Self-assembled liquid-crystalline gels designed from the bottom up

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Liquid crystals are often combined with polymers to influence the liquid crystals' orientation and mechanical properties, but at the expense of reorientation speed or uniformity of alignment. We introduce a new method to create self-assembled nematic liquid-crystal gels using an ABA triblock copolymer with a side-group liquid-crystalline midblock and liquid-crystal-phobic endblocks. In contrast to in situ polymerized networks, these physical gels are homogeneous systems with a solubilized polymer network giving them exceptional optical uniformity and well-defined crosslink density. Furthermore, the unusually high-molecular-weight polymers used allow gels to form at lower concentrations than previously accessible. This enables these gels to be aligned by surface anchoring, shear, or magnetic fields. The high content of small-molecule liquid crystal ($\geq$95%) allows access to a regime of fast reorientation dynamics.

The molecules of a liquid crystal (LC) tend to cooperatively orient in a preferred direction, giving rise to useful properties such as birefringence, dielectric anisotropy, diamagnetic anisotropy and orientational elasticity[1] that are forbidden by symmetry in isotropic liquids. The coupling of order with fluidity makes LCs particularly intriguing materials because their orientation-dependent properties can be influenced by readily accessible fields. Combining LCs and polymers can lead to synergistic orientational coupling between the two, but to date all such materials have either displayed slow reorientation dynamics or lacked uniformity. Liquid-crystal elastomers, composed of crosslinked LC polymers, generally have very slow reorientation dynamics[2–4]. Polymer-dispersed LCs (PDLCs)[5–8] and polymer-stabilized LCs (PSLCs)[9–13] are two-phase systems lacking homogeneity and optical clarity.

A way to retain the fluid nature of the LC in a single-phase LC–polymer material is to create a gel[14,15]. A dilute polymeric network should preserve the fluidity of the small-molecule LC, allowing for fast reorientation dynamics. Recent work[15] with in-situ-polymerized, chemically crosslinked LC gels, demonstrated that the reorientation of the LC director was much slower than for a pure small-molecule LC due to the resistance of the polymer network and that inhomogeneities in the director orientation were visible under an optical microscope. To increase the speed of response to external stimuli, the polymer network must be made more dilute, requiring a network of long, well-solvated polymers. An inherent drawback of in-situ-polymerized networks is that the high rate of termination reactions precludes the formation of long chains and significantly reduces the ability of dilute chain-ends to form a crosslink. Furthermore, the random nature of covalent crosslinking results in a broad distribution in the molecular weight between crosslinks and in the formation of free-floating polymers. These inhomogeneities in the polymeric network give rise to detrimental optical and viscoelastic non-uniformities.

To create LC gels that are homogeneous and well characterized, we use block copolymer self-assembly: we have synthesized polymers having very long LC midblocks flanked by LC-phobic endblocks that allow us to produce more dilute gels than previously obtained.

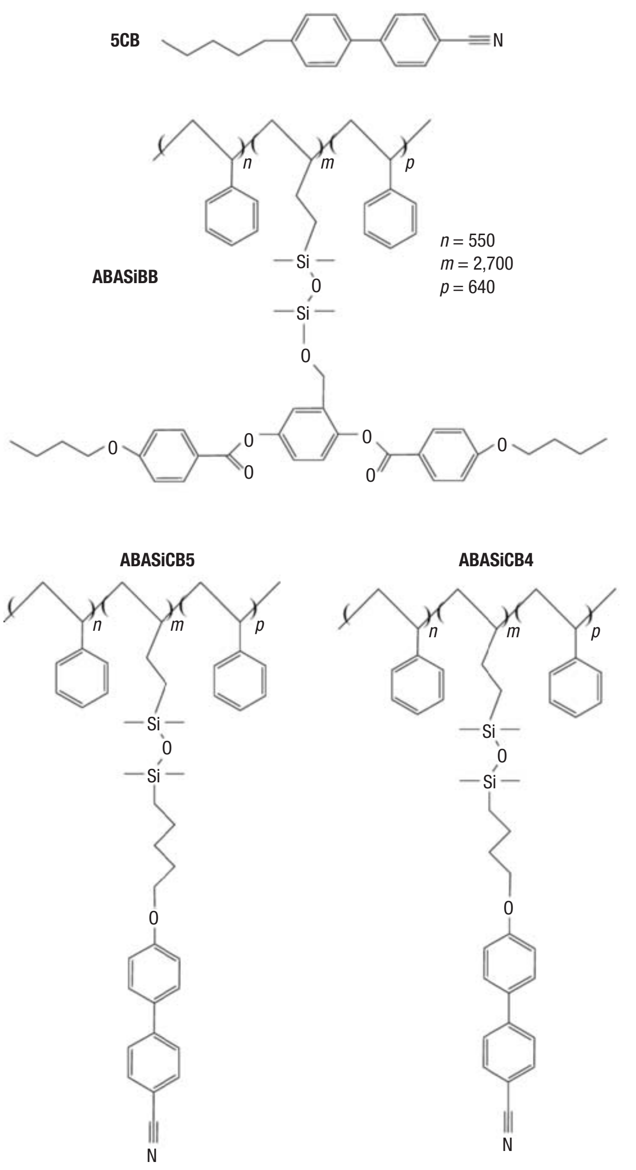

Figure 1 Molecular structure of the nematic solvent 5CB and the ABA liquid crystal polymers. The polymers were also made in a homopolymer form, and named HSiBB, HSiCB5 and HSiCB4, respectively. The polymers were named to reflect their backbone structure, linking group, and mesogen. ABA denotes a triblock copolymer and H signifies a homopolymer. Si represents a siloxane linking group. CB stands for cyanobiphenyl-containing, and BB for butoxybenzoate-containing mesogens. The CB polymers are further distinguished by the number of carbons in the alkyl spacer.

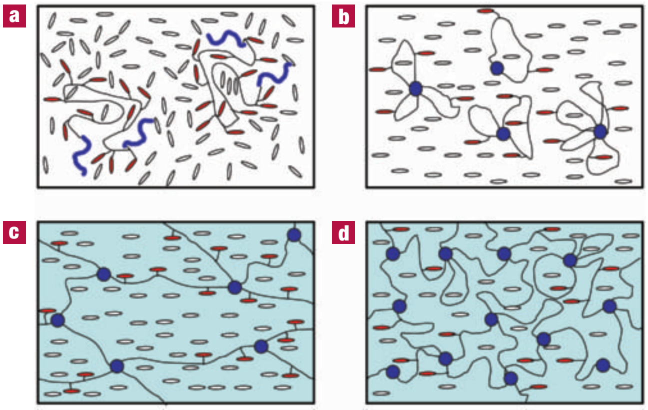

Figure 2 The phase behaviour of the nematic gels. Circles represent polystyrene aggregates and ovals represent mesogenic units. **a**, Non-aggregated ABA block copolymer in the isotropic phase. **b**, Formation of a micellar solution in the nematic phase. **c**, Nematic gel formed with a highly elongated polymer. **d**, Nematic gel formed using a moderately elongated polymer.

When dissolved in a small-molecule LC, the endblocks spontaneously aggregate to form a physical gel with as little as 3-wt% polymer, allowing the fast dynamics of the LC to be preserved. In contrast to chemically crosslinked LC networks, the resulting gel is thermoreversible and exceptionally uniform, as it permits heterogeneities to relax away. In turn, control of the physical network enables control of the coupling between mechanical stress and molecular alignment—the origin of 'soft elasticity' in nematic elastomers[14]. The small-molecule LC dictates the degree of liquid-crystalline order, making the approach quite general to other LC phases. In the following sections, we discuss the synthesis, phase behaviour, alignment, and electro-optic characteristics of the self-assembled liquid crystalline gels.

The ABA block copolymers used in this study (Fig. 1) have polystyrene 'A' endblocks with degree of polymerization (DP) of 640 and 550 (number-average molar masses, M_n, of 67 and 57 kg mol^{-1}), and side-group liquid-crystalline polymer (SGLCP) 'B' blocks with DP of 2,700 (M_n between 1,010 and 1,200 kg mol^{-1}, depending on the side-group). The three different SGLCP structures were selected to confer solubility in the LC 4′-pentyl-4-cyanobiphenyl (5CB) (Fig. 1), a thoroughly characterized small-molecule nematic. Cyanobiphenyl-based ABASiCB4 and ABASiCB5 were chosen because matching the structure of the side-groups and LC solvent is known to increase solubility[16]. Similarly, ABASiBB was chosen because the side-group has been shown to dissolve in cyanobiphenyl-based LCs[17].

A polymer-analogous approach to synthesis allowed a model series of high-molecular-weight polymers to be created with different mesogenic types but with the same degree of polymerization. First, the triblock pre-polymers with polystyrene, 1,2-polybutadiene, and polystyrene blocks were synthesized by anionic polymerization[18]. The various mesogenic units were then attached to the pendant vinyl groups of the 1,2-polybutadiene midblock by hydrosilylation[19–21]. Homopolymers HSiCB4, HSiCB5 and HSiBB were similarly synthesized with DP of 1,200. The details of these syntheses are described elsewhere (M.D.K., R.V., N.R.S., J.L. and J.A.K., manuscript in preparation; Maria L. Auad *et al.*, manuscript in preparation).

To create homogeneous gels, the polymer and 5CB were dissolved together in dichloromethane followed by drying in a vacuum at room temperature for two days with periodic mixing.

The formation of the physical network by aggregation of the endblocks is mediated by the nematic order of the LC host. Dissolution of a polymer in a small-molecule solvent is entropically driven, and in a nematically ordered solution, the entropy of a dissolved polymer is reduced, resulting in lower polymer solubility. The SGLCP midblocks remain dissolved in 5CB because of their intrinsic nematic order. On the other hand, the polystyrene endblocks, which are soluble in the isotropic phase of 5CB (Fig. 2a), aggregate in the nematic phase (Fig. 2b,c,d). Above a critical concentration of polymer, a gel is formed (Fig. 2c,d).

Calorimetric studies confirmed that the phase-transition temperature of the gel did not deviate significantly from that of 5CB.

The nematic-to-isotropic transition temperature (T_{ni}) was measured for each of these gels for concentrations up to 20-wt% polymer and found to be within 3 °C of the T_{ni} of 5CB (35 °C). Optical microscopy showed that the triblock copolymers ABASiCB4 and ABASiBB formed single-phase mixtures with 5CB at all concentrations tested (0.5% to 20%), and ABASiCB5 formed a single-phase mixture for concentrations above 18 wt%. Dynamic mechanical analysis was also performed on these mixtures to determine which satisfy the criteria for being gels[22], that is, a plateau in the storage modulus over an appreciable range of frequencies with the storage modulus greater than the loss modulus. For all concentrations between 18 and 50 wt%, ABASiCB5 formed a homogeneous gel in 5CB. ABASiCB4 formed gels above 5 wt%, and ABASiBB formed gels above 3 wt% (M.D.K., R.V., N.R.S., J.L. and J.A.K., manuscript in preparation). When any of these gels was heated into the isotropic phase, it reversibly turned into a viscous fluid (Fig. 2a). The transition from a viscous fluid to a gel with decreasing temperature coincided with the transition from the isotropic to the nematic phase evident in optical microscopy and in calorimetry. This demonstrates that we have created a thermoreversible nematic gel.

In physical gels composed of ABA block copolymers, the minimum polymer concentration necessary to form a gel varies inversely with the length spanned by the midblock. It is the three-dimensional, space-filling nature of the polymer network that gives solid-like characteristics. The span is largely determined by the degree of polymerization of the midblock, but midblock flexibility is also an important factor. A flexible midblock can form loops, where both endblocks are in the same aggregate. A more rigid midblock will have a higher tendency to form a bridge between two different endblock aggregates. As the flexibility of the midblock is determined by its structure, the side-group can dramatically affect phase characteristics.

Neutron-scattering studies were conducted on solutions of homopolymers in perdeuterated 5CB (D5CB). The polymers had the same backbone length, so the effect of the side-group structure on the polymer anisotropy and molecular dimensions could be isolated.

The end-on SGLCPs (HSiCB4 and HSiCB5) both have oblate conformations with similar anisotropies. The ratio of the radius of gyration perpendicular to the director ($R_\perp$) to that parallel ($R_\parallel$) was approximately 1.6 for HSiCB4 and 1.5 for HSiCB5 (Fig. 3a). In constrast, side-on attachment of the mesogen (HSiBB) produced a strongly prolate conformation (Fig. 3b). A lower bound on the anisotropy obtained from an elliptical approximation fit to the scattering pattern yields $R_\parallel/R_\perp > 5$. The scattering pattern for HSiBB actually has a bow-tie shape, which could be due to the polymer exceeding the overlap concentration or to a rigid cylinder polymer conformation. Previous studies[23–25] on side-on polymers with structures similar to HSiBB, but much lower DP, have found them to have reduced flexibility derived from steric interactions between adjacent side-groups. Further experiments with different molecular weights and concentrations are necessary to fully elucidate this polymer's structure.

For ABA triblocks having matched backbone structures and backbone length, these very different conformational characteristics of the SGLCP midblock can substantially affect gelation. A highly prolate conformation of the midblock is more likely to accommodate a greater distance between crosslinks than a weakly oblate conformation. Indeed, ABASiBB gelled at lower molar concentrations than ABASiCB4 (3-wt% ABASiBB corresponds to half the molar concentration of 5-wt% ABASiCB4).

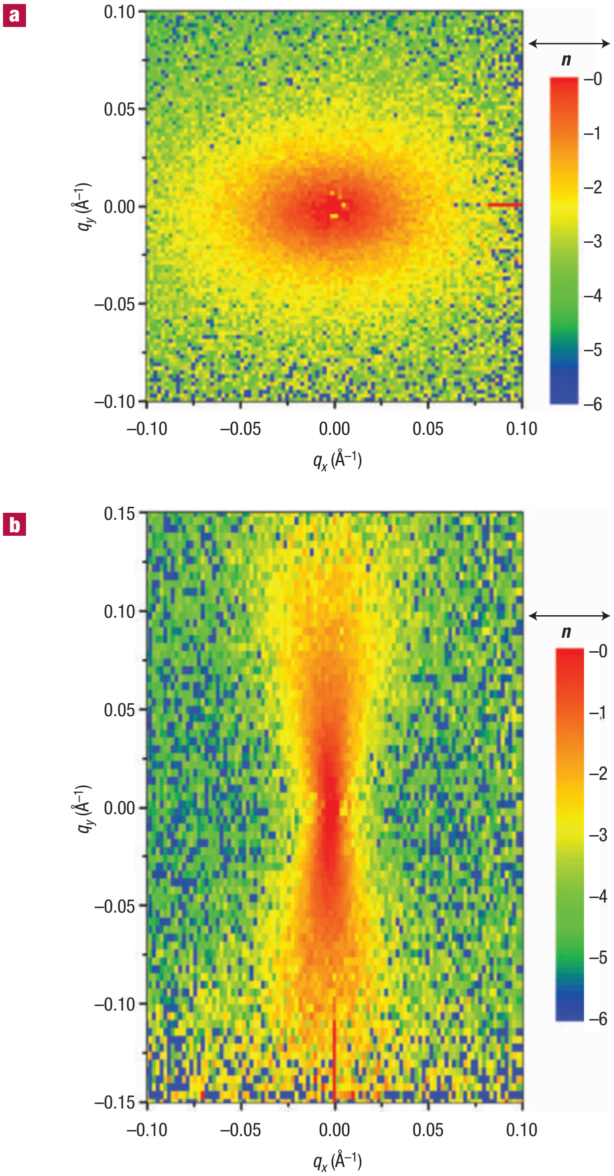

Figure 3 Neutron-scattering patterns for homopolymers dissolved in perdeuterated 5CB[33,34] at a concentration of 5 wt%. a, 470 kg mol^{-1} HSiCB4; **b**, 743 kg mol^{-1} HSiBB. The scale indicates logarithmic values of normalized intensity. The scattering pattern for 500 kg mol^{-1} HSiCB5 is similar to HSiCB4 except for a slightly reduced anisotropy. ***n*** denotes the director. q_x and q_y denote components of the scattering vector. Homopolymer samples were aligned using both surface treatment and a 0.8 T magnetic field. Scattering patterns were collected using the small-angle diffraction (SAD) instrument at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory under experimental conditions identical to Kempe *et al.* (M.D.K., J.L. and J.A.K., manuscript in preparation).

Most applications of LC systems demand macroscopic alignment into a uniform monodomain. In the absence of surface anchoring or an applied external field, an LC typically has a polydomain texture with a high density of orientational defects (disclinations). The network strands in an LC gel or elastomer can act throughout the volume to induce and preserve a uniformly oriented state, even in the absence of applied fields. On the one hand, in-situ-polymerized LC gels can preserve the alignment state present during the polymerization (induced by aligning surfaces or fields)[15]; the rapid relaxation time before gelation precludes strain-induced alignment. On the other hand, LC elastomers can be aligned by mechanical deformation and then further crosslinked to create a 'single liquid crystal elastomer'[2,3,26], but LC elastomers are relatively insensitive to applied fields. The present physically crosslinked LC gels open diverse processing strategies to

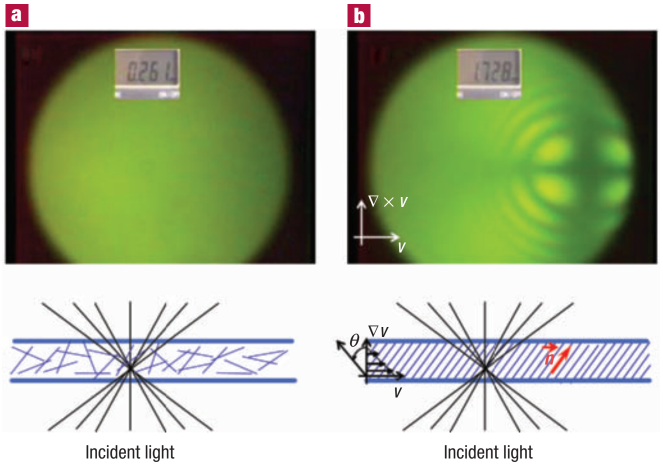

Figure 4 **Conoscopic images of 20-wt% ABASiCB5 gel, 400 μm thick, in 5CB at 25 °C. a**, The gel before shear and **b**, immediately after cessation of shear. The cross-section schematics under each image illustrate how light interacts with the corresponding polydomain (**a**) and single-crystal-like (**b**) orientation of the director. The axes of **b** indicate the direction of shear (v) and define the angle (θ) of the director (***n***). Conoscopic imaging was performed using a Zeiss stereomicroscope equipped with an Olympus 1C20 high-numerical-aperture lens, a custom-made translation stage and a computerized video capture system. The inset images were used to synchronize the measurement of the stage translation with the recording of the conoscopic image.

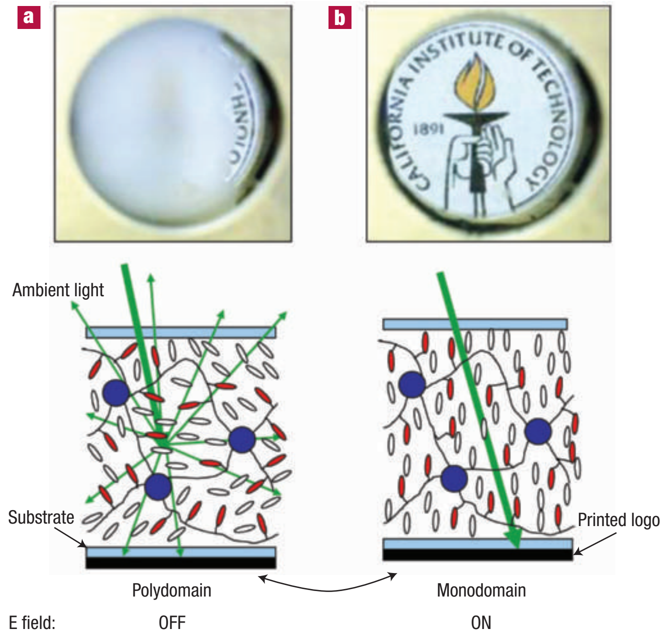

Figure 5 **Photos and cross-section schematics illustrating the electro-optic switching of a 5-wt% ABASiCB4 gel in a 25-μm gap.** A printed logo was placed behind the cell. **a**, Light-scattering voltage OFF state. The cell was intentionally left empty in the area where the word "TECHNOLOGY" is partially legible. **b**, Transmissive voltage ON state switched at $1.6\ \mathrm{V}\ \mu\mathrm{m}^{-1}$. The LC domains are shown schematically with dimensions of the order of the polymer size, when they would actually be much larger, and may slowly transition from one orientation to another. Similarly, the size of the polymers relative to the cell dimensions is greatly exaggerated. Photographs were taken using a Canon EOS D30 digital camera equipped with a Canon EF 50 mm *f*/2.5 macro lens. A California Instruments 25ITL-OP1 a.c. power supply was used to apply electric fields.

create uniformly aligned LCs using surface anchoring, applied fields, or deformation.

Strain-induced alignment is illustrated for a 20-wt% ABASiCB5 gel that is initially in an unaligned, polydomain state (Fig. 4a), and transformed to a monodomain state with excellent optical clarity and uniform director orientation (Fig. 4b). Single-crystal samples produce an interference figure in conoscopic imaging, which can be used to determine the angle of the optic axis relative to the surface normal[27]. In a shear cell that allows for conoscopic examination under the application of a controlled shear strain, the 20-wt% ABASiCB5 gel was heated into the isotropic phase (above 38 °C) and then cooled to room temperature, producing a polydomain, light-scattering structure (Fig. 4a). At 25 °C, after the application of a strain of 3.7 at a rate of $1.2\ \mathrm{s}^{-1}$, an interference figure was observed (Fig. 4b). Observation of an interference figure is a significant achievement, as it requires single-crystal-like optical uniformity over the relatively large sample thickness of 400 μm.

The lifetime of the aligned state depends on the thermal history during shear. When shear was performed at 25 °C, the interference figure lasted one or two minutes, and slowly faded away as the gel relaxed back to a polydomain state. A permanent monodomain was achieved by shear at temperatures between 35 and 38 °C. A permanently aligned state at ambient temperature was achieved when large-amplitude oscillatory shear was applied to the sample while cooling.

The direction of this uniform alignment results from the coupling of the director field to the polymer conformation. As shown above, the pendant mesogens of HSiCB4 and HSiCB5 tend to orient transverse to the backbone. Shear causes the backbone to preferentially orient at an angle between 45° and 90°, in accord with the observed steady-state orientation of the director, θ, at –8° for 20-wt% ABASiCB5 (Fig. 4). The direction of alignment induced by shear varies with molecular structure, in accordance with the conformational characteristics seen in the SGLCP homopolymers using small-angle neutron scattering. Both ABASiCB4 and ABASiCB5 exhibit director alignment near the velocity gradient direction, as expected from the oblate character of HSiCB4 and HSiCB5 (Fig. 3a). In contrast, the director of ABASiBB aligns close to the flow direction under shear, in accord with its prolate character (Fig. 3b). In all these systems, the uniformity of alignment is excellent, as manifest in the formation of conoscopic interference figures.

In addition, the gels may be aligned by more conventional means, albeit slowly. Surface anchoring using rubbed polyimide surface treatment aligned a 10-μm-thick sample of 5-wt% ABASiBB gel after annealing for several weeks at room temperature, resulting in a permanent monodomain. A 3-wt% ABASiBB gel aligned after annealing for several days. Conversely, a 2.5-wt% ABASiBB mixture, which is below the critical gelation concentration, aligned immediately after loading. Alternatively, gels can be aligned by cooling from the isotropic to the nematic phase in a magnetic field. All gels tested—up to 50-wt% ABASiBB, 20-wt% ABASiCB5, and 10-wt% ABASiCB4—were amenable to alignment in approximately one hour (cooling approximately $0.1\ ^{\circ}\mathrm{C\ min}^{-1}$) under a field of 8.8 T.

Single-LC elastomers have been previously described[2,3,26], but these have slow dynamics, precluding electro-optic applications. Rapid electro-optic response has been demonstrated in systems in which the polymer segregates from the LC (for example, PDLCs and PSLCs) at the cost of optical uniformity. Here we show that polymers designed to self-assemble a single-phase physical network at low polymer concentration provide access to LC gels with rapid electro-optic response.

To study their electro-optic characteristics, gels of ABASiCB4 and ABASiBB were heated to the isotropic phase and loaded by capillary action into a gap between glass plates coated with indium tin oxide electrodes. Samples were then cooled to room temperature to produce a polydomain structure that strongly scatters light (Fig. 5a). The intensity of transmitted linearly polarized HeNe laser light was recorded while a 1,000 Hz a.c. voltage was applied across the cell to orient the gel (Fig. 5b). A photodiode detector was set 10 cm behind the sample resulting in an aperture angle of approximately 2°. High-amplitude oscillations of the transmitted intensity with the a.c. voltage were observed at lower frequencies, but oscillations were reduced at 1,000 Hz and above. The transmitted intensity was normalized by the intensity recorded for the same cell with the gel heated to the isotropic state. The transmitted intensity of a layer of gel 25 μm thick was recorded as a function of applied voltage. The transmittance of both 5-wt% ABASiCB4 and 5-wt% ABASiBB was initially linear with voltage above a threshold field of 0.7 V μm^{-1} and 1.2 V μm^{-1}, respectively. With increasing voltage, the transmittance saturated to a maximum that was more than 95% that of the isotropic cell. Saturation was reached at 3.0 V μm^{-1} for ABASiCB4 and approximately 4.5 V μm^{-1} for ABASiBB. The threshold field for switching was insensitive to gap thickness. This phenomenon has been previously observed in chemically crosslinked LC gels[14,15], and originates from the fact that the polymeric network generates an elastic restoring force that acts on the director throughout the volume rather than only at the surface of alignment layers. Hysteresis was observed, meaning that transmitted intensities while ramping voltage up were not superimposable on those recorded while ramping voltage down. Hysteresis may be a result of the reorientation of the polymer network itself under application of a field.

Next, the transmittance of the cells was recorded transiently while an electric field was applied (Fig. 6a) and removed (Fig. 6b). The time required for the transmitted intensity (I) to reach 90% of its maximum is defined as the orientation time, τ_{90}. On removal of the field, the time required for I/I_{max} to fall to 10% is defined as the relaxation time, τ_{10}. The response times were insensitive to gap thickness, but highly dependent on the applied field. For 5-wt% ABASiBB, τ_{90} decreased strongly (from 1,000 ms to 3 ms) as the applied field was increased from 2.4 V μm^{-1} to 6.4 V μm^{-1} (Fig. 6a). For the same gel, τ_{10} increased significantly (from 19 ms to 170 ms) with applied field over the same range (Fig. 6b). These voltage dependencies contrast with the $\tau_{90} \sim V^{-2}$ and $\tau_{10} \sim V^{0}$ behaviour of pure LCs[1] and PDLCs[8]. The observed field dependence of τ_{10} may be due to reorganization of the polymer network under high fields. Switching times were similar for 5-wt% ABASiCB4 with τ_{90} equal to 3 ms and τ_{10} equal to 15 ms when a field of 4.0 V μm^{-1} was applied. For reference, pure 5CB in a cell with a 5-μm gap has relaxation as its rate-limiting response with τ_{10} equal to approximately 38 ms (refs 28,29), which slows quadratically with increasing gap and is independent of the previously applied field.

These experiments suggest that an ABA nematic gel could be effectively used in a reflective electro-optic display by placing a layer of the LC gel in front of a uniform black background[6,30]. Without an applied field, ambient light is scattered to produce a bright state analogous to the blank areas on a sheet of paper. Application of an electric field induces a transparent state that allows incident light to be transmitted and absorbed on the back surface, yielding a dark appearance like ink on a printed page. At intermediate voltages, the ratio of absorbed to scattered light can be modulated to provide greyscale images. The most significant advantage of the present LC gels over PDLCs in a reflective display, is the facile loading and structure formation enabled by the self-assembled gels. Some of the challenges associated with PDLC and other scattering LC materials (hysteresis, high drive voltage and limited contrast ratio[7,31]) would also need to be addressed in the present gel.

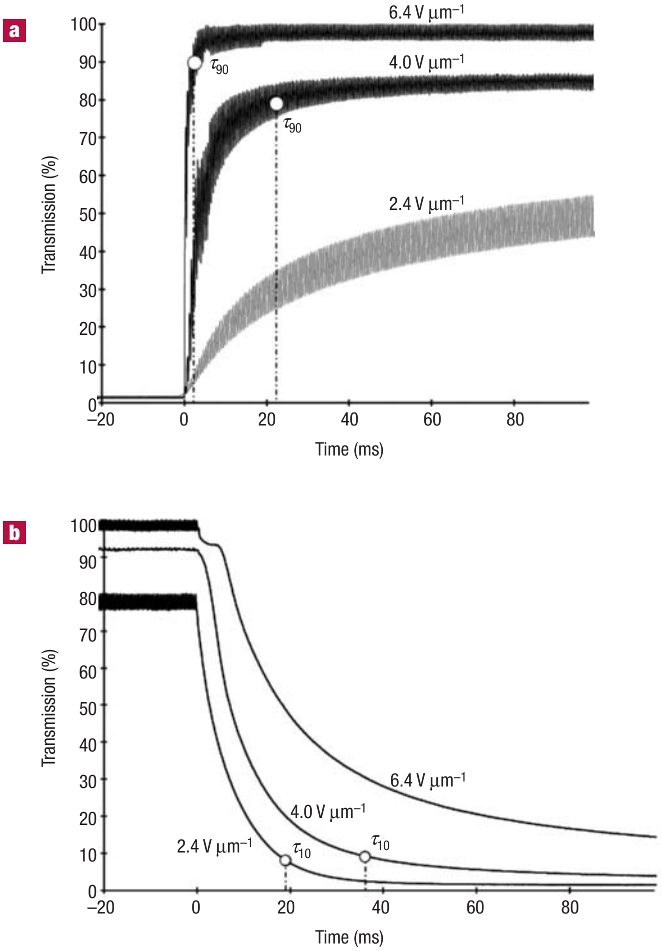

Figure 6 Transient electro-optic properties of a 5-wt% ABASiBB, 25-μm-thick layer, under application of a.c. fields at 1,000 Hz. a, Switching the electric field on. The time required to reach 90% of the maximum transmittance is denoted τ_{90}. At the lowest field of 2.4 V μm^{-1}, the τ_{90} of 1,000 ms is beyond the scale of the graph. **b**, Switching the electric field off. The time required to return to 10% of the maximum transmittance is denoted τ_{10}. At the highest field of 6.4 V μm^{-1}, the τ_{10} of 170 ms is beyond the scale of the graph. The response of the materials is so rapid that substantial oscillations are observed at twice the frequency of the applied field. The intensity of 10-mW HeNe laser light passing through the cell was measured using a Thorlabs PDA55 photodetector and recorded by a computer using a National Instruments PCI-MIO-16XE-50 data acquisition card.

The present approach to creating liquid-crystalline gels is sufficiently general to open the way to a broad range of materials that combine liquid-crystalline order and dynamics with polymer self-assembly and elasticity. In the presence of chiral nematic order, the combination of rapid response and optical uniformity of self-assembled LC gels can be harnessed for tunable wavelength filters and lasers[26]. The ease of alignment of the polymer within these gels may provide facile routes to align currently intractable chiral smectic liquid crystals, such as those exhibiting analog response with excellent speed[32]. The ability to systematically adjust the interplay of polymeric and director orientation and motion through precise control of the polymer concentration, SGLCP length between crosslinks, and the nature of the small-molecule LC in the gel provides molecular insight into the physical properties of LC gels, guiding rational design for diverse technological applications.

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References

1. de Gennes, P.-G. *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
2. Assfalg, N. & Finkelmann, H. A smectic A liquid single crystal elastomer (LSCE): Phase behavior and mechanical anisotropy. *Macromol. Chem. Phys.* **202,** 794–800 (2001).
3. Sanger, J., Gronski, W., Leist, H. & Wiesner, U. Preparation of a liquid single-crystal triblock copolymer by shear. *Macromolecules* **30,** 7621–7623 (1997).
4. Finkelmann, H., Kock, H.-J. & Rehage, G. Investigations on liquid crystalline polysiloxanes 3. Liquid crystalline elastomers — a new type of liquid crystalline material. *Makromol. Chem. Rapid Commun.* **2,** 317–322 (1981).
5. Craighead, H. G., Cheng, J. & Hackwood, S. New display based on electrically induced index matching in an inhomogeneous medium. *Appl. Phys. Lett.* **40,** 22–24 (1982).
6. Huitema, H. E. A. *et al.* Plastic transistors in active-matrix displays. *Nature* **414,** 599 (2001).
7. Coates, D. Polymer-dispersed liquid crystals. *J. Mater. Chem.* **5,** 2063–2072 (1995).
8. Bouteiller, L. & Le Barny, P. Polymer-dispersed liquid crystals: Preparation, operation, and application. *Liq. Cryst.* **21,** 157–174 (1996).
9. Dierking, I. Polymer network-stabilized liquid crystals. *Adv. Mater.* **12,** 167–181 (2000).
10. Guymon, C. A. *et al.* Effects of monomer structure on their organization and polymerization in a smectic liquid crystal. *Science* **275,** 57–59 (1997).
11. Hikmet, R. A. M. & Kemperman, H. Electrically switchable mirrors and optical components made from liquid-crystal gels. *Nature* **392,** 476–479 (1998).
12. Hikmet, R. A. M. Electrically induced light-scattering from anisotropic gels. *J. Appl. Phys.* **68,** 4406–4412 (1990).
13. Hikmet, R. A. M. Anisotropic networks and gels formed by photopolymerisation in the ferroelectric state. *J. Mater. Chem.* **9,** 1921–1932 (1999).
14. Terentjev, E. M., Warner, M., Meyer, R. B. & Yamamoto, J. Electromechanical Fredericks effects in nematic gels. *Phys. Rev. E* **60,** 1872–1879 (1999).
15. Chang, C. C., Chien, L. C. & Meyer, R. B. Electro-optical study of nematic elastomer gels. *Phys. Rev. E* **56,** 595–599 (1997).
16. Kihara, H., Kishi, R., Miura, T., Kato, T. & Ichijo, H. Phase behavior of liquid-crystalline copolymer/liquid crystal blends. *Polymer* **42,** 1177–1182 (2001).
17. Chang, M. C. *et al.* Phase transitions in mixtures of a side-on-side chain liquid crystalline polymer and low molar mass nematic liquid crystals. *Liq. Cryst.* **25,** 733–744 (1998).
18. Sanger, J., Tefehne, C., Lay, R. & Gronski, W. A simplified procedure of anionic polymerization of styrene and dienes using 4,5-methylenephenanthrene as an indicator. *Polym. Bull.* **36,** 19–26 (1996).
19. Ojima, I. *et al.* Reduction of carbonyl-compounds via hydrosilylation.1. Hydrosilylation of carbonyl-compounds catalyzed by tris(triphenylphosphine)chlororhodium. *J. Organometall. Chem.* **94,** 449–461 (1975).
20. Hempenius, M. A., Lammertink, R. G. H. & Vancso, G. J. Well-defined side-chain liquid-crystalline polysiloxanes. *Macromol. Rapid Commun.* **17,** 299–303 (1996).
21. Moment, A., Miranda, R. & Hammond, P. T. Synthesis of polystyrene-polysiloxane side-chain liquid crystalline block copolymers. *Macromol. Rapid Commun.* **19,** 573–579 (1998).
22. Almdal, K., Dyre, J., Hvidt, S. & Kramer, O. What is a gel? *Makromol Chem. Macromol. Symp.* **76,** 49–51 (1993).
23. Li, M. H., Brulet, A., Davidson, P., Keller, P. & Cotton, J. P. Observation of hairpin defects in a nematic main-chain polyester. *Phys. Rev. Lett.* **70,** 2297–2300 (1993).
24. Lecommandoux, S., Achard, M. F., Hardouin, F., Brulet, A. & Cotton, J. P. Are nematic side-on polymers totally extended? A SANS study. *Liq. Cryst.* **22,** 549–555 (1997).
25. Leroux, N., Keller, P., Achard, M. F., Noirez, L. & Hardouin, F. Small-angle neutron-scattering experiments on side-on fixed liquid-crystal polyacrylates. *J. Phys. II* **3,** 1289–1296 (1993).
26. Finkelmann, H., Kim, S. T., Munoz, A., Palffy-Muhoray, P. & Taheri, B. Tunable mirrorless lasing in cholesteric liquid crystalline elastomers. *Adv. Mater.* **13,** 1069–1072 (2001).
27. Van Horn, B. L. & Winter, H. H. Analysis of the conoscopic measurement for uniaxial liquid-crystal tilt angles. *Appl. Optics* **40,** 2089–2094 (2001).
28. Khoo, I.-C. & Wu, S. T. *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993).
29. Skarp, K., Lagerwall, S. T. & Stebler, B. Measurements of hydrodynamic parameters for nematic 5CB. *Mol. Cryst. Liq. Cryst.* **60,** 215–236 (1980).
30. Yang, D. K., Chien, L. C. & Doane, J. W. Cholesteric liquid-crystal polymer dispersion for haze-free light shutters. *Appl. Phys.Lett.* **60,** 3102–3104 (1992).
31. Wu, S. T. & Yang, D. K. *Reflective Liquid Crystal Displays* (ed. Lowe, A. C.) (Wiley, New York, 2001).
32. Walba, D. M. Fast ferroelectric liquid-crystal electrooptics. *Science* **270,** 250–251 (1995).
33. Wu, S. T., Wang, Q. H., Kempe, M. D. & Kornfield, J. A. Perdeuterated cyanobiphenyl liquid crystals for infrared applications. *J. Appl. Phys.* **92,** 7146–7148 (2002).
34. Zimmermann, H. Specifically deuteriated intermediates for the synthesis of liquid crystals and liquid-crystalline polymers. *Liq. Cryst.* **4,** 591–618 (1989).

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Competing financial interests

The authors declare that they have no competing financial interests.