Alignment of Liquid-Crystalline Polymers by Field-Oriented, Carbon Nanotube Directors

Randy A. Mrozek and T. Andrew Taton*

Department of Chemistry, University of Minnesota, 207 Pleasant Street Southeast,
Minneapolis, Minnesota 55455

Received February 28, 2005. Revised Manuscript Received April 6, 2005

Bulk liquid-crystalline polymer (LCP) material can be macroscopically aligned by seeding the growth of LCP domains with preoriented, single-wall carbon nanotubes (SWNTs). SWNT seeds dispersed in a columnar polyoxazoline melt were first oriented by applying an ac electric field across the molten material. Then, cooling the material below the liquid-crystalline transition temperature yielded domains that were oriented in the direction of the applied field. The orientation of these domains was characterized by temperature-controlled polarized light microscopy, static birefringence, and wide-angle X-ray scattering. These experiments demonstrate that domains can be oriented at field strengths that are orders of magnitude lower than those used to pole anisotropic polymers alone, and that the seeded domains can grow together to form homogeneously oriented bulk material. Because the nanotubes act only as nucleants, very little SWNT material is required. We anticipate that this general concept could aid the fabrication of monolithic objects with tailored anisotropic properties from SWNT−polymer composites.

Introduction

Structurally anisotropic polymer materials are technologically useful because molecular or supramolecular order in the material often results in anisotropic physical properties—including mechanical,[1−5] electrical,[6,7] or optical[8] anisotropy. When this anisotropy is a result of macromolecular assembly, rather than processing conditions, the resulting material typically exhibits localized regions of order ranging from nanometers to hundreds of micrometers in size. Beyond the scale of an individual ordered domain, anisotropic properties may not be realized in the bulk polymer due to variation in the orientation of adjacent domains. To maximize structural anisotropy, these individual domains must be macroscopically aligned. Macroscopic alignment of anisotropic polymers has been achieved by several techniques in which a uniform aligning force is applied to bulk material. Domains of anisotropic polymers are commonly aligned by shear forces during extrusion as a fiber or sheet,[9−13] but exposure of thin films to an external electric field has also been shown to induce alignment.[14,15] The dielectric anisotropy of most polymers is low, so high voltages are typically required; for example, field strengths of 150−180 kV/cm were reported to be necessary to align ~100 μm thick samples of lamellar PS−PI block copolymer.[16] Improved methods for electrically aligning anisotropic polymers would allow thicker, more complex objects to be fabricated in which anisotropy is determined by a locally applied field.

Anisotropic polymers have also been aligned by contact with nanostructured or nanopatterned surfaces, as well as crystalline substrates, where epitaxial ordering of a periodic polymer structure adjacent to the surface pattern propagates into the bulk.[17] This method has the advantage that no external force is required, but alignment typically only propagates over a short depth. To some extent, this depth depends on the relative scale of the surface features and the periodicity of the polymer structure. Micrometer-thick films of block copolymers, in which the scale of segregated microdomains is tens of nanometers, have been organized by contact with surface patterns with commensurate periodicity.[18,19] Similarly, columns of some hexagonal-phase liquid-crystalline polymers (LCPs) orient with the six sym-

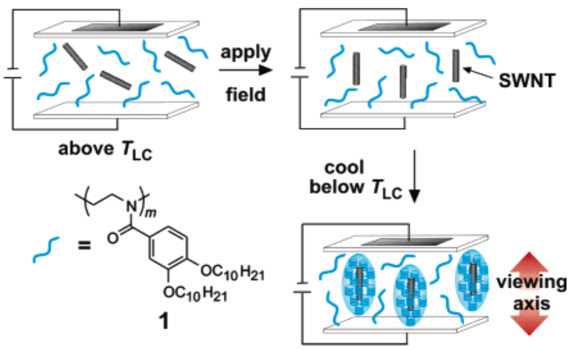
---

* To whom correspondence should be addressed. E-mail: taton@chem.umn.edu.

(1) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307−310.
(2) Harada, T.; Bates, F. S.; Lodge, T. P. *Macromolecules* **2003**, *36*, 5440−5442.
(3) Zheng, W.-Y.; Albalak, R. J.; Hammond, P. T. *Macromolecules* **1998**, *31*, 2686−2689.
(4) Honeker, C. C.; Thomas, E. L. *Chem. Mater.* **1996**, *8*, 1702−1714.
(5) Folkes, M. J.; Keller, A. *Polymer* **1971**, *12*, 222−236.
(6) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384−387.
(7) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; De Leeuw, D. M. *Nature* **1999**, *401*, 685−688.
(8) Edrington, A. C.; Urbas, A. M.; DeRege, P.; Chen, C. X.; Swager, T. M.; Hadjichristidis, N.; Xenidou, M.; Fetters, L. J.; Joannopoulos, J. D.; Fink, Y.; Thomas, E. L. *Adv. Mater.* **2001**, *13*, 421−425.
(9) Hamley, I. W. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 342−350.
(10) Pinheiro, B. S.; Hajduk, D. A.; Gruner, S. M.; Winey, K. I. *Macromolecules* **1996**, *29*, 1482−1489.
(11) Vollrath, F.; Knight, D. P. *Nature* **2001**, *410*, 541−548.
(12) Chen, Z.-R.; Kornfield, J. A.; Smith, S. D.; Grothaus, J. T.; Satkowski, M. M. *Science* **1997**, *277*, 1248−1253.
(13) Zhou, W.-J.; Kornfield, J. A.; Ugaz, V. M.; Burghardt, W. R.; Link, D. R.; Clark, N. A. *Macromolecules* **1999**, *32*, 5581−5593.
(14) Amundson, K.; Helfand, E.; Davis, D. D.; Quan, X.; Patel, S. S.; Smith, S. D. *Macromolecules* **1991**, *24*, 6546−6548.
(15) Thurn-Albrecht, T.; DeRouchey, J.; Russell, T. P.; Jaeger, H. M. *Macromolecules* **2000**, *33*, 3250−3253.
(16) DeRouchey, J.; Thurn-Albrecht, T.; Russell, T. P.; Kolb, R. *Macromolecules* **2004**, *37*, 2538−2543.
(17) Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. *Nature* **2003**, *424*, 411−414.

10.1021/cm050455t CCC: $30.25 © 2005 American Chemical Society
Published on Web 05/24/2005

Scheme 1



metric axes of a highly ordered pyrolytic graphite surface, and this orientation propagates into the bulk phase.[20]

We have recently expanded this concept to demonstrate that order in a bulk polymer mesophase can also propagate from the surface of suspended nanorod templates. Single-walled carbon nanotubes (SWNTs) that were suspended in the columnar LCP **1** were shown to template local alignment of self-assembled columns of polymer in the hexagonal phase.[21] As the LCP−SWNT composite was cooled from the isotropic melt below the liquid-crystallization transition temperature (T_{LC}), the nanorods induced coaxial growth of uniform, ellipsoidal domains with an orientation determined by the direction of the SWNT seed. The local aligning influence was demonstrated at extremely low SWNT loading, indicating that only a small amount of SWNTs are required to template alignment in bulk material. Although cooperative alignment of nanotubes by small-molecule liquid crystals has been previously reported,[22−24] this work demonstrates that nanoscale rods could kinetically template the organization of millimeter-scale domains of anisotropic material. The dimensions of SWNTs are ideal to induce alignment in LCPs because the diameter (∼1 nm) is similar to the molecular dimensions of the polymer and the high aspect ratio ($L/d > 1000$) ensures one-dimensional templating of the surrounding mesophase. However, to translate this local influence into macroscopic alignment, the SWNT seeds must be universally aligned prior to domain growth.[25]

We report that SWNTs suspended in a columnar LCP melt can be oriented by an applied ac electric field, and that subsequent cooling of this material below T_{LC} results in coaxial seeding and global alignment of the LCP material (Scheme 1). The field strength required to achieve bulk alignment was significantly lower than what is typically applied to align other anisotropic polymer materials. In fact, the method reported here succeeded in aligning an LCP material that, in the absence of SWNTs, had failed to respond to electroalignment even at high field strengths. We propose that dispersing and orienting nanorods within anisotropic polymer melts could provide a general method for templating the orientation of the polymer in complex forms and patterns.

Experimental Section

Materials. Poly{*N*-[3,4-bis(*n*-decan-1-yloxy)benzoyl]ethyleneimine} (**1**),[26] which forms a hexagonal (ϕ_h, $p6mm$) liquid-crystalline phase between 60 and 120 °C, was synthesized ($M_n = 6300$ g/mol; PDI = 1.12), and composited with SWNTs (Carbon Nanotechnologies, Houston, TX; length 1−3 μm, diameter 0.79−1.1 nm) to form **1**·SWNT as previously described.[21] The concentration of SWNTs in the **1**·SWNT composite was determined to be 8.76×10^{-4} wt % by UV−vis spectroscopy, using a specific absorptivity of $\epsilon = 0.0286$ mg L^{-1} at $\lambda = 500$ nm.[27]

Polarized Light Microscopy (PLM). Domain formation was observed using an Olympus BX51 polarizing microscope equipped with a 1/10 λ Brace−Köhler compensator. The optical electroalignment experiments were performed using two pieces of indium tin oxide (ITO) coated glass (Delta Technologies, Stillwater, MN) attached to ultra-high-temperature single-conductor wires using a conductive epoxy (Cepoxy 1025, AIM Solder). The sample thickness was controlled with a 125 μm PTFE gasket. This cell was placed in an Instec HCS402 heat stage mounted in the microscope, and the stage temperature was controlled by an Instec STC200 heat controller. The electric field was generated by attaching the electrodes to a Hewlett-Packard 8116A function generator. The field was applied while the sample was heated to 120 °C for 15 min and then cooled to 111.0 °C at 0.1 °C/min where it was held for 5 min before being cooled to 45 °C at 0.1 °C/min.

Static Birefringence. In situ static birefringence measurements were obtained by passing vertically polarized light from a HeNe laser through the sample in the optical electroalignment cell, followed by a horizontal polarizer. The laser intensity was recorded using a photodiode placed after the horizontal polarizer. Intensity measurements were obtained throughout the same heating/cooling protocol described above for the PLM experiments.

Wide-Angle X-ray Scattering (WAXS). In situ wide-angle scattering analyses were performed on a Bruker AXS microdiffractometer using Cu Kα radiation ($\lambda = 1.542$ Å) from a 2.2 kW sealed source operating at 40 kW and 18 mA. A fixed laser pointer and video microscope allowed for precise alignment of the heat-stage aperture with the X-ray beam. The electroalignment cell consisted of two pieces of 125 μm thick, carbon-black-filled PTFE (DeWal, Saunderstown, RI) attached to the function generator by alligator clips. An unfilled piece of PTFE between the two conductive sheets acted as a spacer and prevented electrical contact. The heating elements were covered by 1 mil adhesive Kapton (Bertech, Torrance, CA) to prevent electrical contact while the heat was allowed to conduct. The heat stage was aligned with the beam such that the beam and electric field lines were parallel. The primary beam was collimated to 500 μm. Scattering patterns were collected at a sample to detector distance of 30 cm with a multiwire two-dimensional area detector (Siemens Hi-star). The electroalignment cell did not account for any noticeable scattering or attenuation of the incident X-ray beam.

---

(18) Rockford, L.; Liu, Y.; Mansky, P.; Russell, T. P.; Yoon, M.; Mochrie, S. G. J. *Phys. Rev. Lett.* **1999**, *82*, 2602−2605.

(19) Rockford, L.; Mochrie, S. G. J.; Russell, T. P. *Macromolecules* **2001**, *34*, 1487−1492.

(20) Schoenherr, H.; Manickam, M.; Kumar, S. *Langmuir* **2002**, *18*, 7082−7085.

(21) Mrozek, R. A.; Kim, B.-S.; Holmberg, V. C.; Taton, T. A. *Nano Lett.* **2003**, *3*, 1665−1669.

(22) Lynch, M. D.; Patrick, D. L. *Nano Lett.* **2002**, *2*, 1197−1201.

(23) Dierking, I.; Scalia, G.; Morales, P.; LeClere, D. *Adv. Mater.* **2004**, *16*, 865−869.

(24) Dierking, I.; Scalia, G.; Morales, P. *J. Appl. Phys.* **2005**, *97*, 044309/044301−044309/044305.

(25) SWNTs have been previously aligned in LCPs: Courty, S.; Mine, J.; Tajbakhsh, A. R.; Terentjev, E. M. *Europhys. Lett.* **2003**, *64*, 654−660. Naciri, J.; Srinivasan, A.; Jeon, H.; Nikolov, N.; Keller, P.; Ratna, B. R. *Macromolecules* **2003**, *36*, 8499−8505.

(26) Percec, V.; Holerca, M. N.; Magonov, S. N.; Yeardley, D. J. P.; Ungar, G.; Duan, H.; Hudson, S. D. *Biomacromolecules* **2001**, *2*, 706−728.

(27) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, 193−194.

Results

A primary aim of this work was to apply an electric field to orient SWNTs by dielectrophoresis[28,29] in the LCP melt, prior to cooling the material and seeding domains. Previous work has shown that applying a dc[30] or ac[31] field across a suspension of SWNTs will align the tubes in the direction of the applied field. This effect has been used to orient SWNTs to cross an electrical gap[31] or to direct SWNTs in suspension to the end of STM tips.[32] In the case of a carbon nanotube in a viscous polymer, the aligning field must be strong enough to counteract the rotational rediffusion of the tube. Using Ruoff's expression for the electric field required to overcome Brownian motion in a nonconductive medium (and assuming $\epsilon = 2.5$),[33] a conductive nanoscale rod with a diameter of 1 nm and a length of 3 μm would require a minimum field strength of ~90 V/cm, regardless of viscosity.[34] Although the polymer viscosity does not determine the required field, it does determine the rod alignment time. We estimated that a uniform field of 480 V/cm applied over ~40 min would be sufficient to orient an SWNT suspended in a polymer with a viscosity of 30 Pa•s.[33,34] Electrophoretic migration of the nanotubes toward the electrodes was minimized by applying an ac rather than a dc field,[35] and the parallel-plate electrode geometry ensured field homogeneity. Frequencies in the megahertz range have been reported to have different influences on metallic and semiconducting SWNTs,[36] so only frequencies below this range were studied.

The orientation of nanotube-templated LCP domains was first characterized by polarized light microscopy, where the observation and applied field axes were the same. Under these conditions we expected both the electroaligned SWNT seeds and the resulting ellipsoidal LCP domains to be oriented along this vertical axis. We anticipated that, in contrast to our previous observations of elliptical, highly birefringent domains of **1**•SWNT perpendicular to the viewing axis,[21] vertically aligned domains would appear circular and faint (nonbirefringent) under the polarized light microscope. In the absence of an applied field, domains formed in the electroalignment cell looked similar to those previously reported (Figure 1a–c).[21] On the other hand, when a 480 V/cm, 80 kHz ac field was applied to a 125 μm thick sample of **1**•SWNT, the domains that formed below T_{LC} appeared extremely faint, circular, and mostly uniformly light or dark (Figure 1d–f). The shade of the domains could be switched between light and dark, or made to disappear, by rotating the sample, indicating that the domains were closely but not perfectly aligned with the optical axis.[34] Over time, these domains continued to grow into one another until all isotropic regions of the sample had become weakly birefringent (Figure 2). Near the end of the phase transition, bright elongated domains were also observed. By varying the focal plane of the microscope, we determined that these domains were located near the top or bottom sample surface, and were presumably templated by SWNTs that migrated toward the electrodes and lay flat on the Kapton film. Even though a uniform field should not have induced electro-

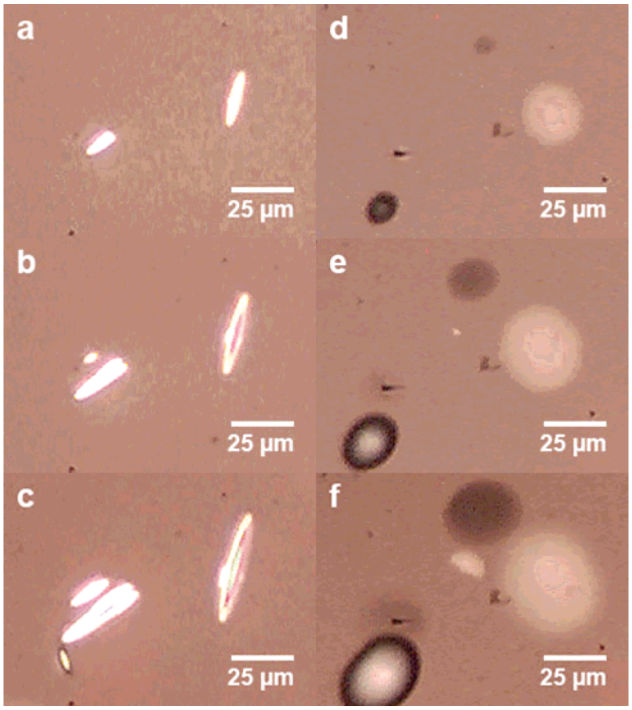


Figure 1. PLM images of **1**•SWNT cooled below T_{LC} without an applied field (a–c) and with an applied ac field of 6.0 V and 80 kHz (d–f). Images in each series were collected 1 min apart. Contrast is enhanced in these images due to the optical influence of a Brace–Köhler compensator placed in the optical train. The compensator also causes the isotropic material surrounding the domains to appear gray (rather than black).

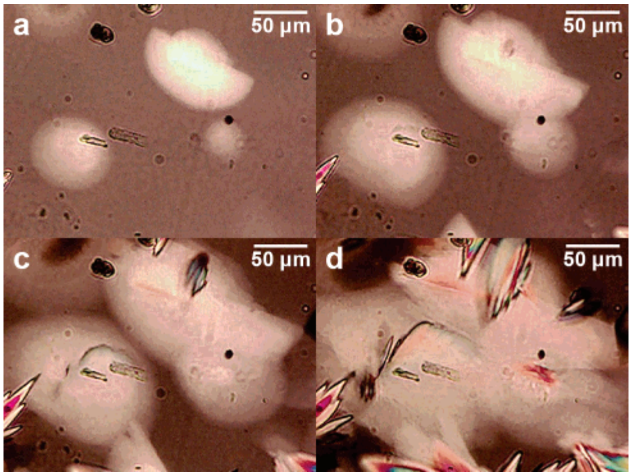


Figure 2. PLM images of a **1**•SWNT sample cooled from isotropic at 0.1 °C/min to 110.8 °C: (a) 120 s, (b) 240 s, (c) 360 s, and (d) 600 s after initial domain nucleation was observed. The small needle-shaped domains that gradually grow above the large white domains are brighter and more brightly colored because their perpendicular orientation maximizes birefringence ($n_x - n_y$).

---

(28) Jones, T. B. *Electromechanics of Particles*; Cambridge University Press: New York, 1995.

(29) Benedict, L. X.; Louie, S. G.; Cohen, M. L. *Phys. Rev. B: Condens. Matter* **1995**, *52*, 8541–8549.

(30) Yamamoto, K.; Akita, S.; Nakayama, Y. *Jpn. J. Appl. Phys., Part 2* **1996**, *35*, L917–L918.

(31) Krupke, R.; Hennrich, F.; Weber, H. B.; Beckmann, D.; Hampe, O.; Malik, S.; Kappes, M. M.; von Loehneysen, H. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *76*, 397–400.

(32) Tang, J.; Gao, B.; Geng, H.; Velev, O. D.; Qin, L.-C.; Zhou, O. *Adv. Mater.* **2003**, *15*, 1352–1355.

(33) Hsu, H.-Y.; Sharma, N.; Ruoff R. S.; Patankar, N. A. *Nanotechnology* **2005**, *16*, 312–319.

(34) See the Supporting Information for further details.

(35) Chen, X. Q.; Saito, T.; Yamada, H.; Matsushige, K. *Appl. Phys. Lett.* **2001**, *78*, 3714–3716.

(36) Krupke, R.; Hennrich, F.; Kappes, M. M.; von Loehneysen, H. *Nano Lett.* **2004**, *4*, 1395–1399.

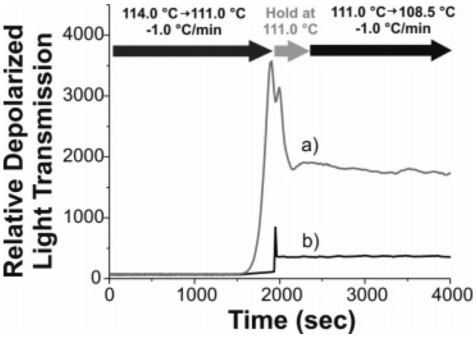


Figure 3. Time-resolved static birefringence of **1**·SWNT as the material is cooled through T_{LC} (a) without an applied field and (b) with an applied field of 6.0 V and 80 kHz. The sharp peak in each graph is attributed to the domain growth passing through the size that produces the maximum phase difference.[38]

phoretic migration of the dispersed SWNT seeds, migration of SWNTs in a uniform ac field has been previously observed,[37] and here appears to have been confined to the edges of the material.

The majority of **1**·SWNT material appeared to have been aligned by the effect of the dispersed, field-oriented nanotubes. By contrast, the pure LCP **1** was not observably aligned by any applied field strength or frequency,[34] and exhibited the characteristic radial growth pattern previously reported.[26] Other dispersed nucleants, such as 2.30×10^{-4} wt % spherical carbon black, reinforced radial growth regardless of whether a field was applied.[34] Electroalignment of **1**·SWNT was observed over a range of applied field strengths, between 300 and 800 V/cm. For applied fields below this range, samples looked identical to those which experienced no applied field. Above this range, all domains appeared to be seeded by nanotubes that had been attracted to the electrode surfaces. Alignment was also observed for a wide range of frequencies, from 1 Hz to 800 kHz, though the amount of time required to align the seeds varied over this range.

To characterize macroscopic alignment in field-oriented **1**·SWNT, bulk birefringence of a 4 mm^2 region of the electroalignment cell was monitored as the sample was cooled. On the basis of our microscope images, this volume should contain approximately 1000 seeded domains. As indicated above in Figure 1, the collective birefringence of these domains should be minimized when aligned parallel to the optical axis. The total birefringence of the sample along the axis of the applied field was roughly 4 times lower when a field was applied than in the absence of a field (Figure 3). If we assume that domains are randomly oriented in the absence of a field, but aligned either parallel or perpendicular to the optical axis after a field is applied (consistent with the microscope images in Figures 1 and 2), then over 80% of the material in the field-oriented sample is vertically aligned.[34]

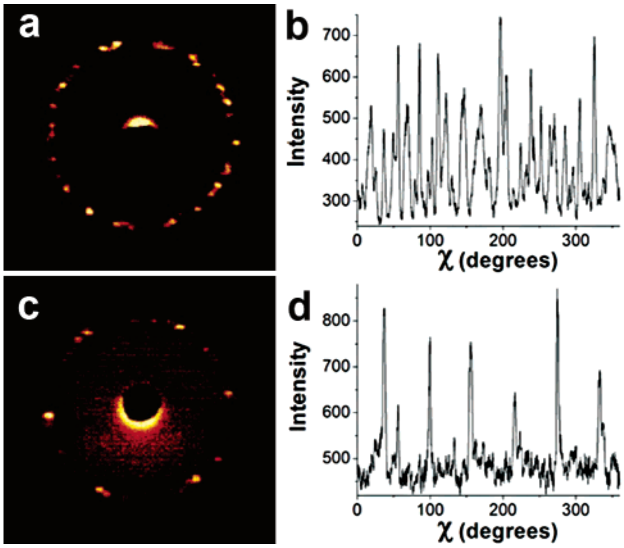


Figure 4. (a) In situ WAXS pattern of **1**·SWNT cooled without an applied field. The radius of observed scattering corresponds to a *d*-spacing of 3.4 nm, consistent with that of pure **1**.[26] (b) Scattering intensity as a function of azimuthal angle χ for image a. (c) In situ WAXS pattern of **1**·SWNT cooled under an applied field of 6.0 V and 80 kHz. (d) Angle-dependent scattering intensity for image c.

The growth and orientation of LCP domains were also monitored by WAXS. For these experiments, the same electroalignment cell used for polarized light microscopy and bulk birefringence was mounted in the X-ray line with coincident beam and applied field axes, and the same temperature program was used. The collimated X-ray beam size (0.25 mm^2) in these experiments was large enough that one or more domains could contribute to the observed scattering pattern. We anticipated that, as is typical for hexagonal columnar phases, scattering peaks with 2-fold radial symmetry should be observed for homogeneously oriented domains perpendicular to the beam axis and 6-fold symmetry for domains parallel to this axis. Pure LCP **1**, in the absence of SWNTs, exhibited a radially isotropic scattering pattern on being cooled below T_{LC}, regardless of whether a field was applied or not.[34] This observation is consistent with the fan-shaped and spherulitic textures observed by polarized light microscopy for this material. WAXS patterns from composite **1**·SWNT, on the other hand, developed multiple sharp peaks as the sample was cooled below 113.0 °C that could be ascribed to homogeneously oriented liquid-crystalline domains. In the absence of an applied field, the density of peaks (and presumably domains) was high enough that it was difficult to pair them or assign symmetry or direction to the component domains (Figure 4a). Presumably, the domains observed in these experiments were randomly oriented as observed previously by polarized light microscopy.[21]

When a 480 V/cm, 60 kHz field was applied to **1**·SWNT as it was cooled from the isotropic phase, the scattering profiles contained sharp peaks with unmistakable 6-fold symmetry (Figure 4b). We attribute this pattern to the hexagonal packing of cylinders in a single growing domain parallel to the X-ray beam. These 6-fold symmetric patterns were observed consistently for electroaligned samples of **1**·SWNT, and were never observed for any samples of **1** or for **1**·SWNT without an applied field. Symmetric peaks were also not observed for **1** composited with other nucleants such as carbon black.[34] The unequal peak intensities in Figure 4b are probably due to slight tilting or misalignment of the symmetry axis relative to the beam.[39,40] The 6-fold symmetry

---

(37) Bubke, K.; Gnewuch, H.; Hempstead, M.; Hammer, J.; Green, M. L. H. *Appl. Phys. Lett.* **1997**, *71*, 1906−1908.

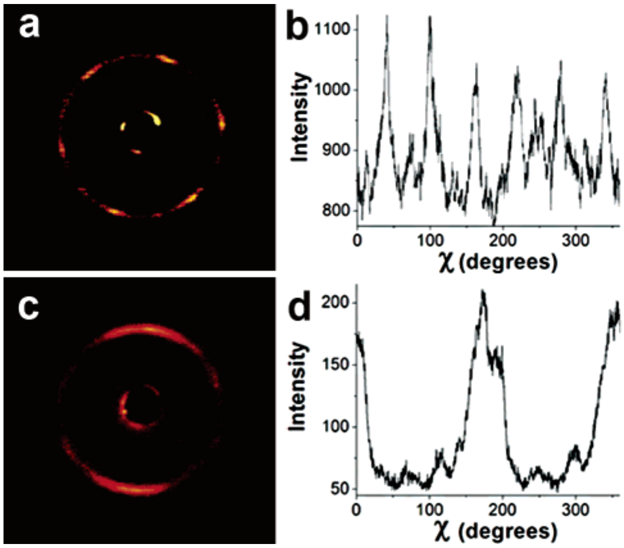


Figure 5. X-ray scattering data from an electroaligned sample cooled to room temperature, with the alignment axis (a) parallel to the X-ray beam and (c) tilted 65° with respect to the X-ray beam. (b, d) Scattering intensity as a function of azimuthal angle χ for images a and c, respectively. Of eight samples tested, seven samples produced a hexagonal pattern. All samples exhibited a 2-fold pattern upon rotation.

pattern persisted throughout the cooling process and was still observed at room temperature, although the background scattering signal had increased and the peaks had broadened.[34] As expected, tilting these samples with respect to the incident X-ray beam produced WAXS patterns with 2-fold symmetry that reached maximum intensities at large tilt angles (Figure 5). These data confirm that orienting SWNT seeds dispersed in **1** with an applied ac electric field results in large, homogeneous LC domains that are primarily oriented along the field axis.

Conclusion

In conclusion, we have demonstrated that applying an electric field to preorient SWNTs dispersed in a model LCP melt results in domain formation parallel to the electric field. Macroscopic alignment was achieved using a low-voltage electric field and an extremely small concentration of dispersed SWNT seeds. We anticipate that this method may apply to other polymers that cannot be aligned by melt dielectrophoresis or that are oriented only under large field strengths.[41] We are currently investigating SWNT alignment of other materials, including nematic-phase liquid-crystalline polymers and anisotropic block copolymers, in which complementary assembly of materials and nanorods leads to templated structural and physical anisotropy.

Acknowledgment. This work was supported by the Research Corp. (Research Innovation Award RI0964) and the University of Minnesota. We thank Thomas Chastek and Jeffrey Haley for help with the static birefringence experiments and Gary Mrozek for designing and constructing the x-ray sample holder.

Supporting Information Available: Field-strength calculations, additional PLM and WAXS data, and static birefringence calibration (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

CM050455T

---

(38) Dierking, I. *Textures of liquid crystals*; Wiley-VCH: Weinheim, Germany, 2003.

(39) Loo, Y.-L.; Register, R. A.; Adamson, D. H. *Macromolecules* **2000**, *33*, 8361−8366.

(40) Imperor-Clerc, M.; Davidson, P. *Eur. Phys. J. B* **1999**, *9*, 93−104.

(41) Boeker, A.; Knoll, A.; Elbs, H.; Abetz, V.; Mueller, A. H. E.; Krausch, G. *Macromolecules* **2002**, *35*, 1319−1325.