Giant soft-memory in liquid crystal nanocomposites

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Supporting Information – SI

Polarized optical microscopy images of samples with different concentrations

To study the effect of concentration of BaTiO$_3$ FNPs in the LC matrix for any possible aggregations, we took the polarized optical microscopy (POM) images of three samples of concentrations 0.175 wt%, 0.275 wt% and 0.375 wt% (Supplementary Figure 1). We found no aggregates that are big enough to cause the nematic director distortion. Above 0.4 wt%, the particle clusters become large enough for causing the electrical shorting between the electrodes.

Macroscopic texture under polarized optical microscope.
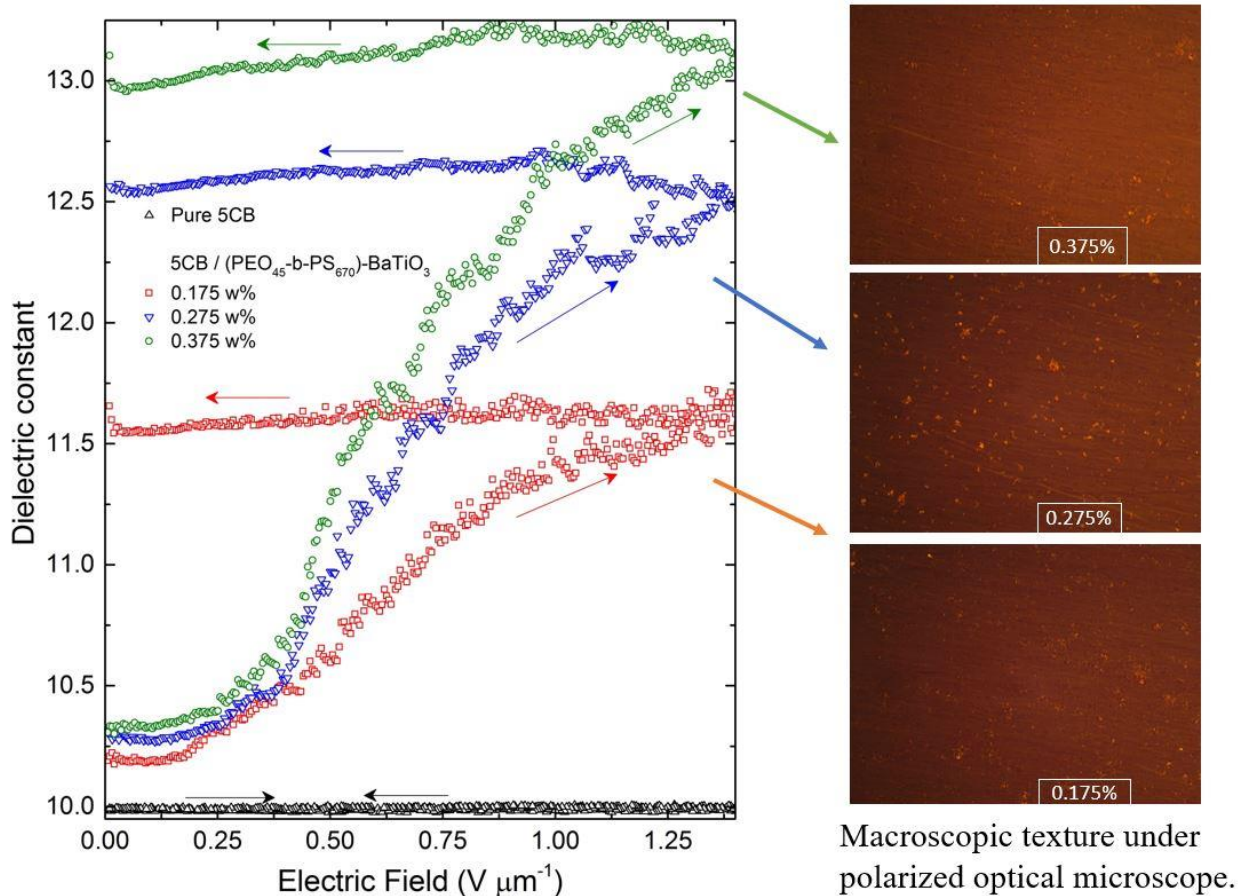
Supplementary Figure 1: Polarized Optical Microscopy study of suspensions of different concentrations.

Scheme of π-π interaction between liquid crystal mesogens and polymer brushes
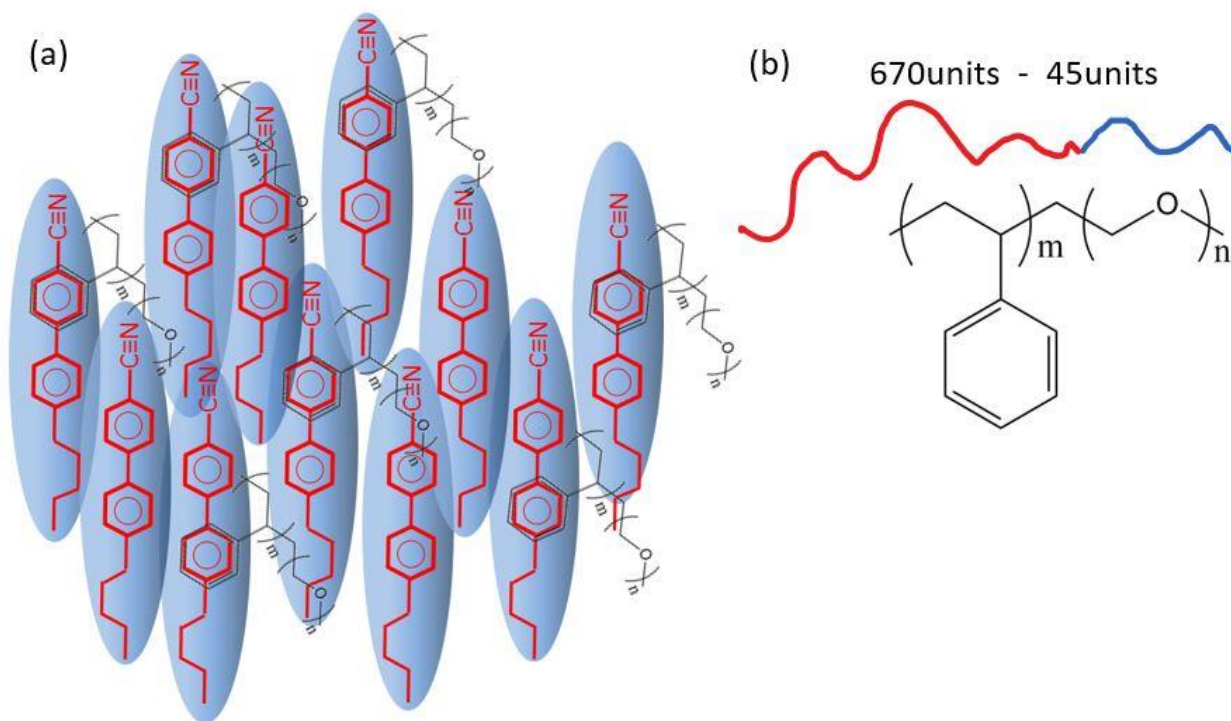
Supplementary Figure 2: (a) Schematic Illustrating the π-π stacking interaction between 5CB mesogens and benzene rings of polystyrene units. (b) PEO_{45}-b-PS_{670}-SH BCP molecular structure.

We hypothesize that such huge increase in dielectric anisotropy occurs because of π-π stacking interaction between electron-rich biphenyl group of 5CB molecules and benzene groups on the long chain polystyrene unit of the block copolymer (BCP). Figure (a) illustrates such π-π stacking interaction that could lead to alignment of the mesogens. Figure (b) shows the molecular structure of PS_{670}-b-PEO_{45} BCP and a sketch depicting the chain-like conformation of these BCPs.

Calculations

Calculations of wt%, approximate grafting density, normalized polymer value etc.

1. Volume of one $BaTiO_3$ nanoparticle $V = \frac{4\pi}{3}(r^3)$, where r = 25nm.

$$V = \frac{4\pi}{3}(25 \times 10^{-9}m)^3 = 65.45 \times 10^{-18}cm^3$$

2. From the supporting info document of reference 12, we used the gold nanoparticle model for our experimental study and equation 1 to approximate the grafting density. Also, from the SEM images, the end-to-end distance (L) of PS_{670}-b-PEO_{45} was found to be ~ 7nm.[30]
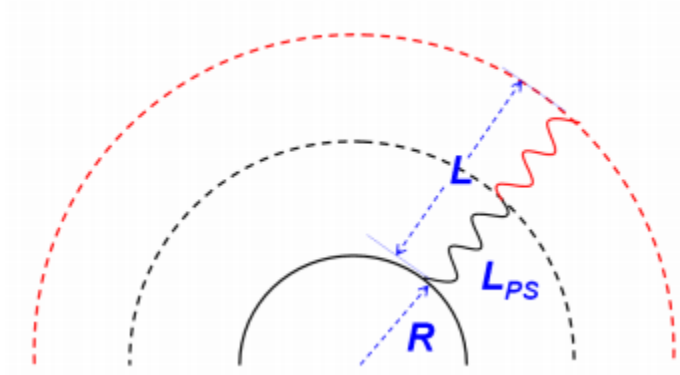
Supplementary Figure 3: Concentric shell-like structure of $BaTiO_3$ nanoparticles covered with polymer brushes.

Here, R = 25nm and L = 7nm

Equation 1: $V_{polymer} = \frac{4\pi}{3}[(R + L)^3 - R^3]$

Equation 2: $N_{polymer} = \frac{\rho V_{polymer} N_{Av}}{M_n}$

Here, ρ and N_{Av} are the density of polymer and the Avogadro number, respectively. We consider the molecular weight (M_n) of PS_{670}-b-PEO_{45} to be 69 Kg/mol. This calculation gives us the $N_{polymer}$ value to be 658 chains per nanoparticle.

Molecular weight of $BaTiO_3$ = 233.19 g/mol. Using this value, we can compute the approximate weight of each polymer brush to be around 75.39 E-18 grams. During the washing process, we lose approximately 10% of the nanoparticles.

4.5mg of $BaTiO_3$ nanoparticles in 10ml THF would have volume of $= \frac{4.5}{6.02} \times 10^{-3} = 0.747 \times 10^{-3}$ cm^3.

Therefore, total number of FNPs $= \frac{0.67 \times 10^{-3}}{65.45 \times 10^{-18}} = 1.142 \times 10^{13}$ nanoparticles.

1.142 E13 nanoparticles correspond to 0.86mg of polymer. So, 0.86mg of PS$_{670}$-b-PEO$_{45}$ was dissolved in 10ml THF and 0.49g of this solution was mixed with 0.1g of 5CB liquid crystal to obtain $(\frac{0.49 \times 0.0561}{0.1}) = 0.275$ wt% mixture. This mixture was further sonicated and annealed to evaporate the volatile THF. Finally, the remaining solution was filled in LC cell to obtain normalized concentration (the amount of polymer that would go on the nanoparticles only). Dielectric measurements were conducted as per the procedure.