEMA brush population (a consequence of the RAFT polymerization). The cleavage was achieved using AIBN via a radical cross-coupling mechanism (AIBN:CTA = 20:1). After the deactivation of RAFT chain ends, the attachment of second-round CPDB on the surface of PTTEMA@BT nanoparticles was achieved using an approach similar to that employed for the first round of RAFT polymerization. Hydroxyl groups on the surface of the PTTEMA@BT nanoparticles, which remained unreacted after the first round of CPDB attachment, were reacted with 3-aminopropyltriethoxysilane (APTS). The small APTS molecule can diffuse to the surface of BT particles and react with hydroxyl groups even in the presence of grafted polymer chains from the first round of polymerization. After functionalization of the PTTEMA@BT nanoparticles with APTS, CPDB was attached via a condensation reaction between mercaptothiazoline activated-CPDB and the amine group in APTS. Ex cess activated-CPDB relative to amine (4:1) was used to ensure complete conversion of amine groups to RAFT chain transfer agents. Second-round CPDB functionalized nanoparticles were washed several times by using THF to remove unreacted CPDB.

Following the attachment of second-round CPDB on PTTEMA@BT, the second round of surface-initiated RAFT polymerization of TTEMA was conducted to produce bimodal PTTEMA-grafted BT nanoparticles (B-PTTEMA@BT). The TTEMA monomer can diffuse to the surface of the BaTiO₃ nanoparticles even in the presence of polymer chains and then react with the chain transfer agent after initiation. A monomer to CTA ratio in excess of 2400:1 was used to keep the conversion low and avoid gelation while ensuring the formation of high molecular weight polymer.

In order to confirm the achievement of bimodal, brush-grafted BT nanoparticles, the PTTEMA chains were cleaved from polymer-grafted BT nanoparticles by treating them with HF, followed by gel permeation chromatography (GPC) characterization. Figure 2 compares the GPC trace of cleaved polymer chains from B-PTTEMA@BT with that obtained from PTTEMA@BT. Table 1 summarizes the quantitative GPC results for both monomodal PTTEMA@BT and bimodal B-PTTEMA@BT. The GPC trace for B-PTTEMA@BT clearly shows that the cleaved polymer has a bimodal distribution of molecular weight. The lower MW mode from B-PTTEMA@BT has the same average molecular weight as the monomodal distribution from PTTEMA@BT. For B-PTTEMA@BT, the average molecular weight of the second, higher MW chain population is approximately 9 times that of the first polymer chain population. This demonstrates successful synthesis of bimodal-graft-functionalized B-PTTEMA@BT with distinct low- and high-MW modes of grafted PTTEMA chains.

The morphologies of these core–shell nanoparticles were characterized by TEM (Figure 2). A stable and dense polymer shell was clearly observed on the surface of BT nanoparticles. The thickness of PTTEMA polymer shells is about 7–9 and 16–20 nm respectively for PTTEMA@BT and B-PTTEMA@BT. FT-IR spectra (Figure S1) manifest all of the characteristic
absorption peaks associated with the grafted PTTEMA polymer brush.

Thermogravimetric analysis (TGA) measurements (Figure S2) show that the weight loss of B-PTTEMA@BT (19.95%) was much larger than PTTEMA@BT (12.22%). DSC measurements (Figure S3) show that the surface-grafted PTTEMA polymers exhibit melting and recrystallization processes similar to those of free PTTEMA homopolymer, although the peaks are less obvious due to the presence of large fractions of BT nanoparticles (>80 wt % based on TGA). These results confirm the successful grafting of bimodal PTTEMA polymer brushes on the BT particle surface and demonstrate that the surfacegrafterd polymers have thermal properties similar to those of nongrafted PTTEMA homopolymer. It suggests that the formation of crystalline domains induced by interactions between terthiophene side chains is likely to occur in such hybrid systems.

Preparation and Characterization of B-PTTEMA@BT-Based Polymer Nanocomposites. The PTTEMA homopolymer was synthesized via free radical polymerization (see 1H NMR and GPC results in Figures S4 and S5, respectively). Polymer nanocomposite films were prepared by solution blending of the PTTEMA homopolymer with two different volume fractions (10 and 20 vol %) of PTTEMA-grafted BT nanoparticles.

Field-emission scanning electron microscopy (FESEM) was used to image the exterior and cross-sectional surfaces of films in order to investigate the microscopic homogeneity of BT nanoparticle dispersion. As shown in Figure 3, all bimodal B-PTTEMA@BT nanoparticles were well dispersed in the PTTEMA matrix at both 10 and 20 vol % BT, with no obvious agglomeration observed in these images (Figure 3a–f). In contrast, agglomeration and voids are observed in the nanocomposite films containing monomodal PTTEMA@BT nanoparticles (20 vol % BT, Figure 3g–i). Visually, the films filled with bimodal B-PTTEMA@BT particles exhibit good quality with smooth surfaces and very few defects. However, films filled with monomodal PTTEMA@BT particles have uneven surfaces with visible cracks. The results demonstrate that the bimodal polymer brush shell can provide stronger interchain forces promoting better entanglement with the PTTEMA polymer matrix compared to composites with BT particles coated with a monomodal polymer brush shell. The uniform distribution of B-PTTEMA@BT nanoparticles in the PTTEMA matrix minimizes the incidence of defects both within the films and on the surfaces, which could be beneficial for improving mechanical and dielectric properties.

In order to understand the effects of different interfacial architectures (bimodal B-PTTEMA@BT versus monomodal PTTEMA@BT) on the microstructure of PTTEMA matrix, these nanocomposites were characterized by differential
scanning calorimetry (DSC) (Figure S6) and wide-angle X-ray diffraction (WAXD) (Figure S7) to evaluate crystalline microstructure. As shown in the DSC profiles obtained in the cooling scan (Figure S6), the crystallization temperature ($T_c$) of all nanocomposites shifted to lower values. In addition, the introduction of either bimodal and monomodal BT nanoparticles led to decreases of heat of fusion, from 16.49 J g$^{-1}$ for the PTTEMA homopolymer matrix to 4.17 and 4.71 J g$^{-1}$ respectively for B-PTTEMA@BT and PTTEMA@BT nanocomposites (20 vol % BT). The results indicated that the inclusion of either kind of BT nanoparticles to the PTTEMA polymer matrix resulted in a decrease of degree of crystallinity in the PTTEMA homopolymer matrix, with a slightly larger decrease in the bimodal B-PTTEMA@BT system. The decrease in the heat of fusion became larger as the BT volume fraction increased from 10 to 20 vol % for both bimodal and monomodal systems, indicating a corresponding decrease in degree of crystallinity with increase in BT volume fraction in the nanocomposites.

**Dielectric Properties of B-PTTEMA@BT-Based Polymer Nanocomposites.** Nanocomposite films were fabricated containing either monomodal PTTEMA@BT or bimodal B-PTTEMA@BT nanoparticles blended with PTTEMA homopolymer. Impedance spectroscopy and polarization testing were then used to characterize their dielectric properties.

Figure 4 shows the dielectric properties of bimodal B-PTTEMA@BT and monomodal PTTEMA@BT nanocomposites (10 and 20 vol % BT nanoparticles) as well as neat PTTEMA homopolymer. The relative permittivity values ($\varepsilon_r$) of both bimodal and monomodal composites are larger than that of the neat PTTEMA matrix. The $\varepsilon_r$ values are nearly constant, decreasing only a few percent over a wide frequency range (1 kHz to 1 MHz), which is distinct from the significant frequency dependence of PVD-based nanocomposites.$^{7,1,13,35,36}$ The $\varepsilon_r$ values clearly increase with the volume fraction of BT. The most significant observation is that at the same BT loading, nanocomposites incorporating bimodal B-PTTEMA@BT exhibited much larger $\varepsilon_r$ values than those containing monomodal PTTEMA@BT. For example, at 20 vol % BT loading, the bimodal B-PTTEMA@BT nanocomposites have $\varepsilon_r$ values (57.2–50.7 from 1 kHz to 1 MHz), 55–60% greater than monomodal PTTEMA@BT nanocomposites (37.1–31.6 from 1 kHz to 1 MHz), and 5 times greater than PTTEMA homopolymer (9.7–9.2 from 1 kHz to 1 MHz). These results demonstrate the great potential of the bimodal strategy for achieving high-permittivity polymer nanocomposites.

All nanocomposite films exhibited dielectric loss (expressed as loss tangent, tan$\delta$, Figure 4b) higher than that of the pure PTTEMA homopolymer. For nanocomposites containing 10 vol % BT, those made with bimodal B-PTTEMA@BT had significantly lower loss tangent than those made with monomodal PTTEMA@BT. The trend was the same for 20 vol % BT nanocomposites, although the difference was smaller. These results indicate that the bimodal PTTEMA polymer shell can better suppress dielectric loss in the composites than the monomodal polymer shell.

The better dielectric performance of bimodal B-PTTEMA@BT nanocomposites can be attributed that the bimodal strategy promotes better, more uniform dispersion of BT nanoparticles$^{27–30}$ which, in turn, results in more uniform distribution of the electric field over the BT nanoparticles and thus higher composite effective permittivity. It is well established that electric field lines in dielectrics tend to pass preferentially through the lower permittivity polymer matrix rather than higher permittivity filler particles, with the field distribution depending on particle shape, size, and aggregation state.$^3$ In addition, strong entanglement of the longer chains in the bimodal strategy should have a positive effect on the quantity and size of the PTTEMA crystalline domains, increasing the density of polarizable dipolar domains and thus effective permittivity.

Dielectric losses are related to charge migration (leakage currents), especially through electrostatic double layers that may be located at polymer–filler interfaces.$^{7,38}$ This mechanism may explain the higher loss tangent values observed in these PTTEMA/BT nanocomposites compared to neat PTTEMA homopolymer. Previous work$^{39}$ showed that PTTEMA grafting on BT resulted in suppression of dielectric loss in PTTEMA/BT nanocomposites compared to that in composites prepared with pristine BT. This is due to the suppression of the double layer by polymer grafts, which reduce surface charges. In this work, the lower dielectric loss in composites containing bimodal B-PTTEMA@BT nanoparticles can be attributed to better BT particle dispersion, which disrupts particle-to-particle conduction paths found in aggregates.$^{7,38}$ The effect is greater for composites with 10 vol % BT because the bimodal graft polymers produce well-dispersed BT with greater interparticle separation. In composites with 20 vol % BT, although the BT particles are well dispersed, the interparticle separation is obviously not as large.

**Figure 4.** (a) Relative permittivity and (b) loss tangent of monomodal PTTEMA@BT and bimodal B-PTTEMA@BT nanocomposites and PTTEMA homopolymer as functions of frequency. All measurements carried out at ambient temperature (23 °C).
Polarization testing was carried out to investigate the dielectric properties of bimodal B-PTTEMA@BT and mono-modal PTTEMA@BT nanocomposites subjected to higher applied fields. Figure 5 shows typical displacement–electric field (D–E) loops. In the earlier report, monomodal PTTEMA@BT nanocomposites enhanced polarization compared with composites prepared with pristine BT. However, monomodal PTTEMA@BT composites prepared with 20 vol % BT exhibited significant hysteresis (electrical energy loss dissipated as heat) upon polarization at relative low electric fields (ca. 240 kV cm⁻¹). In this work, measured D–E loops (Figure 5a) show that bimodal B-PTTEMA@BT composites exhibit both enhanced polarization and reduced hysteresis compared to monomodal PTTEMA@BT composites. The bimodal B-PTTEMA@BT composites clearly have a more linear polarization behavior than the monomodal composites under the same conditions (20 vol % BT, moderate electric field). Moreover, the bimodal B-PTTEMA@BT composites can be polarized to higher electric fields before the hysteresis becomes noticeable (Figure 5b). These observations can be rationalized in terms of the same charge conduction mechanisms mentioned above for dielectric performance at low electric fields.

Figure 6a shows the stored energy density ratios of bimodal B-PTTEMA@BT and monomodal PTTEMA@BT nanocomposites relative to that of neat PTTEMA homopolymer measured at the same electric field. The stored energy density of all nanocomposites improved in comparison with that of pure PTTEMA homopolymer at both 10 and 20% BT loading. Notably, the bimodal B-PTTEMA@BT composites showed greater improvement than the monomodal PTTEMA@BT composites. In addition, the bimodal B-PTTEMA@BT composites also exhibited greater energy extraction efficiency (recovery of stored electrical energy) than the monomodal counterparts (Figure 6b). In fact, bimodal B-PTTEMA@BT containing 20% BT had greater than 95% recovery efficiency. These results can also be rationalized in terms of the superior BT particle dispersion achieved in composites prepared with bimodal B-PTTEMA@BT. Better BT dispersion results in (1) more uniform distribution of electric field lines through BT particles and thus higher stored energy density and (2) disruption of charge conduction along the polymer–filler interface and through particle-to-particle contacts.

Figure 6b shows the energy extraction efficiency measured at 210 kV cm⁻¹ with 1 kHz cycle frequency as a function of various vol % loading of BT nanoparticles.

Compared with the monomodal approach, this bimodal strategy provides distinct advantages for synthesizing polymer nanocomposites for dielectric applications. In this bimodal strategy, the shorter grafted polymer chains with higher graft density minimize particle aggregation due to attractive interparticle forces. The longer polymer chains with a lower graft density promote entanglement with the matrix polymer due to favorable thermodynamics, especially when the polymer shells have the same chemical structure as the polymer matrix. The bimodal architecture significantly enhances the dispersion and energy extraction efficiency.
of BT nanoparticles and improves particle–polymer interfacial adhesion. As a result, the bimodal PTTEMA polymer shell acts as a superior buffer layer that helps alleviate the large contrast in permittivity between nanoparticle and polymer matrix. Better BT particle dispersion results in a more homogeneous electric field with more of the field lines passing through high permittivity BT, resulting in significantly higher dielectric permittivity and lower dielectric loss. In addition, the bimodal PTTEMA polymer shell contributes to the formation of small nanoscale conjugated domains rather than disrupting them. Not only does this contribute to higher permittivity and stored energy density, but it also sustains fast polarizability response and thus low dielectric loss up to high frequencies, all of which are desirable for pulse power applications.

**CONCLUSIONS**

Bimodal thiophene polymer-grafted BT hybrid nanoparticles were successfully synthesized using a step-by-step RAFT polymerization method. PTTEMA nanocomposite films incorporating bimodal B-PTTEMA@BT nanoparticles were fabricated and tested as dielectric materials. In comparison with the monomodal system, the bimodal strategy offers greater improvement in dielectric performance, including higher permittivity and lower dielectric loss over a wide range of frequency. More importantly, at higher applied fields, the bimodal strategy suppresses electric energy dissipation (hysteresis), shifting its onset to higher electric fields.

Overall, the bimodal surface modification technique manifests an impressive influence on composite dielectric properties and offers great potential for fabrication of hybrid polymer–inorganic fillers for application in high performance dielectric nanocomposites. We believe that this robust surface engineering approach could be generalized to introduce other polarizable polymer shells to a variety of nanoparticles.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b02018.

IR, TGA, DSC, and WXRD of the B-PTTEMA@BT/PTTEMA@BT-based nanocomposites; NMR and GPC of the PTTEMA homopolymer matrix (PDF)

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Notes

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