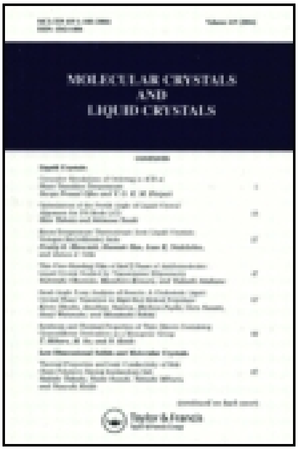

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Parallel Alignment of Poly-γ-Benzyl-Glutamate Nematic Liquid Crystal at a Solid Surface

Victor G. Taratuta [a] , George M. Srajer [a] & Robert B. Meyer [a]

[a] Department of Physics, Brandeis University, Waltham, MA, 02254

Version of record first published: 20 Apr 2011.

To cite this article: Victor G. Taratuta , George M. Srajer & Robert B. Meyer (1985): Parallel Alignment of Poly-γ-Benzyl-Glutamate Nematic Liquid Crystal at a Solid Surface, Molecular Crystals and Liquid Crystals, 116:3-4, 245-252

To link to this article: http://dx.doi.org/10.1080/00268948508074576

Mol. Cryst. Liq. Cryst., 1985, Vol. 116, pp. 245–252
0026-8941/85/1164-0245/$15.00/0

Printed in the United States of America

Parallel Alignment of Poly-γ-Benzyl-Glutamate Nematic Liquid Crystal at a Solid Surface

VICTOR G. TARATUTA, GEORGE M. SRAJER and ROBERT B. MEYER
Department of Physics, Brandeis University, Waltham, MA 02254

(*Received June 5, 1984*)

We have developed a simple practical method of producing large single crystalline nematic samples of poly-γ-benzyl-glutamate aligned parallel on glass or quartz substrates. The substrates were plasma coated with a thin polyethylene film and the sample was then aligned in a 10 K Gauss magnetic field. This produced very uniformly aligned parallel samples with the direction of alignment determined by the magnetic field. The uniformity of the alignment is enhanced by silicon monoxide evaporated obliquely on the substrates prior to coating with polyethylene. The characterization of the polyethylene coating is given, and the properties of the resulting surface are described.

I. INTRODUCTION

The importance of polymer liquid crystals has been widely recognized due to both a fundamental interest in these novel physical systems, and important new technological applications, such as the successful spinning of high modulus fibers from nematic melts and solution.

Poly-γ-benzyl-L-glutamate (PBLG), which belongs to the class of synthetic polypeptides, is a very well characterized macromolecular liquid crystal. It forms a very good model system for the study of these materials due to the inherent rigidity of the molecules in their α-helical conformation, its ready availability in a wide range of mo-

---

PACS numbers: 61.30.Eb, 61.30.Gd, 81.20.Sh

lecular weights, the existence of a number of solvents in which it forms a liquid crystal, and its well-known phase diagram.

There have been a number of experiments proposed to study the elastic and hydrodynamic properties of polymer nematic liquid crystals,[1] but few systematic experimental data have appeared in the literature so far.[2]

The alignment of a nematic liquid crystal at a surface is an important subject. For very long chain polymer nematics it has been argued[3] that the director must be parallel to the surface: for long molecules, condensing many ends at the surface costs a lot of entropy and is therefore unlikely unless there is a strong binding energy for ends at the surface.

For poly(P-benzamide) published photographs suggest that the director is parallel to glass and fluid surfaces.[4,5] For PBLG the previous experiments[6] indicate that all of the standard procedures for producing parallel surface alignment, that proved successful in low molecular weight liquid crystals, have yielded the homeotropic alignment only. This is probably due to some surface binding of the polymer ends.

In the specific case of PBLG we speculate that this is a hydrogen bonding of N—H or C = 0 groups of the amino acid residues at oxide surfaces. To circumvent this problem we attempted coating the substrates with a non-hydrogen bonding polymer layer. Some of the earlier observations[3] indicate that PBLG molecules aligned parallel at a teflon gasket in our samples. The alignment also appeared to be parallel at polyimide coatings spun onto glass substrates.

A technique which allows a greater control over experimental conditions is a vacuum plasma deposition of polymer films. Here a variety of possibilities in the choice of reagent materials exists. We attempted using trifluoromethane (CHF_3) and ethylene (C_2H_4) gases, although other fluorocarbon and hydrocarbon compounds can be explored. Some preliminary observations with CHF_3 suggested a parallel alignment. However, we did not explore this material systematically, since excitation processes in CHF_3 produce highly corrosive species that tend to do a lot of damage to the vacuum system.

This paper reports the successful use of plasma polymerized polyethylene films in producing large single-cyrstalline parallel nematic samples of PBLG, which are often required in specific experimental situations. Our result, therefore, will be immediately useful in many experiments, such as laser light scattering, magnetic and electric field experiments, and flow experiments, as well as in understanding fundamental alignment effects in PBLG.

II. SAMPLE PREPARATION

To obtain a polyethylene coating a chemical purity ethylene gas (Matheson Company product) is polymerized by a glow discharge using inductively coupled RF plasma in a vacuum chamber. The apparatus used is a modified PDS/PDE 500 model of LFE Corporation, originally designed for plasma etching of semiconductor materials. The RF source, a crystal controlled radio frequency generator operating at 13.56 MHz, is connected to a 4 inch long RF coil through an impedance matching network. A cylindrical quartz vacuum chamber, 4 inches in diameter by 8 inches long is positioned inside the coil. The chamber is equipped with a quartz viewing window in the front, vacuum sealed with a silicone rubber gasket during operation. A standard mechanical vacuum pump is connected via a 0.5 inch adapter in the back of the chamber. The total output power of the RF generator is continuously adjustable from 0 to 500 Watts. However, any low power RF generator can be used for this application, as seen from the power requirements below.

The glass substrates are precleaned in soap solution using an ultrasonic cleaner, rinsed in running distilled water, dried with nitrogen gas and placed at the bottom of the vacuum chamber. The substrates are finally cleaned using oxygen burning in glow discharge by flowing air through the chamber. This dehydrates the surfaces of the substrates and improves adhesion properties of the polyethylene film. This procedure typically requires several minutes at the following condition:

a) pressure of 100 to 200 mTorr,
b) total RF power of 10 to 20 W,
c) air flow rate of 2 to 4 cm^3/min (measured at one atmosphere).

The chamber is then evacuated to a pressure of 30 mTorr or less; it is essential that the partial air pressure be sufficiently low, as higher contents of oxygen during a polymerization reaction produce coatings of inferior quality. Ethylene gas is introduced into the chamber through four manifolds with many jets which results in a uniform gas flow distribution (this may not be important; it is the structure of our commercially produced chamber). The flow rate is controlled by an Aalborg Corporation flow meter equipped with a micrometer driven needle valve. The flow rate, measured at atmospheric pressure, is adjustable from 0 to 27 cm^3/min. The optimized conditions for the glow discharge polymerization reaction of ethylene are as follows:

a) Pressure of 500 mTorr (during the discharge the pressure increase to 700 mTorr,

b) Total RF power of 2.5 W, which corresponds to RF power density of 10 mW/cm^3,

c) Steady flow of ethylene gas through the chamber at a rate of 2 cm^3/min.

At these conditions the polyethylene film deposition proceeds at a rate of roughly 100 Å per minute as determined by measurements described below. It should be noted that there is no handling of the substrates involved between the final stage of cleaning in the vacuum chamber and polymer deposition, which improves the effectiveness of cleaning.

The films produced are distinctly hydrophobic, optically transparent and are clearly visible on a substrate as their reflectivity is different from that of glass or quartz. According to the literature,[7] plasma-polymerized ethylene forms highly crosslinked coatings that were found to be insoluble and mechanically very stable.

The film thickness was accurately measured by optical interferometry. A part of the substrate is masked off with a thin microscope cover glass, such that there is a sharp boundary between coated and uncoated parts of the substrate. A small wedge of about 0.25° is introduced between the hybrid substrate and an optical flat. Fizeau wedge interference fringes of equal thickness[8] are visible under a microscope with monochromatic illumination. The fringes are localized in the plane of the substrate and can be seen in reflection or transmission. The film thickness is determined by observing a shift in the interference fringes across the boundary between the unmasked and masked areas on the substrate.

We were able to produce mechanically stable films in the thickness range from 100 Å to 3000 Å. At high thicknesses the films become optically less transparent with a characteristic yellowish color, but they are clearly still suitable for optical work.

In addition to polymer coatings applied directly onto a substrate, we examined the use of oblique vacuum evaporation of SiO[9] in the alignment of PBLG liquid crystal. The polymer film is applied on top of the SiO layer. In low molecular weight liquid crystals it is believed that an irregular surface structure with a streaky texture in one direction, created by oblique SiO evaporation, is responsible for the unidirectional alignment.[10] Thus, the proposed alignment mechanism is by elastic forces. The angle of incidence of evaporant on the substrate plays an important role.[11] The aligning effect of SiO in PBLG appears to be quite different as discussed in the next section. The thickness of the SiO layer was optimized at about 1000 Å: a polyethylene film, when deposited on a thinner SiO layer, tends to obscure whatever topographic surface structure was created by the oblique SiO evaporation, while thicker SiO layers become optically opaque.

In addition, polyethylene films were deposited on indium tin oxide (ITO) surfaces. This creates interesting possibilities for electric field experiments on parallel liquid crystal samples of PBLG.

The adhesion of polyethylene to glass, SiO and ITO remained excellent and the parallel alignment of nematic samples of PBLG was repeatably reproduced within the range of thickness mentioned above.

There was evidence, however, that at thicknesses greater than 3000 Å the films became mechanically unstable. They developed internal strains and cracked. The adhesion properties of thick films became poorer as well. However, for alignment purposes the films one hundred Angstroms thick are perfectly adequate.

The polyethylene films can be removed by burning in an oxygen atmosphere in a plasma chamber, so that the substrates can be reused. Typically, the requirements for this procedure are identical to those described for oxygen plasma cleaning of substrates at the beginning of this section.

III. SAMPLE CHARACTERIZATION

Nematic samples of PBLG were assembled between two coated substrates using a 50μm thick teflon spacer and the resulting alignment was examined with a polarizing microscope. The particular liquid crystal preparation studied is a racemic mixture of left and right handed species, PBLG and PBDG, of the same molecular weight (150,000, purchased from Sigma Chemical Company). To aid in suppressing a cholesteric pitch, a solvent mixture composed of 20% dioxane and 80% methylene chloride is used.[12] The concentration range studied is 16% to 20% polymer by weight.

Two cases of interest arise, distinguished by the absence or presence of an aligning magnetic field. Each of these cases is further detailed by the use of oblique vacuum evaporation of SiO.

i) No aligning magnetic field:

In the course of several hours the samples develop a pattern consisting of large areas with the director varying only very smoothly within each. Typically, these areas are 1 mm in size, but occasionally the whole sample assumes an almost unidirectional alignment. In cases where oblique SiO evaporation is used, we observe a similar pattern in which the director is aligned arbitrarily and not, in general, in the direction one might expect to be imposed by the SiO. This is in sharp contrast to the behavior observed in low molecular weight nematics. For example, in the absence of any surface treatment, MBBA adheres to the surface as many randomly oriented domains typically 1 to 10 μm in size. The time scale for this process is very short. In PBLG, on the other hand, reaching an equilibrum requires typically one hour. An irregular array of disclinations is formed initially on filling the cell. They slowly anneal away with a few disclination lines localized at the surface ultimately remaining. These form the boundaries between the areas of essentially uniform alignment. The final alignment does not appear to be influenced by the inital flow pattern generated by filling the cell.

ii) Samples aligned in the magnetic field:

Freshly assembled samples of PBLG nematic liquid crystal were immediately placed in a 10 kGauss magnetic field until completely aligned, which typically required half an hour to one hour. The samples were then left out of the field for long periods of time. Although the initial uniformity of the alignment produced by the magnetic field was somewhat diminished by thermal fluctuation, the samples remained very well aligned in the direction of the field. A layer of obliquely deposited SiO underneath the polyethylene coating definitely improves the uniformity of alignment of the PBLG nematic single crystal when used in combination with an aligning magnetic field.

The anchoring condition of PBLG molecules at the polyethylene surface was examined by putting a well aligned sample in a magnetic field whose direction was oblique to that of the initial alignment. It was found in all cases that the samples that were realigned in the field in this way restored their initial alignment within a short time, typically one hour, after being removed from the magnet. We conclude that a unique surface orientation of the director at the polyethylene surface develops after the initial (approximately one hour) stage of the alignment, perhaps due to some specific bonding of PBLG molecules. This occurs regardless of the use of the magnetic field in aligning the liquid crystal initially.

The experiments described above were done with polished glass substrates. We repeated them using float glass, which has a molecularly smooth surface, to test the idea that the unusually large areas of uniform alignment observed in our samples could perhaps be attributed to polishing. The result was negative: the general appearance of these samples was identical to that observed on polished glass substrates. Also, the unique surface orientation developed after initial alignment. The other interesting extreme, the "slippery" boundary condition, was not achieved in our experiments.

The unique surface orientation appears to be independent of the use of oblique evaporation of SiO. The published electron micrographs of obliquely evaporated SiO films[13] suggests a topographically rough surface, at which the preferred direction is defined only very poorly. The role of the aligning magnetic field is, perhaps, to hold the molecules in a single orientation at the surface such that they get "locked" in that direction, which produces a superior uniformity of the alignment. The unique surface orientation therefore, is not purely an elastic effect due to the interaction of the liquid crystal with the inhomogeneous surface, but rather it is most likely explained by some specific bonding of PBLG molecules.

To summarize, we can conclude that PBLG liquid crystals align parallel at plasma deposited polyethylene films, and that the surface orientation becomes unique after some initial period. The unusually large areas of spontaneous uniform alignment, the anomalously long periods of time required for the unique surface orientation to develop, and the nature of the surface interaction of PBLG molecules remain important issues we do not yet understand.

As a practical matter, the best quality parallel nematic single crystal of PBLG is achieved by using a combination of oblique vacuum deposition of SiO and an aligning magnetic field applied immediately after filling the sample.

Acknowledgments

The authors are grateful to the Crystal International Corporation for providing samples of float glass.

This research was supported in part by the National Science Foundation through grant No. DMR82-10477, and by the Martin Fisher School of Physics at Brandeis University. One of us (V. G. T.) is grateful to Sony Corporation for support through a Summer Research Fellowship.

References

1. R. B. Meyer in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, Robert B. Meyer (New York, Academic, 1982) pp. 155-163.

2. D. L. Patel and D. B. Dupré, *J. Chem. Phys.* **72**, p 2525 (1980).
3. R. B. Meyer in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, Robert B. Meyer (New York, Academic, 1982) pp. 147-150.
4. P. W. Morgan, *Macromolecules* **10**, p. 1381 (1977).
5. M. Panar and L. F. Beste, *Macromolecules*, **10**, p. 1401 (1977).
6. Donald B. Dupré in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, Robert B. Meyer (New York, Academic, 1982) pp. 165-200.
7. M. Millard in *Thin Film Processes*, edited by J. L. Vossen and W. Kern (New York, Academic, 1978) pp. 177-209.
8. S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films*, (Oxford University Press, 1979).
9. J. L. Janning, *Appl. Phys. Lett.* **41**, p. 73 (1972).
10. D. Berreman, *Phys. Rev. Lett.* **28**, p. 1683 (1972).
11. Jacques Cognard, *Mol. Cryst. Liq. Cryst.*, Supplement 1, p. 1 (1982).
12. Conmar Robinson, *Tetrahedron* **13**, p. 219 (1961).
13. T. Wilson et al., *Mol. Cryst. Liq. Cryst.* **94**, p. 359 (1982).