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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	2/19/95	Final 1 Aug 91 - 31 Jul 94

4. TITLE AND SUBTITLE

see attached

5. FUNDING NUMBERS

DAAL03-91-G-0139

6. AUTHOR(S)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 27863.14-MS

11. SUPPLEMENTARY NOTES

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13. ABSTRACT *(Maximum 200 words)*

The research performed under this contract focused on the molecular engineering of thin polymer films prepared from functionally terminated oligomers by application of Langmuir Blodgett monolayer and multilayer film transfer techniques. The goals of the work were to:

1) Fabricate ultrathin films (i.e. 1-10 nm thickness) with controlled thickness, orientation, and surface chemistry.
2) Use these films to develop boundary lubricants that are stable at high temperatures.
3) Apply these films to stabilize the aging characteristics of bulk acoustic wave oscillators.

19950308 070

14. SUBJECT TERMS

Siloxanes, Monolayers, LB Films, Tribology, Surface Modification

15. NUMBER OF PAGES

6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Molecular Engineering of Thin Polymer Films Prepared from Functionally-Terminated Oligomers

A FINAL REPORT

prepared by
Dr. Jeffrey T. Koberstein

February 19, 1995

U. S. Army Research Office
Grant Number: DAAL03-91-G-0139
to the
University of Connecticut

4. RESEARCH RESULTS

A. Statement of the Problem Studied

The research performed under this contract focused on the molecular engineering of thin polymer films prepared from functionally terminated oligomers by application of Langmuir Blodgett monolayer and multilayer film transfer techniques. The goals of the work were to:

1) Fabricate ultrathin films (i.e. 1-10 nm thickness) with controlled thickness, orientation, and surface chemistry.
2) Use these films to develop boundary lubricants that are stable at high temperatures.
3) Apply these films to stabilize the aging characteristics of bulk acoustic wave oscillators.

B. Summary of Most Important Results

End Group Segregation: The first published manuscript demonstrated where end groups go at polymer surfaces. Three cases were studied: Neutral, attractive and repulsive end groups. When placed on the end of polystyrene, fluorosilane groups are attracted to the air-polymer surface and repelled from the silicon oxide substrate, carboxylic acid groups are repelled from the surface and attracted to the substrate, and the butyl residue from the butyl lithium initiator is attracted to the surface. These experiments demonstrate that the wetting characteristics of polystyrene can be adjusted by controlling the end groups.

Monolayer Properties: The second publication listed summarizes our current understanding of pressure-area isotherms for monolayers of functionally terminated oligomers of poly(dimethylsiloxane) (PDMS). The third publication describes the process control parameters important in transferring good monolayers of these materials and how the transfer requirements differ from those of more traditional fatty acid or crystalline materials. The relationship between the process control parameters and the monolayer properties is described in manuscript #6. In order to fully understand this relationship, the dynamic properties of the floating monolayers were studied as reported in manuscript #8. The surface chemical structure of these monolayers has been examined by X-ray Photoelectron Spectroscopy (manuscript #9). In the case of di-functional oligomers, we find that one functional group lies at the substrate, and the other lies just below the surface of the monolayer. A number of functionally-terminated oligomers with different backbones (such as poly(carbonate), poly(styrene), and poly(butadiene)) have also been purified and characterized, and these results are described in the thesis by J. F. Elman. Current work (J. Pickering) funded by an AASERT extension to the original grant centers

on the study of mixed monolayers and multilayers. The idea of the latter work is to develop means for the formation of controlled nanostructures for smart materials systems. Since the oligomers employed in these studies are polydisperse, we also studied the molecular weight distribution of the materials before and after processing the thin films by the Langmuir Blodgett technique. These results (manuscript #5) demonstrated that low molecular weight species dissolve in the subphase and are thus excluded from the film.

Formation of SiO_X Films. Exposing a transferred monolayer of PDMS to a UV/ozone treatment produces thin films of SiO_X materials with a uniformity much greater than that of traditional sputtering techniques. A manuscript (#4) describing this work has been accepted for publication and a patent regarding this technique is currently being filed. It appears that it may be possible to dope these films by using PDMS-carboxy salts with various metal counterions, producing very thin (less than 100 Angstroms) doped ceramics which may have applicability in coating and waveguiding applications. Thin film metal oxides can also be prepared by a modification of this method as described in manuscript #7.

Aging Control in Resonators. In conjunction with Dr. Ray Sawin of Phonon Corporation and Dr. Aaron Murray of the U.S. Army Laboratory Command in Fort Monmouth, we investigated the use of monolayers of functionally-terminated oligomers to control frequency drift during aging of bulk acoustic wave (BAW) oscillators and to assess the usefulness of surface acoustic wave (SAW) devices for accelerated aging testing. The low surface energy PDMS monolayers showed promise for retardation (or at least control) of the aging process in BAW devices, but questions about film structure and attachment still remain.

The reflective mode SAW devices showed high sensitivity to aging effects. However, the aging process for thin film coated devices appears to depend heavily on specific surface interactions. Since different materials are used to construct the SAW (aluminum) and BAW (gold) devices, the results cannot be directly compared. Cooperative research will continue with Dr. Murray to determine which aspects of the oligomer structure can be optimized to provide better control of the BAW aging process.

Tribology-Thin Film Boundary Lubricants: The friction and wear properties of LB monolayers prepared from functionally terminated oligomers were studied in the thesis of C. L. Mirley. A manuscript (#10) describing these results is in preparation. We found that the siloxanes were poor lubricants, that hydrogenated butadiene oligomers were acceptable lubricants, but that the best lubrication properties were obtained for siloxanes converted to organoceramics by the aforementioned UV/ozone conversion reaction.

C. Publications and Technical Reports

Technical Reports:

1. C. L. Mirley and J. T. Koberstein, "Tribology of Langmuir-Blodgett Films".
2. C. L. Mirley and J. T. Koberstein, "Tribology of Functionally Terminated Oligomer Films".
3. C.L. Mirley, M.G. Lewis, D.H.T. Lee, and J.T. Koberstein, "Surface Pressure Feedback Control for Langmuir-Blodgett Film Transfer. 1. Optimization of Process Control Parameters".
4. T.J. Lenk, D.H.T. Lee, and J.T. Koberstein, "End group Effects on Isotherms of Functionally-Terminated Poly(dimethylsiloxanes)".
5. F. E. Runge, H. Yu, T. Lenk and J. T. Koberstein, "Monolayer Dynamics of Functionally Terminated Poly(dimethyl siloxanes) at the Air/Water Interface".
6. C.L. Mirley and J.T. Koberstein, "A Novel Method for the Preparation of Ultrathin Organoceramic Films from Langmuir-Blodgett Layers".
7. "J. F. Elman, D. H. T. Lee, J. T. Koberstein and P. M. Thompson, "TOFSIMS Measurements of Molecular Weight Distributions for Functionally Terminated Oligomers and Transferred Langmuir-Blodgett-Kuhn Monolayers"
8. C.L. Mirley, M.G. Lewis, D.H.T. Lee, and J.T. Koberstein, "Surface Pressure Feedback Control for Langmuir-Blodgett Film Transfer. 2. Effect of Floating Monolayer Film Properties on Process Control Parameters".
9. C.L. Mirley and J.T. Koberstein, "The Preparation of Ultrathin Metal Oxide Films from Langmuir-Blodgett Layers".
10. C. L. Mirley and J. T. Koberstein, "Triblogical Properties of Ultrathin Films of Functionally Terminated Oligomers Prepared by the Langmuir-Blodgett-Kuhn Method".

Published Manuscripts:

1. J. F. Elman, B. D. Johs, T. E. Long and J. T. Koberstein, "A Neutron Reflectivity Investigation of Surface and Interface Segregation of Polymer Functional End Groups", Macromolecules, 1994, 27, 5341-5349.
2. T.J. Lenk, D.H.T. Lee, and J.T. Koberstein, "End group Effects on Isotherms of Functionally-Terminated Poly(dimethylsiloxanes)," Langmuir, 1994, 10, 1857-1864.
3. C.L. Mirley, M.G. Lewis, D.H.T. Lee, and J.T. Koberstein, "Surface Pressure Feedback Control for Langmuir-Blodgett Film Transfer. 1. Optimization of Process Control Parameters," Langmuir, 10, 2370-2375.

Manuscript Accepted for Publication:

4. C.L. Mirley and J.T. Koberstein, "A Novel Method for the Preparation of Ultrathin Organoceramic Films from Langmuir-Blodgett Layers", accepted by Langmuir, February, 1995.

Manuscripts Submitted for Publication:

5. "J. F. Elman, D. H. T. Lee, J. T. Koberstein and P. M. Thompson, "TOFSIMS Measurements of Molecular Weight Distributions for Functionally Terminated Oligomers and Transferred Langmuir-Blodgett-Kuhn Monolayers", Langmuir, May, 1994.
6. C.L. Mirley, M.G. Lewis, D.H.T. Lee, and J.T. Koberstein, "Surface Pressure Feedback Control for Langmuir-Blodgett Film Transfer. 2. Effect of Floating Monolayer Film Properties on Process Control Parameters", submitted to Langmuir, February, 1995.
7. C.L. Mirley and J.T. Koberstein, "The Preparation of Ultrathin Metal Oxide Films from Langmuir-Blodgett Layers", submitted to Langmuir, February, 1995.

Manuscripts in Preparation:

8. F. E. Runge, H. Yu, T. Lenk and J. T. Koberstein, "Monolayer Dynamics of Functionally Terminated Poly(dimethyl siloxanes) at the Air/Water Interface".
9. J. Pickering, D. H. T. Lee, T. J. Lenk and J. T. Koberstein, "An XPS Investigation of Transferred Monolayers and Multilayers of Functionally Terminated Poly(dimethyl siloxanes)".
10. C. L. Mirley and J. T. Koberstein, "Triblogical Properties of Ultrathin Films of Functionally Terminated Oligomers Prepared by the Langmuir-Blodgett-Kuhn Method".

D. Scientific Personnel Supported by this Project:

1. James F. Elman, Ph.D. in Polymer Science awarded September, 1993.
2. Christopher L. Mirley, Ph.D. in Polymer Science awarded September, 1994.
3. Jerry A. Pickering, Chemical Engineering Ph.D. Student.
4. Dr. Thomas J. Lenk, Postdoctoral Research Associate (partial support)

5. Report of Inventions

A patent is being filed to cover the process that we developed for the preparation of ultrathin SiO_X, organoceramic, and metal oxide films by treatment of the appropriate LB films by exposure to UV/ozone. This work is described in the thesis of C. L. Mirley, and in manuscripts #4 and #7.