Giant soft-memory in liquid crystal nanocomposites

Ravindra Kempaiah,1 Yijing Liu,1 Zhihong Nie,1,a) and Rajratan Basu2,b)
1Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20740, USA
2Department of Physics, The United States Naval Academy, Annapolis, Maryland 21402, USA

(Received 21 December 2015; accepted 5 February 2016; published online 23 February 2016)

A hybrid nanocomposite comprising 5CB liquid crystal (LC) and block copolymer (BCP) functionalized barium titanate ferroelectric nanoparticles was prepared. This hybrid system exhibits a giant soft-memory effect that was detected by dielectric hysteresis. Spontaneous polarization of ferroelectric nanoparticles couples synergistically with the radially aligned BCP chains to create nanoscopic domains where LC mesogens can align directionally. Such domains can be rotated electromechanically and locked in space even after the removal of the applied electric field. The resulting non-volatile memory is several times larger than the non-functionalized sample and provides an insight into the role of non-covalent polymer functionalization on enhancing the size of the nanoscopic domains. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4942593]

The use of liquid crystals (LCs) for electronic data storage has attracted interest in both fundamental and applied research communities.1–6 Inorganic nanoparticles (NPs) in LC matrices bear a great potential for this application due to the synergistic interactions between NPs and LCs.7–10 Creating programmable memory devices holds great promise in multi-level data storage systems.11 Non-volatile memory effects in the nematic phase of ferroelectric LCs doped with bare and polymer capped gold nanoparticles (Au NPs) have been studied using low-frequency dielectric spectroscopy.12,13 The presence of ferroelectric NPs (FNPs) like barium titanate (BaTiO3) enhances electro-optical properties of LC composites without distorting the global nematic director.14–19 In the nematic phase of nanocomposites, the global director trumps individual molecular orientation and the effect of FNPs on the molecular orientation is hard to distinguish.16,20 However, non-volatile memory effect has been reported in the isotropic phase of nanocomposites made of 5CB (4-cyano-4’-pentylbiphenylcarbonitrile) LC and FNPs of BaTiO3.21 When polymers are attached on the surface of FNPs like BaTiO3, the system is found to exhibit interesting physical22,23 and chemical properties.24–26

Here, we report a giant soft-memory effect, studied by the dielectric hysteresis effect, found in 5CB LC doped with block copolymer (BCP) functionalized BaTiO3 FNPs. The soft-memory effect we are referring to in this report is a non-volatile electromechanical effect at the interface of LC molecules and FNPs’ surface. The 5CB LC, obtained from Sigma Aldrich, has a nematic to isotropic transition (NI) temperature TNI of 35 °C. BaTiO3 FNPs with a diameter of 50 ± 5 nm were purchased from U.S. Research Nanomaterials Inc. BCP of polyethylene oxide-b-polystyrene (PEO45-b-PS670-SH) containing a small polyethylene oxide block (45 repeating units) and a long polystyrene (670 repeating units) terminated with a thiol functional group was synthesised following the reversible addition-fragmentation chain transfer (RAFT) polymerization procedure as described in the previous report. Another type of BCPs of polystyrene-b-poly (acrylic acid) (PS-b-PAA) with varied polystyrene block length was also produced using the same synthetic approach.27

Surface functionalization of BaTiO3 FNPs was performed in several stages. First, 5 mg BaTiO3 powder was dispersed in N,N-dimethylformamide (DMF) and sonicated for 3 h. Sonicated solution was centrifuged at 6000 rpm for 20 min to collect the FNPs and washed with tetrahydrofuran (THF) for three more cycles. Finally, the FNPs were dispersed in 5 ml of THF. This sample was used a control for measuring the soft-memory effect arising from pristine, non-functionalized FNPs. Note that this functionalization process of BaTiO3 for our experiment was carried out at room temperature. Therefore, it is unlikely that BaTiO3 FNPs’ surface crystal structure would be modified by this process without reaching above its Curie temperature, 130 °C.28

To attach the polymer ligands, 2.5 mg of amphiphilic PEO45-b-PS670-SH BCP was dissolved in 5 ml of THF and it was mixed with 5 ml premade THF solution containing non-functionalized BaTiO3 FNPs. The mixture was sonicated for 30 min and left for 1 h to promote attachment of the ligands on FNPs’ surface. The result is a homogeneous colloidal solution containing BaTiO3 FNPs with BCPs tethered to their surface. Block copolymer chains attach to the FNPs surface via intermolecular interaction and/or van der Wall’s forces. The solution was thermally annealed and degassed to remove any residual organic solvent and sonicated again for an hour. Three concentrations for 5CB/BaTiO3 and 5CB/BCP-modified-BaTiO3 were prepared for investigation, i.e., c1 = 0.175 wt. %, c2 = 0.275 wt. %, and c3 = 0.375 wt. %. The surface topology of these polymer-modified FNPs can be affected by the external stimuli, and hence, both kinetics and thermodynamic pathway play a role in alignment of mesogens around these particles.29

Dielectric measurements were carried out using an automatic liquid crystal tester (Instec, Inc.) that was attached to a precision temperature controller. Commercially available LC cells (SA100A200uG180, planar rubbed) with 1 cm² semi-transparent indium tin oxide electrode area, 1° pretilt angle,
and a spacing \( d = 20 \mu m \) were used for our experiments. Scanning electron microscopy (SEM) imaging was done using Hitachi SU-70 field emission scope.

The 5CB LC shows positive dielectric anisotropy, \( \Delta e = \epsilon_{||} - \epsilon_{\perp} \), where \( \epsilon_{||} \) and \( \epsilon_{\perp} \) are the dielectric components parallel and perpendicular to the nematic director, respectively. In a parallel-plate planar cell, 5CB exhibits Fréedericksz transition, where under an applied electric field (\( E \)) the nematic director orients from a planar configuration (\( \epsilon_{\perp} \)) to a homeotropic configuration (\( \epsilon_{||} \)). This director reorientation occurs because the LC experiences a torque proportional to \( \Delta e E^2 \) in the presence of \( E \). When the \( E \) is switched off, the director reorients back to planar configuration due to the LC’s long range splay elastic interaction and the surface anchoring mechanism in the cell. When the temperature is raised above \( T_{NI} \), the global nematic order is destroyed (i.e., \( \Delta e = 0 \)) and the Fréedericksz transition is no longer observed.

Figure 1 shows the dielectric constant \( \varepsilon \) as a function of \( E \) (\( f = 1 \text{ kHz} \)) in nematic phase for pure 5CB, 5CB doped with bare BaTiO\(_3\) (5CB/BaTiO\(_3\)) and 5CB doped with polymer functionalized BaTiO\(_3\) (5CB/BCP-modified-BaTiO\(_3\)), at a doping concentration of 0.275 wt. % of FNPs. A typical Fréedericksz transition with a threshold field of 0.04 V/\( \mu m \) is observed for all three samples. No dielectric hysteresis was observed on turning \( E \) down to zero.

Since BaTiO\(_3\) FNPs carry a spontaneous polarization \( P = 0.26 \text{ Cm}^{-2} \),\(^{31}\) they enable very strong local electric fields \( \sim 10^{10} \text{ Vm}^{-1} \) near the surface. This local field, \( E_{\text{FNP}} \), attenuates as \( 1/r^3 \). The presence of \( E_{\text{FNP}} \) creates nanoscopic domains where LC mesogens orient along \( E_{\text{FNP}} \) surrounding the FNPs, and we call these regions—pseudonematic domains. In the nematic phase, these short-range domains align with the global nematic director to reduce the free energy of the nematic matrix. These domains collectively increase the nematic orientational order, increasing \( \Delta e \) in the nematic phase of the LC + FNP system, as shown in Figure 1.

The dipole moment magnitude for a 5CB molecule is \( p = 6.5D = 2.15 \times 10^{-29} \text{ Cm} \).\(^{32}\) When the LC molecules align with \( E_{\text{FNP}} \) close to the FNP, the associated energy can be written as \( U_{\text{FNP}} = -\vec{p} \cdot \vec{E}_{\text{FNP}} \sim -10^{-19} \text{ J} \). The thermal energy in the isotropic phase of 5CB at \( T = 42 \text{ °C} \) is 315 K (well above the transition temperature) is \( U_{\text{thermal}} \sim k_B T \sim 10^{-21} \text{ J} \). Apparently, the thermal energy is too small to eliminate the FNP-induced LC-order in the isotropic phase. Due to the presence of these domains, the isotropic phase of 5CB/BaTiO\(_3\) maintains a net \( \Delta e \) and is expected to interact with the external \( E \).

Figure 2 shows \( \varepsilon \) as a function of \( E \) in the isotropic phase (\( T = 42 \text{ °C} \)) for pure 5CB, 5CB/bare BaTiO\(_3\), and two different 5CB/BCP-modified-BaTiO\(_3\) samples as listed in the legend. Pure 5CB shows a featureless behaviour in the electric field. The hybrid systems show an increase in \( \varepsilon \) above a threshold field, exhibiting a Fréedericksz-like transition. The dielectric constant for these nanocomposite systems does not relax back to its original value on turning the \( E \) down to zero, manifesting a dielectric hysteresis effect. The hysteresis area correlates to the soft-energy memory effect in the hybrid samples. The memory effect for 5CB/BaTiO\(_3\) can be seen from the (red) curve in Figure 2; the \( \Delta e \) holds its value (\( \Delta e_{\text{5CB}} / 5CB = 0.4 \)) even when the \( E \) is switched off. The hysteresis curve for 5CB/PEO\(_{45}\)-b-PS\(_{670}\)-SH polymer functionalized BaTiO\(_3\) FNPs (blue curve) clearly shows a giant increase in the magnitude of \( \Delta e \) (\( \Delta e_{\text{5CB}} / 5CB = 2.4 \)) and a six-fold increase in the hysteresis area compared to 5CB/BaTiO\(_3\) at the same wt. % concentration. If we compare this value to \( \Delta e \) of nematic 5CB, (\( \Delta e_{\text{5CB}} \approx 12 \)), we can estimate that even in isotropic phase, 20% of all the mesogens have directional orientation compared to fully nematic 5CB. This indicates an interesting way of aligning the mesogens in the isotropic phase.

Even though the hybrid system contains short-range pseudonematic domains, the global nematic order is still...
absent in the isotropic phase. Therefore, there is no long-range elastic interaction present in the isotropic phase. Accordingly, these isolated pseudomorphic domains do not interact with the aligning layers of the LC cell. Therefore, when the field is turned off, there is no restoring force to mechanically torque these domains back into original orientation in the isotropic phase and the domains stay oriented, as schematically shown in Figure 3. In addition, the absence of the back flow in the thin LC cell also allows the domains to stay oriented. The thermal diffusion mechanism in this case takes days to randomize the domains in the cell, as can be seen from the inset in Figure 2. An electric field of 1.3 V/µm \(^{-1}\) was first applied to a hybrid system for 30 s to initiate the reorientation of pseudomorphic domains and then switched off. The dielectric constant was monitored as a function of time for the next 72 h and plotted in the inset in Figure 2. No significant change was observed in this time period. This is the essence of a non-volatile nano-electromechanical memory effect; i.e., the domains at the nanoscale are rotated mechanically and locked in thermodynamically.

When the FNP\(_s\) are functionalized with a BCP of PS-b-PAA, the PAA block is expected to bind strongly with BaTiO\(_3\) FNPs’ surface via a combination of chemical and van der Wall’s interaction.\(^{33}\) Even with a shorter PS chain in the PS-b-PAA BCP, the hysteresis effect is found to be comparable to that of the PEO\(_{45}\)-b-PS\(_{670}\)-SH polymer (see Figure 2). This can be explained by the stronger binding of PS-b-PAA to BaTiO\(_3\) than PEO-b-PS-SH BCP, because of the multiple binding sites on PAA block. However, our measurements were limited by the availability of polymer that had longer PS block and higher affinity PAA block.

To understand this huge increase in dielectric hysteresis in detail, we studied (i) the effect of only pure PEO\(_{45}\)-b-PS\(_{670}\)-SH in 5CB, and (ii) the dispersibility of BaTiO\(_3\) when functionalized with PEO\(_{45}\)-b-PS\(_{670}\)-SH. The repeating units of hydrophobic PS block of BCPs have electron-rich benzene ring that can interact with biphenyl group of 5CB via \(\pi-\pi\) stacking interaction. Therefore, a polymer that has more units of hydrophobic PS block will favour aligning with 5CB molecules because of this \(\pi-\pi\) stacking interaction. We then doped 5CB with pure PEO\(_{45}\)-b-PS\(_{670}\)-SH such that the wt. % of the dopant is approximately equal to the weight of the polymer chains tethered on the BaTiO\(_3\) FNPs’ surface. This normalized weight was essential as not all polymers we use for functionalization go onto the surface of the FNPs. In this case, we also noticed a hysteresis curve (purple) as shown in Figure 2. This result clearly suggests that the presence of pure PEO\(_{45}\)-b-PS\(_{670}\)-SH in 5CB also forms pseudomorphic domains due to the \(\pi-\pi\) stacking interaction between the LCs and the polymer chains. These domains also interact with the external \(E\), showing a hysteresis effect. However, as clearly seen in Figure 2, the hysteresis effect of 5CB/PEO\(_{45}\)-b-PS\(_{670}\)-SH polymer functionalized BaTiO\(_3\) is significantly larger than the sum of individual contributing components, i.e., the pure polymer and the pure BaTiO\(_3\) FNPs.

Due to the dipole-dipole interaction between the FNPs, it is expected that some FNPs are present in aggregates form resulting in antiparallel-dipole configuration. An antiparallel-dipole can be approximately treated as a quadrupole, whose field magnitude drops as \(\sim 1/r^4\) and hence the pseudomorphic domains formed by the FNP-clusters would have smaller \(\Delta \varepsilon\). On the other hand, the presence of the polymer ligands on the FNP surface prevents the aggregation of FNPs to a large extent. To visually examine the effects of polymer ligands on aggregation and dispersibility, we prepared two samples: (i) 5CB and bare BaTiO\(_3\) FNPs and (ii) 5CB and BaTiO\(_3\) FNPs functionalized with PEO\(_{45}\)-b-PS\(_{670}\)-SH polymer. After preparation, they were allowed to stabilize for 10 h and then a drop of each of sample in THF solution was deposited on a silicon substrate for SEM imaging. Figure 4 shows representative SEM images of these samples. It was apparent that bare 50 nm BaTiO\(_3\) sample formed several micron-sized aggregates (Figures 4(a) and 4(c)), whereas PEO\(_{45}\)-b-PS\(_{670}\)-SH polymer functionalized BaTiO\(_3\) FNPs showed a much better dispersion (Figures 4(b) and 4(d)). Without large clusters, therefore, the polymer functionalized BaTiO\(_3\) FNPs retain their strong dipolar electric field that drops as \(\sim 1/r^4\) and create pseudomorphic domains with a higher \(\Delta \varepsilon\) and a larger size, as illustrated in the schematic in Figure 3. Due to this enhancement in the pseudomorphic domains, the polymer-functionalized-BaTiO\(_3\) samples exhibit a giant hysteresis effect.

**FIG. 3.** Schematic diagrams. (a) Schematics for each component of the system. (b) Isotropic phase of 5CB with randomly oriented mesogens, (c) The effect of introduction of FNP’s into 5CB. BaTiO\(_3\) molecules carry inherent polarization, and as a result, 5CB molecules orient themselves along the dipole field near the interface. A small arrow represents the direction of polarization. (d) An illustration of the role of polymer functionalization of BaTiO\(_3\) FNPs with amphiphilic block copolymers. Polymer tethers expand the pseudomorphic domains and act as scaffold for the radial alignment of 5CB mesogens. (e) Pseudomorphic domains of mesogens (created by BCP functionalized BaTiO\(_3\)) mechanically rotate in the direction of the field. The density of mesogens is greater along the poles. (f) The domains stay oriented when the field is turned off.
It is reported that the size of the inorganic NP’s, the concentration of the dopant, the chemical nature, and the length of polymer chain all play a major role in affecting the dispersibility, long-range ordering, and electro-optic properties. To further understand the roles of these factors on this soft-memory, especially the role of polymer chemistry and FNP’s concentration, we have studied three different concentrations of 5CB/PEO_{45-b}-PS_{670}-SH modified BaTiO_3: 0.175 wt. %, 0.275 wt. %, and 0.375 wt. %. The schematics in Figures 5(a) and 5(b) explain the π-π stacking interaction. Figure 5(c) shows the effect of the dopant concentration on the hysteresis effect. With increasing concentration of the dopant, we see larger dielectric hysteresis, indicating the presence of more number of pseudonematic domains at higher concentrations. The inset in Figure 5(c) explains the role of different polymer chemistry on the dielectric hysteresis area. Homopolymer of PAA_{600} alone (without the PS block) cannot produce the same effect as PS-b-PAA which contains PS block, due to absence of π-π stacking interaction (red curve). However, an introduction of even small PS block (PS_{260}) with PAA_{100} can produce much larger dielectric hysteresis (green curve). The end-to-end length of each hydrophobic PS_{670} block in a polymer chain is calculated to be around 6–7 nm. Increasing the thickness of polymer brushes, depending on the conformation, results in bigger pseudonematic domains, enhancing the soft-memory effect.

In conclusion, we have shown that 5CB/BCP functionalized BaTiO_3 samples yield giant enhancement of soft-memory effect in the isotropic phase. Here, Δε is enhanced multi-fold by simple attachment of BCP chains on the surface of NPs. Both polymer chemistry and concentration dependent studies have been conducted to understand these physical phenomena. The results presented here are expected to advance the conceptions about, and methodology toward, nanoscale manipulation of nanomaterials via LCs and LC orientation control using their interactions with functionalized nanomaterials. These studies will also lead directly to the central role played by LC-influenced organizational themes in the development of nanoscale directed self-assembled systems, such as the pseudo-nematic domains—which can be used as a nano-electromechanical memory function.

FIG. 4. Scanning electron microscopy images of the pure BaTiO_3 and BCP (PEO_{45-b}-PS_{670}-SH) functionalized BaTiO_3 FNP’s. From (a) and (c), we can infer that clusters and random aggregates are prevalent. Functionalized samples as shown in (b) and (d) provide evidence of uniform colloidal dispersion.

FIG. 5. (a) Molecular structure of PEO_{45-b}-PS_{670}-SH BCP. (b) Schematic illustrating the π-π stacking interaction between 5CB mesogens and benzene rings of polystyrene units. (c) Dielectric hysteresis area of PEO_{45-b}-PS_{670}-SH BCP functionalized BaTiO_3 nanocomposite as a function of concentration of dopants. The inset shows the dielectric hysteresis for various polymers that were used to functionalize BaTiO_3 doped 5CB liquid crystal; solid circle: 5CB/BaTiO_3, solid square: 5CB/(PAA_{100-b}-PS_{260})-BaTiO_3, solid triangle: 5CB/(PAA_{100-b}-PS_{260})-BaTiO_3, solid star: 5CB/(PEO_{45-b}-PS_{670})-BaTiO_3.
Zhihong Nie is grateful for the support from the National Science Foundation grant (CHE-1505839) and startup fund from University of Maryland.

Rajratan Basu is grateful for the support from the Office of Naval Research grant (Award No. N0001415WX01534) and investment fund from the U.S. Naval Academy.