Nanoscale

Block copolymer/ferroelectric nanoparticle nanocomposites†

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Nanocomposites composed of diblock copolymer/ferroelectric nanoparticles were formed by selectively constraining ferroelectric nanoparticles (NPs) within diblock copolymer nanodomains via judicious surface modification of ferroelectric NPs. Ferroelectric barium titanate (BaTiO3) NPs with different sizes that are permanently capped with polystyrene chains (i.e., PS-functionalized BaTiO3NPs) were first synthesized by exploiting amphiphilic unimolecular star-like poly(acrylic acid)-block-polystyrene (PAA-b-PS) diblock copolymers as nanoreactors. Subsequently, PS-functionalized BaTiO3 NPs were preferentially sequestered within PS nanocylinders in the linear cylinder-forming polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymer upon mixing the BaTiO3 NPs with PS-b-PMMA. The use of PS-b-PMMA diblock copolymers, rather than traditional homopolymers, offers the opportunity for controlling the spatial organization of PS-functionalized BaTiO3 NPs in the PS-b-PMMA/BaTiO3 NP nanocomposites. Selective solvent vapor annealing was utilized to control the nanodomain orientation in the nanocomposites. Vertically oriented PS nanocylinders containing PS-functionalized BaTiO3 NPs were yielded after exposing the PS-b-PMMA/BaTiO3 NP nanocomposite thin film to acetone vapor, which is a selective solvent for PMMA block. The dielectric properties of nanocomposites in the microwave frequency range were investigated. The molecular weight of PS-b-PMMA and the size of BaTiO3 NPs were found to exert an apparent influence on the dielectric properties of the resulting nanocomposites.

Introduction

Nanocomposite materials offer a vast design space of potential material properties, depending on the properties of the constituents and their spatial arrangement.¹ Nanocomposites of a polymer and nanoparticles (NPs) yielded by incorporating NPs into a polymer matrix often exhibit advantageous optical, electrical, and mechanical performance enhancement when compared to non-hybrid counterparts.² The spatial control of NPs in different polymeric domains is of great interest for practical applications such as nanostructured solar cells,³ high efficiency catalysts, photonic band-gap materials,⁴ high-density magnetic storage media,⁵ microwave devices,⁶ sensors,⁷ capacitors,⁸ and so on.¹ In this regard, block copolymers (BCPs) composed of chemically dissimilar chains offer the possibility to precisely control the NP organization at the nanoscale.⁹,¹¹

Two major approaches have been developed for incorporating inorganic NPs into BCPs to form BCP-based nanocomposites. The first approach involves the in situ synthesis of NPs within a BCP domain containing the NP precursors.¹² In contrast, the second approach uses the cooperative self-organization of preformed NPs and BCPs,¹² where the location of NPs within the BCP can be controlled by exploiting the enthalpic interaction between the BCP and the surface-modified (e.g., polymer-coated) NPs.¹³ The polymeric ligands on the NP surface control and stabilize the NP formation, allowing the initial small size to be retained by preventing NPs from aggregation. Meanwhile, by specifying the chemical nature of these polymeric ligands so they interact more favorably with one block in the BCP (i.e., preferential segregation within the target block), they provide an ability to control the placement of NPs within the BCP.¹¹,¹³ However, this strategy requires the synthesis of polymeric ligands that are chemically identical or similar to one of the blocks in the BCP for the surface functionalization of NPs.¹²

Barium titanate (BaTiO3) is one of the most extensively studied ferroelectric materials due to its high dielectric constant and ferroelectric properties at temperature below 130 °C where it assumes a ferroelectric phase.¹⁴ It finds use in a variety of areas that include multilayer capacitors, transducers,
actuators, and electro-optical devices. The ferroelectric and dielectric properties of BaTiO3 depend heavily on its size and density. Conventionally, BaTiO3 is prepared by heating a mixture of BaCO3 and TiO2 at a temperature above 1300 °C. This procedure leads to powders that are coarse and inhomogeneous in size. Another problem concerned with this synthesis is the high cost required due to high-temperature sintering. Novel strategies that allow for the preparation of homogeneous BaTiO3 at relatively low temperature are highly desirable to obtain fine particles for myriad applications. Soft-chemical processes such as the hydrothermal method, the sol-gel process, and the precursor decomposition method have been intensively used to prepare BaTiO3 NPs. These approaches carry advantages over the conventional solid state reactions as the nucleation in aqueous solution and subsequent crystalline growth proceed at much lower temperature.

Herein, we report the formation of nanostructured composites based on block copolymers, incorporating ferroelectric nanoparticles within the target block of the copolymer. Polystyrene-capped BaTiO3 nanoparticles (PS-functionalized BaTiO3 NPs) with different average sizes were first synthesized by utilizing a new class of amphiphilic unimolecular star-like poly(acrylic acid)-block-polystyrene (PAA-b-PS) diblock copolymers, prepared by sequential atom transfer radical polymerization (ATRP), as nanoreactors. As the surface of BaTiO3 NPs was permanently capped with PS chains, it dispensed with the need for further surface modification of NPs as in copious past work. Subsequently, hybrid nanomaterials composed of linear cylinder-forming polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) diblock copolymers and PS-functionalized BaTiO3 NPs were yielded upon mixing. The BaTiO3 NPs were selectively dispersed in the cylindrical PS nanodomains of PS-b-PMMA due to the selective chemical affinity of PS-functionalized BaTiO3 NPs to the PS block against aggregation, i.e., possessing a neutral XNP-Polymer, where XNP-Polymer represents the chemical affinity of the NP to the PS block (i.e., enthalpic interaction). By exposing a thin film of PS-b-PMMA-PS-capped BaTiO3 NP nanocomposites to acetone vapor, which is a selective solvent for PMMA, vertically oriented PS nanocylinders containing BaTiO3 NPs were achieved. Finally, the dielectric properties of nanocomposites as a function of microwave frequency from 2 GHz to 15 GHz were explored, revealing that the dielectric properties of these ferroelectric nanocomposites are dependent on the molecular weight of PS-b-PMMA and the size of BaTiO3 NPs.

**Experimental section**

**Materials**

Two asymmetric linear PS-b-PMMA diblock copolymers ($M_{PS} = 45,900$ g mol$^{-1}$ and $M_{PMMA} = 138,000$ g mol$^{-1}$) with polydispersity, PDI = 1.10; $M_{PS} = 315,000$ g mol$^{-1}$ and $M_{PMMA} = 785,000$ g mol$^{-1}$ with PDI = 1.20) were purchased from Polymer Source Inc. Three amphiphilic 21-arm, star-like poly(acrylic acid)-block-polystyrene (PAA-b-PS) diblock copolymers with different molecular weights were synthesized according to our previous work. $N,N$-Dimethylformamide (DMF, Fisher Scientific, 99.9%) was distilled over CaH2 under reduced pressure prior to use. Barium chloride dihydrate (BaCl2·2H2O, ≥99.0%), titanium(IV) chloride (TiCl4, ≥99.0%) and sodium hydroxide (NaOH, ≥98%) were purchased from Sigma-Aldrich, and used as received.

**Synthesis of BaTiO3 NPs with different sizes**

Three amphiphilic 21-arm, star-like PAA-b-PS diblock copolymers (Table S1†) with tailorable architectures, different molecular weights, and different ratios of PAA to PS blocks were then used as nanoreactors to produce BaTiO3 NPs capped with PS chains. Ferroelectric BaTiO3 NPs were synthesized via a wet chemistry approach by reacting NP precursors with the inner PAA chains of star-like PAA-b-PS diblock copolymers. In a typical process, 10 mg star-like PAA-b-PS (sample-2 in Table S1) template was dissolved in 10 mL DMF at room temperature, followed by the addition of an appropriate amount of precursors (i.e., BaCl2·2H2O + TiCl4 + NaOH; 0.081 g + 0.0658 g + 0.0139 g) that were selectively incorporated into the space occupied by the inner PAA blocks through the coordination bonding between the carboxyl of PAA and the metal ions of precursors as there were no active functional groups in the outer PS blocks to coordinate with the precursors. The solution was then refluxed at 180 °C under Ar for 2 h, yielding ferroelectric BaTiO3 NPs (sample-b; diameter, $D = \sim 11$ nm) capped with PS. BaTiO3 NPs of different diameters capped with PS (i.e., sample-a, $D = \sim 6$ nm; sample-c, $D = \sim 27$ nm) were also prepared using the same approach with star-like PAA-b-PS of different molecular weights as templates (i.e., sample 1 and sample 3 in Table S1,† respectively).

**Sample preparation**

Two linear PS-b-PMMA diblock copolymers (i.e., $M_{PS} = 45,900$ and $M_{PMMA} = 138,000$; $M_{PS} = 315,000$ and $M_{PMMA} = 785,000$) were dissolved in toluene, forming 5 mg mL$^{-1}$ solutions. To prepare nanocomposite samples, PS-functionalized BaTiO3 NP powder was added into 5 mg mL$^{-1}$ PS-b-PMMA diblock copolymer toluene solution to produce a series of nanocomposites with different weight fractions of BaTiO3 NPs. Thin films of nanocomposites of PS-b-PMMA–PS-functionalized BaTiO3 NPs were formed on freshly cleaned Si wafers by spin-coating the toluene solution at 3000 rpm for 40 s. These thin films were then immediately placed in an airtight 30 cm$^3$ glass vessel containing 50 μL acetone for a certain period of time at room temperature (i.e., a solvent vapor annealing process). After being exposed to the acetone vapor for a certain period of time, the samples were then quickly removed from the vessel and dried in air at room temperature.

**Characterization**

The size and morphology of PS-functionalized BaTiO3 NPs, and morphology of thin films of PS-b-PMMA/BaTiO3 NP nanocomposites were examined by transmission electron microscopy (TEM) (JEOL 1200EX scanning/transmission electron microscope (STEM); operated at 80 kV). The PS-functionalized BaTiO3 NPs were dissolved in toluene at a very low
Weir algorithm.

complex permittivity by application of the Nicholson
a Vector Network Analyzer (Anritsu 37347C) incorporating a
complex permittivity of the nanocomposites was measured with
the coaxial transmission/re
frequency region. The
parameter test set and operating in the 2
/C6
shape (with rectangular surface of revolution) with inner and
nm, PS-BTO27 (sample-c)) were hot-pressed into a toroidal
nanocomposite TEM sample, the nanocomposite thin
annealing was also characterized by TEM. To prepare the
nanocomposite TEM sample, the nanocomposite thin film formed on the Si substrate coated with 200 nm thick SiO2 on its
surface was immersed into dilute hydrofluoric acid (HF)
aqueous solution; the film was then spontaneously delaminated
from the Si surface and floated on the top of water. Subsequently, a TEM grid was placed in contact with the floating film,
thereby transferring the film onto the surface of the TEM grid.
Finally, the grid was exposed to ruthenium tetroxide (RuO2),
with which the PS phase was preferentially stained. As a result,
PS nanodomains appeared dark in the TEM images. Energy dispersive X-ray spectroscopy (EDS) analysis of nanocomposites
was performed using a field-emission scanning electron microscope (FESEM; FEI Quanta250 operating at 10 kV in high
vacuum). The crystalline structures of the nanocomposites were measured by X-ray diffraction (XRD; SCINTAGXDS-2000, Cu Kα
radiation (λ = 0.154 nm)). The weight fraction of the polymer
phase in the nanocomposites was determined by thermogravi-
metric analysis (TGA; TA Instrument TGA Q 50). The thickness
of the films was measured by Atomic Force Microscopy (AFM;
Dimension 3000). To characterize the dielectric properties of
nanocomposites in the microwave frequency range, two pure
PS-b-PMMA diblock copolymers (MPS = 45 900 and MPMMA =
138 000; MPS = 315 000 and MPMMA = 785 000) and their cor-
responding nanocomposites containing approximately 10–11%
(by volume) of PS-functionalized BaTiO3 NPs of different sizes
(i.e., D = ~11 nm, denoted PS-BTO11 (sample-b), and D = ~27
nm, PS-BTO27 (sample-c)) were hot-pressed into a toroidal
shape (with rectangular surface of revolution) with inner and
outer diameters of 3.00 ± 0.05 mm and 7.00 ± 0.05 mm,
respectively, and thickness in the range from 0.5–1.0 mm. The
complex permittivity of the nanocomposites was measured with
a Vector Network Analyzer (Anritsu 37347C) incorporating a S-
parameter test set and operating in the 2–15 GHz microwave
frequency region. The S-parameters were determined by using the
coaxial transmission/reflection method and converted to
complex permittivity by application of the Nicholson–Ross–
Weir algorithm.27,28

Results and discussion

In contrast to traditional approaches such as high-temperature sintering,15 or the soft-chemical approach,16,29,30 BaTiO3 NPs
with tunable sizes were prepared by exploiting a series of star-
like PAA-b-PS diblock copolymers as nanoreactors. The star-like
PAA-b-PS was composed of inner hydrophilic PAA blocks and
outer hydrophobic PS blocks with each arm covalently linked to
a small molecule β-cyclodextrin (β-CD).23 Three star-like PAA-b-
PS diblock copolymers with different molecular weights and
ratios of PAA to PS blocks were synthesized by sequential atom
transfer radical polymerization (ATRP),26,12 in which β-CD-based
star-like 21-Br-β-CD with 21 initiating sites was used as a
macrorinitiator (Scheme S1†).26 These star-like diblock copoly-
mers with well-controlled molecular architectures and molec-
ular weights form structurally stable spherical unimolecular
micelles. The inner PAA block in the micelles is highly hydro-
philic and facilitates the preferential incorporation of BaTiO3
precursors in the space occupied by PAA blocks via a strong
coordination bonding between the metal ion of precursors and
functional groups of PAA (i.e., carboxyl). Notably, there was no
such coordination with the outer PS chains. Subsequent
hydrolysis and condensation of precursors in pure DMF yielded
BaTiO3 NPs, in which the surface of NPs was permanently
connected with PS chains (i.e., PS-functionalized BaTiO3 NPs),
rendering the solubility of PS-functionalized BaTiO3 NPs in
organic solvents (Scheme 1A).

The diameter of BaTiO3 NPs can be readily altered by varying
the chain length of the PAA block during ATRP of tert-butyl
acrylate (i.e., forming poly(tert-butyl acrylate) (PbBA)), which was
subsequently hydrolyzed into PAA (Scheme S1†). Three BaTiO3
NPs with diameters of D = 6.3 ± 1.3 nm, 11.2 ± 1.9 nm, and
27.1 ± 3.1 nm (Fig. 1) were obtained by utilizing three different
star-like PAA-b-PS as nanoreactors with molecular weights of
PAA blocks, M_{PAA} = 4500, M_{PAA} = 8400, and M_{PAA} = 28 100,
respectively (Table S1†). The representative high resolution
TEM (HRTEM) characterization revealed that these BaTiO3 NPs
possessed a continuous crystalline lattice. It is noteworthy that
the presence of intimately connected hydrophobic PS chains on
the surface of BaTiO3 NPs is crucial as they promote the

![Image](https://example.com/image.png)
m miscibility of BaTiO3 NPs within the host environment (e.g., the polymer matrix as in polymer–NP nanocomposites), and thus further surface modification of NPs is not necessary. The existence of capped PS chains on the surface of BaTiO3 NPs was confirmed by 1H-NMR measurement. The PS-functionalized BaTiO3 NPs can be easily dissolved in toluene (Fig. S1†). The weight fractions of polymers in BaTiO3-PS NPs were determined by TGA (Fig. S2†).

Fig. 2 shows the XRD patterns of PS-functionalized BaTiO3 NPs with different sizes (2θ = 43–47°; patterns with 2θ = 20–60° are shown in Fig. S3†). For the BaTiO3 NPs with ~6 nm in diameter (sample-a), a single peak with 2θ at around 43–47° (corresponding to (200) lattice plane) was observed, suggesting the cubic phase of BaTiO3 NPs. However, as the diameters increased to ~11 nm (sample-b) and ~27 nm (sample-c), the peak at 2θ around 43–47° split into two peaks. Detailed crystal structure refinement indicates that these BaTiO3 NPs are largely tetragonal, with some detectable amounts of orthorhombic phase.35 We note that theoretical and experimental studies14–26 have been conducted on BaTiO3 in order to identify the critical size, below which BaTiO3 retains its cubic paraelectric structure at room temperature, yet there has still been no consensus on this issue.27–29 Clearly, our results are in accordance with reports where the critical size of BaTiO3 NPs was estimated to be on the order of 10–20 nm.30 Moreover, the energy dispersive X-ray spectroscopy (EDS) microanalysis also substantiated the success in synthesizing PS-functionalized BaTiO3 NPs (Fig. S4†).

To prepare linear PS-b-PMMA diblock copolymer/PS-functionalized BaTiO3 NP nanocomposites, two linear PS-b-PMMA diblock copolymers, in which PS blocks form the nanocylinders in the PMMA matrix (MPS = 45 900 and MPMA = 138 000; and MPS = 315 000 and MPMA = 785 000, respectively), were dissolved in toluene to make 5 mg mL−1 PS-b-PMMA toluene solution, in which PS-functionalized BaTiO3 NP powder at different weight fractions of NP was added. Thin films of nanocomposites were prepared by spin-coating the toluene solution on the Si substrate and annealed under the saturated acetone vapor for a certain period of time at 25 °C. The key to using block copolymers to produce ordered block copolymer-based materials relies on the control over the orientation of nanodomains. The preferential interaction of the PMMA block with the Si substrate, together with the lower surface energy of the PS block in a cylinder-forming PS-b-PMMA diblock copolymer would favor orientation of cylindrical PS nanodomains parallel to the surface. To achieve closely packed arrays of PS nanocylinders oriented normal to the film surface in PS-b-PMMA as well as in PS-b-PMMA–PS-functionalized BaTiO3 NP nanocomposites, selective solvent vapor annealing in a glass vessel was performed. Acetone was chosen as the selective solvent for the PMMA block as the polymer–solvent interaction parameter between PMMA and acetone χPMMA/acetone = 0.18 is much lower than that between PS and acetone χPS/acetone = 1.1.40–43 The complete polymer–solvent miscibility can be realized at χpolymer–solvent < 0.5.44

The AFM and TEM images of pure PS-b-PMMA (MPS = 45 900 and MPMA = 138 000) thin films before and after annealing with acetone vapor for 6.5 h (i.e., without the addition of PS-functionalized BaTiO3 NPs) are shown in Fig. 3. Compared to thin films before annealing where a featureless topology was observed (Fig. 3A and B), nearly hexagonally packed nanodomains were formed (Fig. 3C–F). This is not surprising as the saturated acetone vapor annealing process effectively enhanced the chain mobility for PS-b-PMMA by acting as a plasticizer. As a result, the PMMA matrix was swollen due to the absorption of acetone, and pulled from the PMMA/Si interface to contact preferentially with the acetone vapor (i.e., air surface).45 Since the PS domains can be selectively stained by ruthenium tetraoxide (RuO4), the darker domains in the TEM images

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**Fig. 1** TEM and HRTEM images (insets) of BaTiO3 NPs with different diameters (A) ~6 nm; (B) ~11 nm; (C) ~27 nm) using star-like PAA-b-PS diblock copolymers with different molecular weights as nanoreactors (sample-1, sample-2 and sample-3 in Table S1† respectively).

**Fig. 2** XRD patterns of PS-functionalized BaTiO3 NPs with different sizes. A (sample-a, D = ~6 nm), B (sample-b, D = ~11 nm), and C (sample-c, D = ~27 nm) are prepared by using different star-like PAA-b-PS block copolymers, i.e., sample-1, sample-2, and sample-3 (Table S1), respectively, as nanoreactors.
correspond to the PS nanocylinders, while the PMMA matrix appears white. The spacing between adjacent PS nanocylinders is approximately 46 nm.

Clearly, after the addition of PS-functionalized BaTiO$_3$ NPs (e.g., sample-b) into PS-b-PMMA, the BaTiO$_3$ NPs were preferentially located in the PS nanocylinders (Fig. 4). This is a direct consequence of the surface capping of NPs with PS chains that is chemically identical to the PS block in PS-b-PMMA. Such permanent surface capping not only prevented BaTiO$_3$ NPs from aggregation by van der Waals forces, but also offered selective chemical affinity of BaTiO$_3$ NPs to the PS block against aggregation, i.e., possessing a neutral $\chi_{\text{NP-PS}}$, where $\chi_{\text{NP-PS}}$ represents the chemical affinity of the NP to the PS block (i.e., enthalpic interaction). Interestingly, compared to some PS cylinders in Fig. 4 where no PS-functionalized BaTiO$_3$ NPs were present, the existence of BaTiO$_3$ NPs enlarged cylindrical PS nanodomains due to the additions of surface-capped PS chains on the BaTiO$_3$ NPs to the PS nanodomains in PS-b-PMMA. Moreover, with the increased volume fraction of BaTiO$_3$ NPs, the size of PS nanodomains became larger (e.g., comparing Fig. 4A-1 with Fig. 4B-1).

Similar to vertical PS nanocylinders formed in pure PS-b-PMMA upon annealing in the acetone vapor as discussed above (Fig. 3), the formation of vertically oriented PS nanocylinders containing BaTiO$_3$ NPs is illustrated in Scheme 1B, depicting the morphological reconstruction of the mixture of PS-b-PMMA–PS-functionalized BaTiO$_3$ NPs upon acetone vapor annealing. Such structural rearrangement was primarily due to the migration of the PMMA matrix, which interacted preferentially with acetone vapor. As PS and PMMA blocks are covalently linked at one end, the PS nanodomains rearranged themselves accordingly, thereby leading to a BaTiO$_3$ NP-containing nanocylinder normal to the surface of the nanocomposite film. The weight loss and volume fractions of BaTiO$_3$ NPs in nanocomposites were determined by TGA (Fig. S5†). Based on the mass density of BaTiO$_3$ [6.02 g cm$^{-3}$], PS (1.05 g cm$^{-3}$) and PMMA [1.18 g cm$^{-3}$], the volume fractions of BaTiO$_3$ calculated from the mass loss in TGA tests were 11.5% and 16.3%, respectively ($M_{\text{PS}} = 45,900$ and $M_{\text{PMMA}} = 138,000$; $D = \sim 11$ nm) (Fig. S5†).

When asymmetric PS-b-PMMA with larger molecular weights of each block was used (i.e., $M_{\text{PS}} = 315,000$ and $M_{\text{PMMA}} = 785,000$), closely packed nanodomains were also observed after the thin film was annealed in the acetone vapor for 6 h.

Fig. 3 AFM and TEM images of a pure PS-b-PMMA thin film ($M_{\text{PS}} = 45,900$ and $M_{\text{PMMA}} = 138,000$). (A) AFM height and (B) phase images of an as-prepared PS-b-PMMA thin film; image size = 5.0 x 5.0 µm$^2$, Z range = 6 nm for (A) and 3.3 nm for (B). (C-F) TEM images of a PS-b-PMMA thin film after exposing to the acetone vapor for 6.5 h. The closely packed arrays of PS nanodomains appeared dark in the bright PMMA matrix. The average diameter of PS nanocylinders is estimated to be 31.6 ± 3.8 nm, obtained by using standard image analysis software ImageJ. The film thickness was 42 nm.

Fig. 4 TEM images of a thin film of PS-b-PMMA–PS-functionalized BaTiO$_3$ NP nanocomposite (sample-b, $D = \sim 11$ nm; $M_{\text{PS}} = 45,900$ and $M_{\text{PMMA}} = 138,000$) formed upon the exposure to acetone vapor for 6.5 h. (A-1 and A-2) The volume fraction of BaTiO$_3$ NPs = 11.5%. (B-1 and B-2) The volume fraction of BaTiO$_3$ NPs = 16.3%. The closely packed cylindrical PS nanodomains containing BaTiO$_3$ NPs appeared dark. The average diameters of the PS nanocylinders after the addition of BaTiO$_3$ NPs are estimated to be 86.9 ± 20.4 nm (A-1 and A-2) and 112.5 ± 22.8 nm (B-1 and B-2), obtained by using standard image analysis software ImageJ. The film thickness was 52 nm in A-1 and A-2, and 55 nm in B-1 and B-2, respectively. The average numbers of BaTiO$_3$ NPs in the PS nanocylinders are approximately 54 (A-1 and A-2) and 76 (B-1 and B-2), respectively, calculated based on the volume fraction of BaTiO$_3$ NPs and the size of the PS nanocylinders.
range of $D$ and $C_24$. The complex permittivity of nanocomposites prepared using mode conversion caused by non-uniformities in the sample. Similarly, as the volume fraction of BaTiO$_3$ NPs increased, the size of PS nanodomains in the BaTiO$_3$ NP-loaded sample became larger than the unloaded sample.

The dielectric properties of PS-$b$-PMMA diblock copolymers and their corresponding nanocomposites in the frequency range of $f = 2$–15 GHz are shown in Fig. 5. The PS-$b$-PMMA diblock copolymers with relatively low molecular weight ($M_{PS} = 45\,900$ and $M_{PMMA} = 138\,000$) had a larger real part of permittivity ($\varepsilon' = 2.64 \pm 0.4$) than that of PS-$b$-PMMA with high molecular weight ($M_{PS} = 315\,000$ and $M_{PMMA} = 785\,000$) ($\varepsilon' = 2.45 \pm 0.2$) from $f = 2$–15 GHz. The decrease in $\varepsilon'$ with an increase in molecular weight of diblock copolymers may be attributed to the higher degree of chain coiling for higher molecular weight polymers (i.e., longer polymer chains) than for the low molecular weight polymers.$^4$ The nearly zero value of the imaginary part of permittivity $\varepsilon''$ indicates the dielectric lossless property of PS-$b$-PMMA diblock copolymers (Fig. 5A). The complex permittivity of the PS-$b$-PMMA ($M_{PS} = 45\,900$ and $M_{PMMA} = 138\,000$)/BaTiO$_3$ NP nanocomposites with the NP size of $\approx 11$ nm and $\approx 27$ nm is shown in Fig. 5B. For the nanocomposite loaded with $\approx 27$ nm BaTiO$_3$ NPs, the real part of permittivity, $\varepsilon'$, was $21.11 \pm 1.22$, which is larger than that loaded with $\approx 11$ nm BaTiO$_3$ NPs ($\varepsilon' = 17.91 \pm 0.61$). This is likely due to the higher dielectric constant measured in the $\approx 27$ nm BaTiO$_3$ NPs compared with the $\approx 11$ nm BaTiO$_3$ NPs, i.e., $\approx 405$ compared with $\approx 260$ measured at 1 MHz.$^{33}$ The imaginary part of permittivity, $\varepsilon''$, exhibited a steady value from $f = 2$–8 GHz, followed by an apparent increase from 8–15 GHz, indicative of the approach towards a resonance or relaxation at a frequency above the measured range, possibly a microstructural effect or a measurement artifact due to the microwave mode conversion caused by non-uniformities in the sample. The complex permittivity of nanocomposites prepared using the same series of BaTiO$_3$ NPs but PS-$b$-PMMA with higher molecular weight ($M_{PS} = 315\,000$ and $M_{PMMA} = 785\,000$) is shown in Fig. 5C. Both $\varepsilon'$ and $\varepsilon''$ were found to be decreased when compared with the low molecular weight PS-$b$-PMMA ($M_{PS} = 45\,900$ and $M_{PMMA} = 138\,000$) NP nanocomposites. The $\varepsilon'$ of PS-$b$-PMMA ($M_{PS} = 315\,000$ and $M_{PMMA} = 785\,000$)/BaTiO$_3$ NP nanocomposites displayed a similar trend as the PS-$b$-PMMA ($M_{PS} = 45\,900$ and $M_{PMMA} = 138\,000$)/BaTiO$_3$ NP nanocomposites. The $\varepsilon''$ of two nanocomposites increased slightly over the entire frequency range, this may be because the resonant frequency of the resonant cavities is close to the higher end frequency (i.e., 15 GHz). For the nanocomposites consisting of BaTiO$_3$ NPs of the same size but PS-$b$-PMMA with different molecular weights, the TGA results showed the nearly same volume fraction of NPs. Thus, the dielectric property difference between nanocomposites (i.e., Fig. 5B and C) with the same sized BaTiO$_3$ NPs was due most likely to the PS-$b$-PMMA matrix of different molecular weights,$^{48}$ which displayed different dielectric properties as shown in Fig. 5A. On the other hand, due to the toroidal shape of samples needed for the dielectric measurements by a Vector Network Analyzer, the dielectric properties of PS in the microwave frequency range ($f = 2$–15 GHz) cannot be measured because of the brittle nature of PS and its low mechanical resistance. Therefore, the $\varepsilon'$ of BaTiO$_3$ NPs in the GHz range with different sizes cannot be extracted from their nanocomposites. However, our previous study indicates that the $\varepsilon'$ of the $\approx 27$ nm BaTiO$_3$ NPs in the MHz range is

![Fig. 5](image_url)
significantly higher than that of the ~11 nm particles. Thus, the difference in dielectric properties of nanocomposites with the same PS- \( b \)-PMMA matrix used can be attributed to the size effect of BaTiO\(_3\) NPs.\(^{18-20}\) Obviously, the results shown in Fig. 5 suggest that both the molecular weight of PS- \( b \)-PMMA as the matrix and the size of BaTiO\(_3\) NPs as the inclusion have an effect on the resulting dielectric properties of PS- \( b \)-PMMA–PS-functionalized BaTiO\(_3\) NP nanocomposites.

**Conclusions**

In summary, we demonstrated the formation of nanocomposites composed of linear cylinder-forming PS- \( b \)-PMMA diblock copolymers and PS-functionalized BaTiO\(_3\) NPs in which the latter was selectively constrained within the PS block of PS- \( b \)-PMMA. Ferroelectric BaTiO\(_3\) NPs with different sizes, permanently capped with PS chains, were first synthesized by capitalizing on amphiphilic unimolecular star-like PAA- \( b \)-PS block copolymers as a template. The linear PS- \( b \)-PMMA offered a matrix for controlling the spatial organization of BaTiO\(_3\) NPs in nanocomposites. Vertically oriented PS nanocylinders containing PS-functionalized BaTiO\(_3\) NPs were achieved by annealing the thin film of PS- \( b \)-PMMA/BaTiO\(_3\) NP nanocomposites with acetone vapor. The resulting nanocomposites displayed a high dielectric constant in the microwave frequency range. The dielectric properties of ferroelectric nanocomposites were dependent on the molecular weight of PS- \( b \)-PMMA and the size of BaTiO\(_3\) NPs. The use of star-like diblock copolymers as nanoreactors to yield functional NPs that are intimately and permanently connected with polymer chains on the surface may open an avenue to produce a large variety of NPs with superior chemical affinity to the target block in block copolymers. As such, by minimizing the enthalpic interaction between the block copolymer and NPs, block copolymer-based nanocomposites can be readily crafted, thereby facilitating the fundamental study of their structure–property relationships. Block copolymer/ferroelectric nanoparticle nanocomposites may find potential applications in capacitors, actuators, transducers, pyroelectric sensors, photorefractive materials, and optical modulators.

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**References**


