

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Conducting Polymers as Alignment Layers and Patterned Electrodes for Twisted Nematic Liquid Crystal Displays				5. FUNDING NUMBERS Grant N00014-94-1-0270 R & T Code 31321 01 Kenneth Wynne	
6. AUTHOR(S) Jerome BI Lando, J. Adin Mann, Jr., Andy Chang, Chin-Jen S. Tseng, David Johnson					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Case Western Reserve University, Department of Macromolecular Science and Department of Chemical Engineering, Cleveland, OH 44106, and Kent State University, Department of Physics, Kent, OH 44242				8. PERFORMING ORGANIZATION REPORT NUMBER 10	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800North Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Initial work was performed on the preparation of poly(p-phenylene vinylene) and poly(p-phenylene) alignment layers for twisted nematic liquid crystal displays. Soluble precursor amphiphilic polymers, spread at the gas-water interface, were aligned during Langmuir-Blodgett deposition. The structure or the precursor multilayers has been investigated before and after curing of the multilayers to the desired polymers. Initial tests have indicated that the precursor multilayers are good alignment layers for liquid crystal displays.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT UL	

19960418 071

CONDUCTING POLYMERS AS ALIGNMENT LAYERS AND PATTERNED ELECTRODES FOR TWISTED NEMATIC LIQUID CRYSTAL DISPLAYS

*Jerome B. Lando, Case Western Reserve University
J. Adin Mann, Jr. Case Western Reserve University
Andy Chang, Case Western Reserve University
Chin-Jen S. Tseng, Case Western Reserve University
David Johnson, Kent State University*

Abstract

Initial work was performed on the preparation of poly(p-phenylene vinylene) and poly(p-phenylene) alignment layers for twisted nematic liquid crystal displays. Soluble precursor amphiphilic polymers, spread at the gas-water interface, were aligned during Langmuir-Blodgett deposition. The structure of the precursor multilayers has been investigated before and after curing of the multilayers to the desired polymers. Initial tests have indicated that the precursor multilayers are good alignment layers for liquid crystal displays.

Introduction

The construction and basic operation of TN displays is illustrated in Figure 1. The upper and lower substrate plates carry patterned, transparent conductive coatings of Indium-Tin Oxide (ITO) on their inner surfaces. In general, the transparent electrodes have a thin polyimide coating several hundred angstroms thick that is unidirectionally rubbed to align the local optic axis (director) of the liquid crystal at the surface parallel to the rubbing direction. The upper substrate is rubbed at right angles to the rubbing direction of the lower substrate. Thus, in the inactive state (off), the local liquid crystal director undergoes a continuous 90° twist in the region between the substrates. Polarizers sheets are laminated on the outside of the plates so that the direction of vibration of the linear polarized light is parallel to the rubbing direction of the adjacent alignment layer of each substrate. The linear polarized light from the upper polarizer propagates through the layer, rotates its plane of polarization in step with the twisted structure, and emerges at the bottom of the layer polarized parallel to the transmission axis of the lower polarizer. Applying an electric field across the upper and lower electrodes orients the optic axis in the central portion of the LC layer predominantly parallel to the electric field and the twisted structure disappears (on). The polarization direction of the light is no longer rotated and light passing through the cell intersects the second polarizer in the crossed position where it is absorbed, causing the activated portion of the display to appear dark.

We have successfully prepared ultrathin polyimide alignment layers by utilizing the dipping

direction in Langmuir-Blodgett film formation to orient a soluble low T_g precursor polyamic acid, which forms a monolayer at the gas-water interface. Subsequent to deposition of the precursor polymer the oriented multilayer is converted to oriented polyimide.^(1,2) Such alignment layers eliminate the disadvantages inherent in the rubbing technique, which is used commercially at present.

In the present work we intend to eliminate the Indium, Tin Oxide (ITO) electrodes by utilizing dopable conducting polymers as alignment layers. In the present work precursor polymers, which can be converted to the desired conducting polymers after orientation during Langmuir-Blodgett deposition, are again utilized.

Experimental

Materials. The precursor polymer shown in figure 2 poly(p-xylylene- α -diethylsulfonium chloride) was synthesized for this study by Kakimoto. 0.5 mMol solutions of the precursor were prepared by mixing equal amounts of the poly-sulphonium salt with sodium perfluorononanoate in 1:1 EtOH:1,1,1 trichloroethane solution. After formation of precursor multilayers conversion to poly(p-phenylene vinylene) (PPV) was attempted by thermal treatment (2,3) for seven or more hours at 235°C.

The precursor polymer for poly(p-phenylene) (PPP) poly(2,5-dicarboxyl-1,4-phenylene)(PDCP) was provided by Professor Virgil Percec. The tertiary amine o,o',o"- trihexadecanoyltriethanolamine used for salt formation was provided by Kakimoto (1). See figure 3.

PDCP was dissolved in DMSO (dimethyl sulfoxide) and tertiary amine was dissolved in DMAc (dimethyl acetamide). Mixing the above solutions with benzene, the PDCP precursor salt was obtained such that 50% of the carboxyl group are substituted with tertiary amine in the ideal case.

The spreading solution was mixed DMSO, DMAc and Benzene in a volume ration of 1:1:2 respectively. The PDCP precursor (salt) concentration was 0.770 mg/ml.

After multilayer formation side chain removal was attempted by a combination of chemical treatment followed by heat treatment.

Deposition substrates were fused quartz, needed for UV spectra, glass slides, Ge, ZnSe and Si.

Description of Methods

Formation of Monolayers and Multilayers.

Monolayer manipulations were performed on a commercial Lauda film balance that employs the floating barrier method of measuring surface pressure. The brass trough was coated with Teflon. An IBM PC was interfaced with the film balance for data acquisition and processing. All the isotherm collection and deposition experiments were done in class 10 laminar flow areas inside a class 100 clean room. Subphase water was obtained from a Millipore water system. In addition, a "shake test" of subphase water in a clean volumetric flask was used to show the complete absence of any tendency to foam; the surface tension is always within the experimental uncertainty of the literature value for pure water. Capillary ripple damping of the pure water in also checked.

Initial spreading areas were greater than $70\text{\AA}^2/\text{molecule}$ and dwell times of 10 min were used to ensure complete evaporation of the spreading solvent. Compression rates were 3.25 cm/min. The water temperature was controlled by circulating thermostated water underneath the brass trough. The temperature of the water in the trough was measured by a surface probe to a precision of $\pm 0.1^\circ\text{C}$.

Surface pressure area isotherms and compressive creep tests were performed on each of precursor films. Creep tests were performed at the temperatures and surface pressures utilized for deposition of Langmuir-Blodgett multilayers.

Multilayer deposition was accomplished for the PPP precursor at 21°C and a surface pressure of 25 mN/M, while for the PPV precursor a temperature of 13.4°C and a surface pressure of 25 mN/M were used.

Characterization. Multilayers of the precursors were investigated before and after curing treatments as a function of the number of molecular layers by X-ray diffraction (glass substrate) using a Phillips diffractometer and by UV spectroscopy (fused quartz substrate) using a Varian Cary UV - vis spectrophotometer.

Results and Discussion

Surface pressure area curves of the two precursor polymers are shown in figure 4. The compressive creep curves of the two precursors are shown in figure 5. It is clear that the PPV precursor at or near the deposition conditions (13.8°C and 25 mN/M) is far less stable at the gas-water interface than the PPP precursor at its deposition

conditions (21°C and 25mN/m). This is attributed to the fact that ideal packing of the single stranded side chains of the PPV precursor can not accommodate in the area of the head group. However, between 10°C and 15°C PPV precursor is stable to compressive creep for 30 to 60 minutes. Thus stable deposition can be obtained for both materials although it is clear from the surface pressure area curves that the modulus of the PPP precursor monolayer is much higher than that of the PPV precursor. Note that the PPP precursor is stable to compressive creep for long times.

UV (190 - 640 nm) spectra of the precursors before and after curing treatment were obtained as a function of the number of layers on the fused quartz substrate. PPP precursor films at 9, 15 and 31 layers all have two peaks, one at 245 nm and the other at 315 nm. The peak at 245 is attributed to aromatic π electron to π^* transition while the peak at 315 nm is an n electron to π^* transition from the carbonyl group. The intensity changes with the number of layers follows Beer's law. A multilayer sample was tested after treatment. No new peaks were observed.

UV spectra for the PPV precursor as a function of the number of layers were also obtained before and after curing treatment. Absorbencies for the precursor were observed at 195, 225, 260 and 325 nm. After heat treatment there are absorbencies centered at 200, 250, 330, and 390 nm. This observed shift in absorbencies to lower energy radiation would support the hypothesis that significant side chain removal takes place after heating at 235°C for 7 hours. Further heat treatments at higher temperatures for longer durations did not yield changes in the observed spectra. A plot of peak absorbency versus the number of layers shows that layer uniformity was maintained after the heat treatment. Also, Beer's law is followed before and after treatment. We suspect the peak at 390 nm corresponds to π - π^* transition that is affected by the proximity of the polymer-substrate interface since thicker samples (15 or more layers) have similar intensities. As a result the 390 nm peak was not used for the absorbance versus layers plot.

X-ray diffraction plots of the PPV precursor before and after heat treatment both show a peak intensity at $2\theta=2.6^\circ$ which corresponds to a layer thickness of 3.39 nm. This result is in agreement with the fact that deposition is occurring in well-ordered layers. In addition, the presence of the same peak after heat treatment, although reduced in intensity, shows that side chain removal is not complete. Kakimoto *et. al.* observed layer thickness to be 0.34 nm by ellipsometric techniques after heat treatment.⁽⁴⁾ We do not observe the corresponding peak at $2\theta = 26.2^\circ$, although that could be a consequence of low intensity.

X-ray diffractometry of 61 layers of the PPP precursor yielded indexing schemes as shown in Table I. In scheme A two different layer structures are assumed and in scheme B a single structure is assumed with a doubled basic

Y structure spacing of approximately 10 nm. An 11 layer sample had only the X-ray maximum at 2.56 degrees indicating a tilted structure as in scheme A. At some point (after 11 layers) in the deposition an orthogonal side chain packing occurs. Thus scheme A in Table I is correct. It should be noted that after heating the 61 layer sample at 280°C for four hours only the peak is at 2.56 degrees is present. This indicates that only layers near the multilayer upper surface had their side chains removed and/or a phase transformation occurred during treatment. Given the similar intensity of the peak at 2.56 degrees before and after treatment the former explanation is favored.

Conclusions

Langmuir-Blodgett films of both the PPV and PPP precursors have been successfully prepared. However, subsequent treatment indicates that the side chains have only been partially removed by chemical and/or thermal treatments. This work is continuing.

Acknowledgments

This work was supported by the National Science Foundation under the Science and Technology Center ALCOM DMR 89-20147 and by the Office of Naval Research under Grant No. N000 14-94-1-01270.

References

- 1) M. Kakimoto, M. Suzuki, T. Konishi, Y. Imai, M. Iwamoto and T. Hino, Chem. Lett, 823 (1986).
- 2) A. Albarici, Master of Science Thesis, "Langmuir-Blodgett Films as Alignment Layers for Twisted Nematic Liquid Crystal Displays," Case Western Reserve University, December 1994.
- 3) Y. Nishikata, M. Kakimoto, Y. Imai, J. Chem. Soc., Chem. Commun, 1040 (1988).
- 4) Y. Nishikata, M. Kakimoto, Y. Imai, J. Chem. Soc., Chem. Commun., 1042 (1988).

Figures

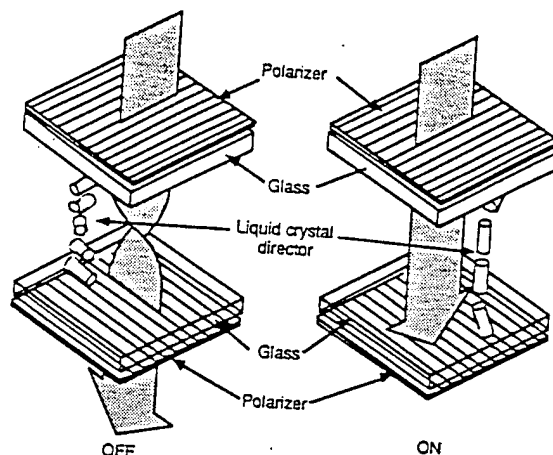


Figure 1. Construction and basic operation of a TN display.

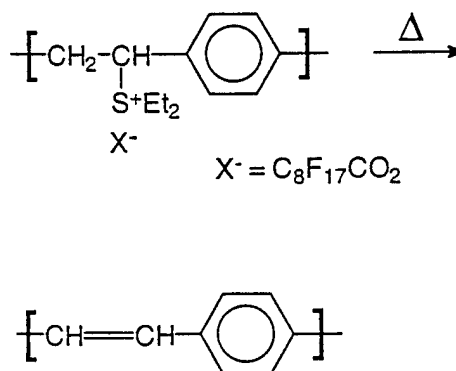


Figure 2. The conversion of precursor multilayers to PPV.

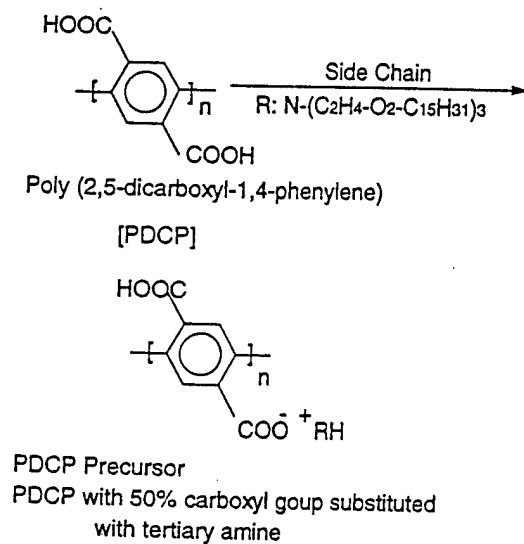


Figure 3. Salt Formation.

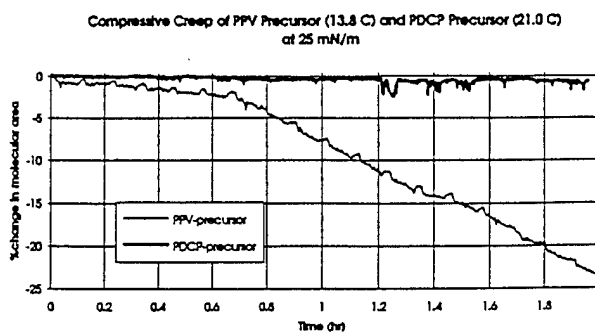


Figure 5. Compressive Creep of PPV-precursor (13.8°C) and PDCP-precursor (21°C) at mN/m

Key Words

Conducting Polymer, Alignment Layers, Langmuir-Blodgett Films

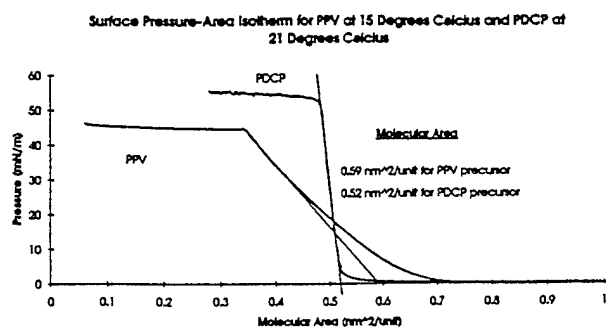


Figure 4. Surface Pressure-Area Curves for the PPV-precursor (13.4°C) and PDCP (21°C).

Table I

Anylsis From X-ray Diffraction (CuK α with λ = 0.1542 nm)

2 Theta Degrees	Relative Intensity	d-spacing nm	00l Indices A	00l Indices B
1.933	3705	4.570	001	002
2.56	993	3.451	001'	003
3.62	786	2.441	002	004
5.34	3770	1.655	003 and/or 002'	006
7.08	888	1.249	004	008

Jerome B. Lando

EDUCATION

1963, Postdoctoral research in solid state polymerization with Professor H. Morawetz, Polytechnic Institute of Brooklyn, New York.

1963, Ph.D. in Physical Chemistry (Polymer Science) with Professor H. Morawetz, Polytechnic Institute of Brooklyn, New York (1956-1963).

1953, A.B. in Chemistry, Cornell University, Ithaca, New York (1949-1953).

EXPERIENCE

12/92 - 3/93 Lady Davis Professor, Technion, Haifa, Israel.

1/87 - 6/87 Visiting Professor, Weizmann Institute of Science Rehovot, Israel, Michael Awardee.

1987 - Present Director, Polymer Microdevice Laboratory.

1985 - Present Director, Macro/EPIC.

1978 - 1985 Chairman, Department of Macromolecular Science.

1974 - Present Professor of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio.

1/74 - 6/74 Visiting Professor, University of Mainz, West Germany. Alexander Von Humboldt Senior American Scientist Awardee.

1968 - 1974 Associate Professor of Macromolecular Science, Case Institute of Technology, Cleveland, Ohio.

1965 - 1968 Assistant Professor of Polymer Science and Engineering, Case Institute of Technology, Cleveland, Ohio.

1963 - 1965 Chemist, Camille Dreyfus Laboratory, Research Triangle Institute, Durham, North Carolina.

PROFESSIONAL ASSOCIATIONS

Society of Plastics Engineers, American Chemical Society, Fellow of the American Physical Society, Editorial Board - Polymers for Advanced Technologies, Editorial Board - Journal of Composite Materials, Past Member of Editorial Board of 5 other journals.

SELECTED PUBLICATIONS

1. "Polar Polymeric Langmuir-Blodgett Films Containing Nitrobiphenyl Groups", with S.H. Ou, V. Percec and J.A. Mann, J.B. Lando, L. Zhan and K.D. Singer, *Macromolecules*, **26** 7263 (1993).

2. "Fabrication of Alternating Diacetylenic Multilayers and the Role of Subphase Condition", S.P. Walsh and J.B. Lando, *Langmuir* **10**, 246(1994).

3. "Monolayer-Properties of an Amine-Based Diacetylene", S.P. Walsh and J.B. Lando, *Langmuir*, **10**, 252 (1994).

4. "Noncentrosymmetric Langmuir-Blodgett Films Containing Nitrobiphenyl Groups", S.H. Ou, V. Percec, J.A. Mann and J.B. Lando, *Langmuir*, **10**, 905 (1994).

5. "Long Period Structure of Langmuir-Blodgett Multilayer Assemblies", S.P. Walsh and J.B. Lando, *Mol. Cryst. Liq. Cryst.*, **240**, 201 (1994).