Graphene-Augmented Polymer Stabilization: Drastically Reduced and Temperature-Independent Threshold and Improved Contrast Liquid Crystal Device

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ABSTRACT: Polymers reinforced with nanofillers, especially graphene in recent times, have continued to attract attention to realize novel materials that are cheap and also have better properties. At a different level, encapsulating liquid crystals (LCs) in polymer networks not only adds mechanical strength, but could also result in device-based refractive index mismatch. Here, we describe a novel strategy combining the best of both these concepts to create graphene-incorporated polymer-stabilized LC (PSLC) devices. The presence of graphene associated with the virtual surface of the polymer network besides introducing distinct morphological changes to the polymer architecture as seen by electron microscopy brings out several advantages for the PSLC characteristics, which include 7-fold lowered critical voltage, its temperature invariance, and enhanced contrast ratio between field-off scattering/field-on transparent states. The results bring to fore the importance of working at very-dilute-concentration limits of the filler nanoparticles in augmenting the desired properties. These observations open up a new vista for polymer—graphene composites in the area of device engineering, including substrate-free smart windows.

1. INTRODUCTION

Depending on the characteristics of the imbibed nanoparticle (NP), polymer nanocomposites (PNCs) can exhibit unique properties ranging from tunable plasmonic absorption to enhanced electrical conductivity. Improved mechanical properties and flammability have also been achieved by adding NPs that impart strength and limit combustion, respectively, to the host polymer. In addition to adding functionality to polymers, nanoparticle mobility influences fundamental properties of the PNC, such as melt flow and viscosity, as well as the effectiveness of self-healing materials to limit crack propagation. Therefore, an improved understanding of nanoparticle diffusion in polymer melts is of both technological and fundamental importance. Carbonaceous nanofillers such as graphene and carbon nanotubes (CNT) are promising materials owing to their extraordinary physicochemical properties. Development of polymer composites incorporating these nanofillers depends on several features not limited to the properties of the nanofillers, their dispersion within the confining polymer matrix, interaction between the two, and any morphological changes in the matrix.

Devices based on confinement of nematic liquid crystals (LCs) in a polymeric matrix have huge potential for use in spatial light modulation and electrically controlled transparency applications. Depending on the concentration of the polymer content, they are divided into two types: polymer-dispersed liquid crystals (PDLCs), in which the polymer content is higher than that of the liquid crystal, and polymer-stabilized liquid crystals (PSLC), in which polymer is the minority component. Owing to the higher polymer content, PDLCs have higher mechanical strength, and thus are less prone to damage due to mechanical shocks. But the threshold voltage, i.e., the minimum operating voltage for the device to switch from the transparent ON state to the scattering off state, is high, due to the large number of polymer strands, which increase the anchoring strength of the system. But for PSLC, due to lower polymer content, the threshold voltage is lower than that of PDLC, but it is not as robust as PDLCs due to the lower concentration of polymer. Thus, the challenge is to strengthen the polymer part without adversely affecting the operating voltage. Obvious candidates for the purpose are nanocomposites of appropriate kind. In point of fact, substantial attempts have been made in investigating the influence of nanocomposites on the LC properties, and effects, including reduction in the threshold voltage, are observed in such nanocomposites. However, with hardly any exception, these efforts are based on pure liquid crystal composites and not on any polymeric system. It may be mentioned that a combination of PSLC-in-PDLC has been just reported to achieve the dual requirement of mechanical strength, but lower operating voltage. It is notable that to achieve this, the authors employed three different polymerizable monomers, a complex system indeed: while two polymers provided the droplet...
mixture was heated at 90°C for 2 h and allowed to cool down, followed by stirring overnight (12–15 h). During this time, the color of the dispersion turned charcoal. The dispersion was repeatedly washed by centrifugation until neutral pH was obtained. Finally, the dispersion was filtered and washed with water and ethanol. The product was collected and dried in vacuum. The final product had a grayish color and was not as shiny as the starting graphite. The flakes thus obtained were characterized by Raman spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The characterization data are given in the Supporting Information. Raman spectra show intense G (1577 cm$^{-1}$) and 2D (2700 cm$^{-1}$) bands characteristic of good-quality graphene (Figure SI-1 of the Supporting Information). The $I_p/I_G$ ratio of 0.3 and the $I_{2D}/I_G$ ratio of 0.5 indicate that the flakes consist of more than five layers of graphene with extended conjugation of sp$^2$ carbon network. SEM (Figure SI-2) and AFM (Figure SI-3) images show the average flake size to be 1–2 μm with 5–15 nm thickness. The above procedure for exfoliation without the use of KMnO$_4$ has shown to produce graphene with very less extent of oxidation, but rather NO$_3^-$ and SO$_4^{2-}$ ions intercalate to give the exfoliated flakes (Supporting Information of ref 40). The graphene used in this work also possess similar characteristics.

The host liquid crystal used here is the well-known 4-pentyl-4’-cyanobiphenyl (5CB for short), which was procured from E-Merck. As expected, incorporation of graphene into the LC material increases the electrical conductivity of the composite. Since the aim is to perform electrical switching measurements, the sample conductivity had to be kept reasonably low, and therefore a minute concentration (0.01 wt % of the total mixture) of graphene is employed.

Two different kinds of cells have been used for the measurements, which we refer to as in situ and template. The cells were made using indium tin oxide-coated glass plates, the inner surfaces of which had a thin polymer layer to facilitate planar alignment of the LC molecules; the cell gap was ~25 μm. The in situ polymer network cells without and with graphene are labeled PSLC and PSLGC, respectively, whereas the template one that contained the network with graphene is referred to as PSLGC-t. In all of the cases, the polymer network is obtained using a photoreactive monomer, RM82 (from E-Merck), along with a photoinitiator BME. RM82 is also a mesogen in its monomeric form, exhibiting the nematic phase, a feature that helps in getting a good homogeneous mixture with SCAB. The molecular structures and transition temperatures of these materials are given in Figure SI-4. The RM82 concentration was kept constant at 3 wt %, and the photoinitiator, 2% of RM82. Photopolymerization of RM82 was carried out by illuminating the cells filled with the appropriate material using an intensity-stabilized UV source (Hamamatsu LSS) in conjunction with a fiber-optic light guide. A 365 nm bandpass filter and an IR filter were introduced between the light guide and the cells. The actual power of the UV light received at the cell surface, measured using a UV power meter (Hamamatsu C6080-03), was 3 mW/cm$^2$. Before filling the cells, weighed amounts of the constituents were physically mixed at 100 °C and then polymerized at room temperature. For the PSLGC-t case, after polymerization, the cells were immersed for 48 h in a beaker containing acetone to remove the active LC (5CB), graphene not attached to the polymer strands, and any unreacted monomer (RM82). Subsequently, the solvent was removed and the cells were dried. Microscopy observation of these cells

2. EXPERIMENTAL SECTION

2.1. Materials and Cell Preparation. Graphene was prepared by exfoliation of graphite powder employing a mild oxidation route adopted from Choi et al.$^{41}$ The procedure was slightly modified and briefly about 0.5 g of graphite powder was mixed with 20 mL of a 1:3 mixture of HNO$_3$ and H$_2$SO$_4$, followed by stirring at room temperature for 2 h. The whole mixture was heated at 90 °C for 2 h and allowed to cool down,
containing the templated polymer showed the presence of the network. The cells were then filled with SCB, to achieve the PSGLC-t configuration.

2.2. Measurements. Dielectric measurements were carried out using an LCR meter (Agilent E4890A) capable of providing an oscillatory voltage up to 20 V. Electro-optical response measurements were done by placing the sample in a polarizing optical microscope (Leitz DMRXP). The microscope illumination was used as the light source, and a photodetector in the beam path, placed after the sample, measured the transmission through the cell, recorded using a digital oscilloscope (Agilent DSO5054A). The voltage needed for switching the state of the LC was provided by a function generator (HP 33120 A) amplifier (TREK model 50/750) combination. The morphology was examined using a TESCAN MIRA3 LM (Czech Republic) field emission scanning electron microscope and Agilent Technologies 5500 AFM. Raman spectra were acquired using a Horiba Jobin Yvon XploRA confocal Raman microscope with 532 nm laser excitation.

3. RESULTS AND DISCUSSION

3.1. Microscopy. Optical microscopy images for PSLC and PSGLC cases are shown in Figure 1a,b, respectively. The images were captured by maintaining the sample in the isotropic phase and for obtaining good contrast, no polarizers were employed. Even on a cursory look, substantial differences are seen between the two images. The PSLC case shows very coarse and spread out strands, providing an apparent feeling of increased density (it must be borne in mind that the polymer content is the same in both the cases). Also, the image could not be brought to a fine focus, which perhaps suggests a non-negligible traverse of the polymer strands from the substrate plane. In contrast, the PSGLC case shows very fine strands, which are sparse; branching of the bundles is also evident. The spacing between the bundles is approximately 20 μm. The image in Figure 1a suggests that the spacing in the PSLC case must be less than 10 μm. The fact that the image for PSGLC could be sharply focused indicates that the polymer bundles must be essentially restricted to the substrate plane. The electro-optic characters to be discussed below appear to be influenced by these features.

The scanning electron microscopy (SEM) images are shown in Figure 2a–c for PSLC and Figure 2d–f for PSGLC. The morphologies in the two cases are clearly seen to be quite different: while PSLC has a strong tendency to form polymer bundles of sizeable thickness (Figure 2b), PSGLC seems to favor thinner fibers (Figure 2e). This leads to, keeping the same polymer content, larger surface area offered by the polymer fibers to the neighboring LC regions. Since the entire PSLC concept is based on the virtual surfaces provided by the polymer fiber, having a larger number of thinner fibers is certainly advantageous. The second feature is the focus of the image is not very uniform over the imaging area even on linear dimensions of 30 μm (Figure 2a,b). In contrast, the focus is always sharp in the case of PSGLC. This suggests that the out-of-plane traverse is much less in the case of PSGLC. In addition to the fact that the PSGLC situation mimics the droplet or swiss-cheese morphology, these features indicate the much stronger polymer fibers caused by graphene acting as a nano-filler. It is common knowledge that the different carbonaceous forms when nanofillers are used in polymeric materials result in significant mechanical strengthening of the polymer.42 Having recently observed similar features in another case, wherein the polymer strands were reinforced by carbon nanotubes, we suggest that incorporation of rigid nanostructures into the polymer matrix yields thinner but stronger polymer bundles, which enhance the virtual surface effect for PSLC applications. To obtain an unequivocal evidence for the presence of graphene in the polymer matrix we carried out Raman spectroscopy measurements on PSGLC and PSLC cells. The results, which are described in the next section, were carried out the same way as for the SEM analysis, by washing out the LC and opening the cells.

3.2. Raman Spectroscopy. To visualize the presence of graphene in the polymer matrix, we have obtained Raman mapping of macroscopic areas (80 μm × 80 μm) of PSGLC. The contour maps of the G band are given in Figure 3a, and those for the D and G′ bands are given in Figure SI-5 of the Supporting Information. While the graphene-rich regions have higher intensity (green), the entire polymer region has low intensity (blue). The exemplary Raman spectra over a larger wavenumber range are given in Figure 3b for the PSLC sample as well as at different spatial positions of the PSGLC film. The latter sample exhibits the signatures of the graphene flakes corresponding to D (1354 cm⁻¹), G (1581 cm⁻¹), and 2D (2705 cm⁻¹) bands, indicating the presence of graphene in PSGLC films. It is noted that for the PSGLC, the G band position is shifted by 4 cm⁻¹ in comparison to that for pristine graphene (Figure SI-2), arguably due to charge-transfer interaction between graphene and the soft materials, viz. RM82 and SCB. The profile for PSLC, which lacks the graphene content, is contrastingly different from that of PSGLC. The D, G, and 2D bands are naturally missing in this case. We identify the most prominent peak seen at 1600 cm⁻¹ carbon–carbon bond stretching of aromatic rings contained in RM82. A family of Raman profiles covering a traverse of 80 μm in the plane of the film is shown in Figure SI-6. Again the graphene-rich and graphene-poor regions stand out clearly.

In view of the information from microscopy and Raman measurements, we propose that the graphene-incorporated polymer network would be like a “loofah” network with the graphene flakes decorating the surface of the fibers in a spatially random way, a scenario that is illustrated schematically in Figure 4. The graphene decoration is highlighted in the inset of the illustration, a feature that is more realistic in the case of the template PSLC, a situation that will be discussed later.
3.3. Permittivity. Temperature-dependent permittivity measurements were carried out at a fixed frequency of 10 kHz with two different magnitudes of the alternating current field: 0.1 and 20 V. While the former, which is well below the Freedericksz threshold voltage \(V_{th}\), gives \(\varepsilon_\perp\), the latter being much larger than \(V_{th}\) yields \(\varepsilon_\parallel\). There is a slight reduction (increase) in \(\varepsilon_\parallel (\varepsilon_\perp)\) for PSGLC in comparison to those for the PSLC material (Figure 5). Concomitantly, the anisotropy \(\varepsilon_\parallel (\varepsilon_\perp)\) also has a decrease (by \(\approx 16\%\) at room temperature) for the graphene composite. This could be suggesting a little lowering of the order parameter for PSGLC or a slightly enhanced antiparallel correlation between the neighboring LC molecules, a feature known to be strongly favored in alkyl cyanobiphenyls, such as the presently used LC. Since \(T_{NI}\), the isotropic–nematic transition temperature, is hardly altered by the addition of graphene (PSGLC), we may ignore the former cause. However, \(\varepsilon_\parallel\) and permittivity in the isotropic are lower than those for the PSLC system. Thus, we argue that the enhancement of the antiparallel correlation between the 5CB molecules is primarily responsible for the observed dielectric features.

3.4. Electrical Switching. The positive dielectric anisotropy of the system couples to the applied electric field in a quadratic fashion. If the field is applied normal to the director,
then a positive torque $\propto \varepsilon E^2$ acts on the molecules and sets up a competition between the surface (elastic) forces trying to retain the equilibrium situation and the electric field demanding reorientation. At a certain threshold voltage ($V_{th}$), the latter wins and the reorientation gets initiated. For $V \gg V_{th}$, the reorientation gets completed with the molecules becoming parallel to the electric field. Concomitantly, significant birefringence changes take place with the equilibrium situation (planar) giving the largest contribution, and the field-driven case (homeotropic), the least (ideally zero). This phenomenon is referred to as the Freedericksz transformation, and lies at the heart of a variety of electrically driven LC device principles. The director reorientation can be probed response functions such as optical transmission, sample capacitance, etc. Figure 6 shows the Freedericksz transformation behavior for PSLC and PSGLC systems presenting the variation of sample capacitance ($C$) as a function of the applied voltage; for better visualization, the data are shown normalized using $C_{norm} = (C - C_{\perp})/(C_{||} - C_{\perp})$, with $C_{\perp}$ being the equilibrium capacitance value obtained in the planar orientation of the LC molecules. The PSLC sample actually shows two-stepped variation; however, we take the threshold to be the voltage at which the larger change in capacitance gets initiated. The PSGLC sample exhibits a dramatic lowering of $V_{th}$ in comparison to the mixture without graphene (PSLC); the value decreases by nearly an order of magnitude (in PSLC, the threshold for even the smaller first step is higher than that for PSGLC). It is interesting to note that while the $V_{th}$ for PSLC is much higher than for SCB (the pure LC), the confinement in the PSGLC matrix reduces it even below that of the pure LC (see Table 1). Thus, the graphene-reinforced matrix provides the double benefit of mechanical rigidity combined with lowered threshold voltage. Besides, above $V_{th}$, the rise in capacitance is much sharper for the PSGLC sample (see inset of Figure 6). Since the associated slope is inversely proportional to the bend elastic constant, the observed behavior is quite attractive for achieving higher resolution in grayscale capabilities of a display device. This slope given by the ratio $\frac{dC}{dV}$ is a factor of 4 higher for the PSGLC mixture ($0.12 \pm 0.002$) than its nongraphene counterpart ($0.031 \pm 0.001$). In addition to PSGLC, the composite with 0.01% concentration of graphene, three more compositions PSGLC$_{0.005}$, PSGLC$_{0.0085}$, and PSGLC$_{0.11}$, with 0.005, 0.0085, and 0.1% graphene, respectively, were investigated for their Freedericksz behavior. All of these composites have a $V_{th}$ higher than for PSGLC. As seen from Table 1, the graphene composition dependence of $V_{th}$ appears to be nonmonotonic, showing a minimum for PSGLC. Experiments with a higher loading of graphene could not be performed owing to the high electrical conductivity of the samples (the conductivity values obtained at room temperature for the planar aligned sample are shown for a few materials in Table S2). It is important to note that higher concentrations could have, in fact, led to increase in the magnitude of the threshold voltage as has been observed in general for polymer-stabilized systems (see, e.g., ref 43). It may, however, be pointed out that a previous study of ours$^{44}$ did indeed point to this possibility that very low concentrations of the additive can result in an improvement of the properties. Inclusion of nanoparticles, such as ZnO,$^{45}$ Gold,$^{46}$ ZnS/Mn,$^{47}$ Sb$_2$O$_5$,$^{48}$ and clay,$^{49}$ has been seen to lower $V_{th}$. However, the extent of improvement seen in the present studies with very small concentrations of graphene is unprecedented.

One of the primary results of this work is displayed in Figure 7 comparing the temperature dependence of $V_{th}$ for PSLC and PSGLC. The behaviors are drastically different: While PSLC has the usual nonlinear variation with a strong rise in the vicinity of the isotropic phase and a limiting situation at lower temperatures, PSGLC has zero dependence on temperature. Thus, for the PSGLC system, the threshold voltage is not only substantially lower, but also remains invariant with temperature.
we have recently reported similar results in another PSLC various kinds have been incorporated, in the PSLC/PDLC systems, wherein nanostructures of

Template Counterpart

Network, PSLC (No Graphene Content), PSGLC0.005 (0.005\% Graphene), PSGLC (0.01\% Graphene), and PSGLC-t, Its fact that is evident from the morphology seen in the SEM owing to better a
times tau-on and tau-off between the non-CNT and CNT systems

Table 1. Threshold Voltage in Volts at Room Temperature for Host LC, and in Situations Having Different Types of Polymer Network, PSLC (No Graphene Content), PSGLC0.005 (0.005\% Graphene), PSGLC (0.01\% Graphene), and PSGLC-t, Its

| system          | host LC   | PSLC     | PSGLC0.005 | PSGLC-t | PSGLC0.005 | PSGLC-t |
|-----------------|-----------|----------|------------|---------|------------|---------|
| threshold voltage (V) | 1.31 ± 0.01 | 3.5 ± 0.03 | 0.45 ± 0.01 | 0.85 ± 0.03 | 1.05 ± 0.01 | 0.5 ± 0.01 |

Figure 7. Thermal variation of the threshold voltage for the PSLC and PSGLC cases exhibiting strikingly different behaviors, while PSLC shows the standard variation; the temperature-independent value seems for PSGLC quite attractive.

and features very attractive from the viewpoint of designing the display driving circuits, owing to the nonrequirement of correcting for the ambient temperature variation of $V_{th}$. In fact, we have recently reported similar results in another PSLC system, wherein the network was strengthened by the incorporation polymer-decorated carbon nanotubes. However, the reduction in $V_{th}$ between the non-CNT and CNT systems was only about 20\%, in contrast to a factor of 7 diminution seen in the current studies for the graphene-incorporated system. In fact, such a large reduction in $V_{th}$ is unprecedented in the PSLC/PDLC systems, wherein nanostructures of various kinds have been incorporated, especially so considering that the concentration of the graphene employed here is extremely small (0.01\%). The fact that the lowered $V_{th}$ and its thermal invariance have been achieved without any special functionality imposed on the nanostructure (graphene) is attractive and suggests that there is a huge potential for generalization of the methodology, which allows for various nanostructures to be incorporated for strengthening the polymer fibers. It is interesting that graphene, vis-à-vis decorated CNT, as a very-low-concentration filler has been able to achieve a much larger diminution in $V_{th}$. This could be owing to better affinity of graphene to the polymer surface, a fact that is evident from the morphology seen in the SEM images, as well as the results of the template technique to be described below. This invariance in temperature could be arising owing to effective manipulation of the anchoring strength by graphene getting adhered to the polymer surface at the time of the photoconversion of the monomer to a polymer fiber. We now elaborate on the role played by the altered anchoring strength. The influence of the surface on the elastic behavior of the nematic liquid crystal can be described in terms of the anchoring strength of the surface. Of course, unlike in non-network systems, the PSLC architecture can be thought of to provide virtual surfaces at every interface between the polymer and the liquid crystal, and thus over the entire bulk of the sample and not merely at the two substrate surfaces. Following Seo et al., we consider the anchoring strength to be given by the ratio of $K_{11}$, the splay elastic constant, to the surface extrapolation length $l_s$. In the polymer–LC interfacial region, $l_s$ has two contributions: $l_{s1}$ from the order parameter variation and $l_{s2}$ from the direct interaction of the LC molecules with the surface. For PSLC, the contribution is dominated by $l_{s1}$, whereas for PSGLC with its mechanically stronger surface, $l_{s2}$ dominates. This causes the anchoring energy and consequently threshold voltage to become temperature-invariant, supporting the experimental observations.

3.5. Electro-Optical Switching. The dynamics associated with the reorientation from planar to homeotropic and back is shown in Figure 8. The responses are obtained by collecting, with the help of a photodiode and an associated differential amplifier, the intensity of a light beam transmitted through the sample kept between crossed polarizers. The field-on response was recorded on applying a sinusoidal voltage of 20 Vrms and at 1 kHz, while the field-off response was obtained after switching the applied field off. Both the field-on ($\tau_{\text{on}}$) and field-off ($\tau_{\text{off}}$) responses, defined as the duration for the output to change between 10 and 90\% of the total, are comparable between the two systems, with $\tau_{\text{on}}$ and $\tau_{\text{off}}$ being 20 and 120 ms, respectively. However, the backflow feature, an undesirable effect seen in the PSLC system, is absent for PSGLC.

3.6. Device. A device based on these features and operating between the field-off scattering and field-on transparent states

Figure 8. Dynamics of the electro-optical switching for PSLC and PSGLC presenting the (a) field-on and (b) field-off responses. The response times tau-on and tau-off for the two processes appear to be impervious to the presence of graphene. However, in the PSGLC system, the undesirable backflow effect is eliminated.
is presented in Figure 9. While the conventional PSLC device (panels (a) and (b)) has a good transparent condition, wherein the printed text placed behind the device is very clearly visible, its scattering state suffers from light leakage. The PSGLC device (panels (c) and (d)), on the other hand, has excellent characteristics with hardly any light leakage. This could be due to two reasons: (i) the well-defined polymer morphology aided by the presence of graphene and (ii) light absorption by graphene, as can be visually seen in the device. The attractive part is that the contrast ratio, given by the light level transmitted in the field-on to field-off states, gets doubled for the graphene-incorporated device, with the contrast ratios being 53 and 25 for the PSGLC and PSLC systems, respectively.

3.7. Polymer–Template System. In a further development in having carbon-reinforced PSLC devices, we now demonstrated that a new strategy in terms of templated architecture can be realized by the studied system. As is expected for template systems, such a realization holds the potential of the option to employ different host systems, optimized for the chemical nature, magnitude of the physical parameters, etc. For this purpose, we employ a wash and refill technique to build templated systems. The protocol is shown in the block diagram depicted in Figure 10.

Figure 9. Visual performance of the devices having (a) PSLC and (b) PSGLC architectures. The devices exhibit a field-off scattering state switching to a transparent one upon application of voltage. The blocking of the background text is better in the PSGLC case, leading to a much better contrast for the device, given by the ratio of the light transmission in the field-on to the field-off situation.

Figure 10. Block diagram showing the steps involved in the fabrication of the templated PSGLC (PSGLC-t).

Briefly, after the PSGLC is formed, the device was immersed in acetone for 48 h to wash out the host LC, any unpolymerized RM82, and graphene flakes, which are not contained inside the polymer network. The cell was left for drying over extended periods of time (~48 h) for the solvent to be completely removed. Observation of the cell under polarizing optical microscopy showed the complete absence of the LC in the cell. We refer to the cell as PSGLC-t. Subsequently, the cell was refilled with the host LC (without any graphene content) and then the Freederickz transformation measurements were conducted. Figure 11 shows the comparative C−V profiles for PSLC, PSGLC, and PSGLC-t cells. As seen in Table 1, $V_{th}$ slightly increases for the templated system, but is certainly much lower than the PSLC device. The marginal difference could be due to any possible effect of the solvent on the surfaces of the polymer network. This clearly demonstrates the robustness of the PSGLC network and provides a path to use this architecture as a template for a variety of LC devices.

4. CONCLUSIONS

We have delineated an attractive strategy to create a novel type of polymer-stabilized liquid crystal by incorporating small amounts of graphene. Even at these trace levels, the presence of graphene has significant effects on the virtual surfaces of the polymer network, as evident from (a) distinctly different morphologies as imaged by scanning electron microscopy and (b) desirable improvements to the PSLC device characteristics. The most notable is the influence on the critical voltage for device operation: In addition to the value decreasing by a factor of 7, the parameter itself becomes independent of temperature. From the point of view of designing the driver circuitry, this is especially advantageous. The device which displays field-off scattering and field-on transparent states shows an enhanced contrast ratio upon inclusion of graphene. The expected increase in mechanical strength, owing to the presence of the carbon form in the polymer network, has the potential to realize substrate-free flexible devices. In this regard, the presence of graphene would certainly enhance the mechanical rigidity of the system, while still maintaining the operating voltages low. This double benefit in the described simple system, contrasts with far more complicated situations reported recently. The strengthening of the polymer strands, which is the feature behind the large reduction in the threshold voltage and its temperature independence, was achieved in the previous case using a nanostructure (CNT), which was specially designed for the purpose and made to have an outer shell to match chemically the host polymer. The present study has shown that with graphene the need for chemical modification of the nanostructure is altogether obviated. We have further confirmed this feature by creating a template structure, wherein any unattached graphene is leech out. These features are well supported by Raman mapping of the ensuing structures. Hence, the method paves way for better devices without appealing to tedious chemical methods. Even quantitatively, the current report stands out because the magnitude of reduction in the threshold voltage is an
unprecedented factor of 7. Importantly, the studies emphasize the importance of nanofillers at very low concentrations to the device operating characteristics and thus have the potential to be generalized to a variety of situations.

**ACKNOWLEDGMENTS**

Funding support from the Thematic project (SR/NM/TP-2/5/2016), Nano Mission, DST, New Delhi, India, is gratefully acknowledged.

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