and sharp changes in density and refractive index at the pore boundary.[18] The PMMA sol-gel composites showed transmissivities of 0.992 (at 500 nm). Absorptivities of our films were unmeasurable and were buried within the absorption of the substrate glass.

The coefficient, d_{33}, can be calculated using the oriented gas model:[19]

$$d_{33} = \tfrac{1}{2} N\beta f^{2\omega}(f^{\omega})^2\langle\cos^3\theta\rangle \tag{3}$$

where N is the chromophore density (mol/cm^3), f is the Lorentz local field factor, and θ is the angle between the dipole moment of the chromophore and the poling direction. This angle can be estimated from the order parameter:[20]

$$\Phi = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{4}$$

The calculated value for d_{33} using the pure TDP film as an example was 15.4 pm/V, close to the measured value of 11.7 pm/V. Further work comparing calculated and experimentally determined values for d_{33} is premature and will be undertaken once film processing procedures have been optimized.

In conclusion, the sol-gel process can be used to incorporate nonlinear chromophores directly into an inorganic network to make nonlinear optical materials possessing properties of both organic and inorganic materials. Since each Si atom contains an attached chromophore, the nonlinear susceptibilities of the films are higher than physically doped sol-gels and are within the range of commercially available inorganic crystals. By mixing trifunctional organo-substituted silanes with TEOS, the physical properties of the films can be improved without sacrificing their optical properties. Future work will involve optimizing the film fabrication and poling process and synthesizing new silane monomers with chromophores of higher susceptibility than those used here.

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Registry No. TDP, 71783-41-0; FPT, 72136-46-0; 2,4-dinitroaniline, 97-02-9; *p*-methoxybenzaldehyde, 123-11-5.

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Incorporation of C_{60} in Langmuir-Blodgett Films

JoAnn Milliken,* Dawn D. Dominguez,
H. H. Nelson, and William R. Barger

Chemistry Division, Code 6100
U.S. Naval Research Laboratory
Washington, D.C. 20375

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Developments in the synthesis of macroscopic quantities of buckminsterfullerene[1] (C_{60}) have led to numerous studies of the properties of this new and exciting material. In this paper, we describe the preparation of an ultrathin mixed film of C_{60} and 1-octadecanol, $C_{18}H_{37}OH$ (abbreviated here as $C_{18}OH$) on fused silica using the Langmuir-Blodgett (L-B) method.[2,3] Thin films of C_{60} are of interest for several reasons. Most noteworthy is the recent discovery that superconducting films are produced when films of C_{60} are exposed to alkali-metal vapor.[4] In addition, thin films of C_{60} have been used in electrochemical studies[5] and in nonlinear optical (NLO) experiments.[6] Recently, Obeng and Bard[7] have reported results of L-B experiments on pure C_{60} and C_{60} mixed with arachidic acid ($C_{19}H_{39}COOH$).

Table I. Spreading Solutions

film type	concn, M	added,[a] μL
C_{60}	3.583×10^{-4}	750
	1.250×10^{-4}	1500
	5.972×10^{-5}	200
$C_{18}OH$	1.831×10^{-3}	300
$C_{60}/C_{18}OH$	2.986×10^{-4} (C_{60})	500
	3.051×10^{-4} ($C_{18}OH$)	

[a] Added in 5.0-μL increments.

Film pressure vs area (π-A) isotherms were determined for three Langmuir film types: (1) C_{60}, (2) $C_{18}OH$, and (3) a 1:1 mole ratio mixture of the two compounds. C_{60} was prepared following the procedures described by Haufler et al.[8] and Aije et al.[9] The C_{60}:C_{70} ratio was greater than 99:1 as determined by negative ion chemical ionization mass spectrometry. C_{60} for these studies was recrystallized from benzene prior to preparation of the spreading solutions described in Table I. Octadecanol (99.5%, LaChat) was used as received. The more dilute (5.972×10^{-5} M) solution of C_{60} was used to check for dependence of π-A characteristics on concentration. Results for the low-concentration run were similar to the runs using higher concentration solutions. The 1.250×10^{-4} M C_{60} solution was from a different preparation batch and was recrystallized from chlorobenzene. Triply distilled water (second and third distillations from a quartz still) used as the subphase was changed for each run.

π-A studies and depositions of L-B multilayer films were carried out in a constant-temperature room at 25 °C using a KSV 5000 Langmuir-Blodgett system (KSV Instruments, Helsinki, Finland). The system had a 10-mm-deep Teflon Langmuir trough with a water surface area of 150 mm × 510 mm. Surface tension (γ) was measured with a Wilhelmy plate. Film pressure is the difference between the surface tension of the clean water and the film-covered water, i.e., $\pi = \gamma_w - \gamma_f$. Solutions were spread on the trough by adding drops in 5-μL increments at different locations on the water surface. Films were compressed at a rate of 1 mN/(m min), resulting in a slowing of the rate of change of area as pressure increased. Fused silica slides 25 mm × 50 mm × 1 mm were cleaned in sulfuric acid/sodium dichromate solution and rinsed with

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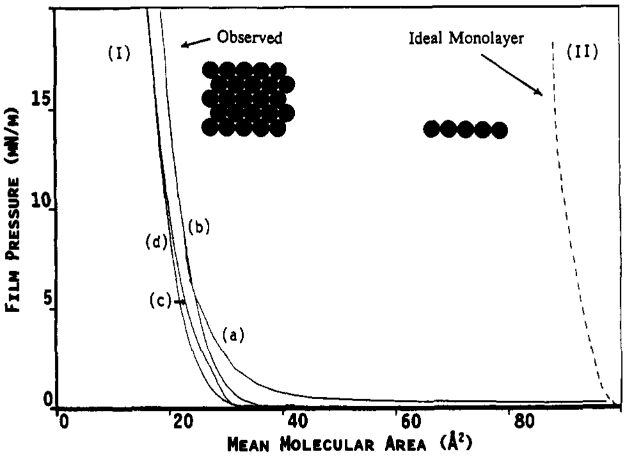

Figure 1. (I) π–A isotherms observed for Langmuir films of pure C_{60} deposited from benzene solutions of varying concentration: (a) 5.972×10^{-5} M, (b) 1.250×10^{-4} M, (c) and (d) 3.583×10^{-4} M. (II) Approximate position expected for the isotherm of an ideal monomolecular film of C_{60}.

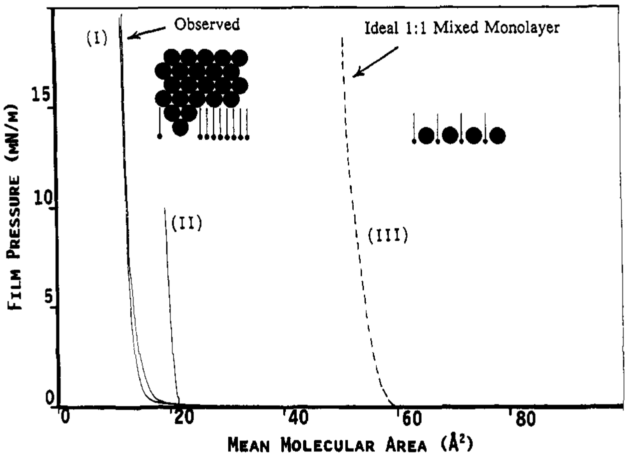

Figure 2. π–A isotherms (I) observed for a 1:1 molar mixed film of C_{60} and $C_{18}OH$, (II) observed for pure $C_{18}OH$, and (III) expected for an ideal 1:1 molar mixed monolayer film.

triply distilled water. They were then washed in a Soxhlet extractor with freshly distilled chloroform. All depositions began with the slides submerged. The dipping speed was 10 mm/min. Spectra were recorded using a Perkin-Elmer Lambda-5 UV-visible spectrophotometer.

Figure 1 (II) shows the π–A isotherm expected for an ideal monomolecular layer of C_{60} molecules, assuming a cross-sectional area of 92 Å²/molecule, which was estimated from the radius reported by Hawkins et al.[10] Figure 1 (I) shows the π–A isotherms obtained for pure C_{60} in this experiment. The apparent cross-sectional area at high film pressure is <20 Å²/molecule, suggesting that the C_{60} film becomes multilayered at high compression, i.e., binding to water is weak. Attempts to transfer Langmuir films of pure C_{60} to a fused silica slide were not successful. A UV–vis spectrum of a slide that was passed repeatedly through a compressed C_{60} film on water showed no difference from a blank slide.

Successful transfers of thin films containing other compounds difficult to transfer have been accomplished in the past by preparing mixed films with classical monolayers such as $C_{18}OH$.[11] Therefore, we prepared a $C_{60}/C_{18}OH$ mixture. Figure 2 (III) shows the π–A isotherm expected for a 1:1 molar mixed monolayer film of C_{60} and $C_{18}OH$. If the films were segregated, a molecular area of approximately 56 Å² would be expected based on a cross-sectional area of 20 Å² for $C_{18}OH$ (Figure 2 (II)) and 92 Å² for C_{60}. Figure 2 (I) shows the π–A isotherm obtained for the 1:1 molar mixture used in this experiment. The apparent average cross-sectional area of <15 Å²/molecule again indicates that the C_{60} does not remain in a monomolecular layer bound to the water surface.

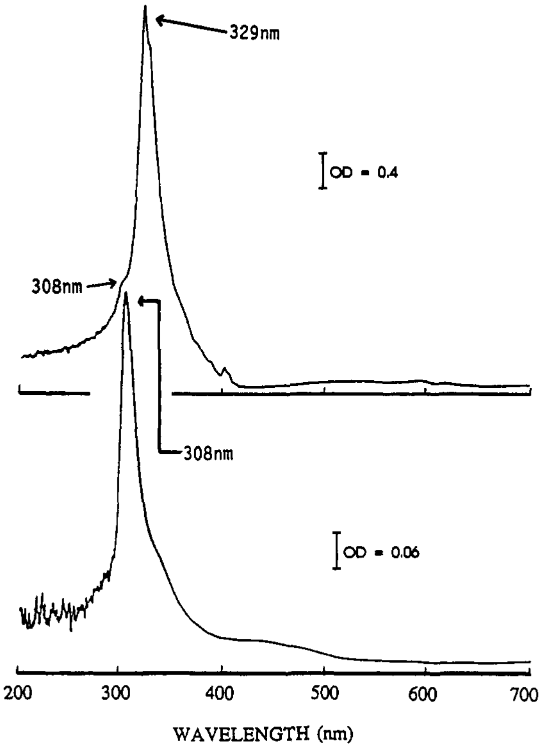

Figure 3. Top: UV–vis spectrum of a 9.389×10^{-5} M solution of pure C_{60} in benzene, maximum absorbance = 3.73 absorbance units at 328 nm. Bottom: UV–vis spectrum of a 1:1 molar mixed Langmuir film of C_{60} and $C_{18}OH$ transferred to fused silica (10 layers), maximum absorbance = 0.552 absorbance units at 308 nm. OD indicates optical density.

In spite of the fact that the $C_{60}/C_{18}OH$ films were not monomolecular, we verified by spectroscopy that they could be transferred to a fused silica slide. While the film pressure was maintained at 20 mN/m, a slide was passed through the interface five times. Figure 3 (top) shows the UV–vis spectrum of a 9.289×10^{-4} M solution of C_{60} in benzene recorded in a 1-cm path-length quartz cell. The absorption at 329 nm and shoulder at 308 nm are consistent with those reported by Hare et al.[9] Figure 3 (bottom) shows the UV–vis spectrum obtained for a solid 1:1 mixed L–B film of C_{60} and $C_{18}OH$ transferred to fused silica. Because both sides of the slide were coated, this spectrum shows the absorbance due to 10 layers. The solution peak at ~329 nm is greatly diminished in the solid state, leaving the most prominent absorption at ~308 nm. The blue shift may be due to the formation of aggregated states in the solid, as has been observed in systems such as cyanines and chlorophylls.[13]

Consistent with Obeng and Bard,[7] we have shown that pure and mixed films of C_{60} can be spread from volatile solvents to form Langmuir films on water, giving repro-

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ducible pressure vs area isotherms. The apparent cross-sectional area (<20 Å^2/molecule) at high film pressure for C_{60} suggests that on compression the films become multilayered. However, we were unable to produce a film of pure C_{60} that remained as a monolayer at pressures above 65 mN/m; our films collapsed at pressures of 32-36 mN/m. Nor were we able to produce a monolayer having a molecular area near 90 Å^2 by spreading from a dilute solution.

In conclusion, we have shown that $C_{60}/C_{18}OH$ mixtures give reproducible pressure vs area isotherms with small apparent areas per molecule. We have successfully transferred the mixture to fused silica by the L-B technique as an ultrathin film which can be used for further study.

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Registry No. C_{60}, 99685-96-8; $C_{18}OH$, 112-92-5.

Electrooxidation of Soluble α,α-Coupled Thiophene Oligomers

J. Guay and A. Diaz*

IBM Almaden Research Center
650 Harry Road, San Jose, California 95120

Ruilian Wu and James M. Tour*

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

Le H. Dao

LRMA INRS-Energie, 1650 Montee Ste-Julie
Varennes PQ J3X 1S2, Canada

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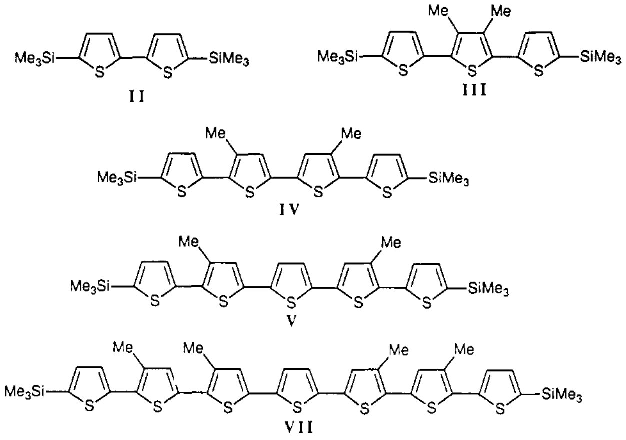
The electrooxidation reactions of polythiophene films produce complicated cyclic voltammograms. The waves are often broad and deformed and appear at the foot of a large anodic current which often continues to rise until the films are decomposed or "burned" off of the electrode.[1-10] There is often a prewave as a shoulder,[4-10] and its visibility varies with the film thickness, substituents on the polymer,[5-7] and electrolyte.[4,8] A recent electrochemical ESR study showed that the prewave is associated with the one-electron oxidation to produce the polaron state and the main peak corresponds to the formation of bipolarons.[4] In contrast, the electrochemical oxidation of the thiophene dimer, trimer, tetramer, and hexamer in liquid SO_2 at -44 °C, in CH_3CN and in nitrobenzene leads to well-separated anodic processes.[11-13] The electrochemistry of the higher oligomers has not been reported even though there are many recent studies on the chemistry of these compounds.[13-20] In this study, α,α-coupled thiophene oligomers with terminal α-$(CH_3)_3Si$ groups (α-TMS) and β-CH_3 groups are used to study the importance of the second oxidation reaction at room temperature as a model study for the polymer segments in the absence of irregular couplings,[21] molecular weight distributions,[22] lattice interactions,[23] capacitance,[24,25] and resistance[26] as may occur in a film.

Table I. Summary of Electrochemical Data

oligomer	E_{pa_1}, E_{pa_2}, V	ΔE_p, mV	n_1, $n_1 + n_2$	$E(h\nu)$, eV
VII	0.86, 1.04	60, 80	1.06, 2.05	2.36
V	0.98, 1.20	60, 70	1.04, 1.98	2.52
IV	1.04, 1.36	70, 100		2.68
III	1.16, 1.53	80	0.95	3.04
II	1.46[a]			3.43

[a] Reported E_{pa} values for II and bithiophene are 1.14 and 1.32 V in CH_3CN, respectively.[30]

Chart I



The soluble α,α-coupled thiophene oligomers with the terminal α-TMS groups and β-methyl groups were prepared by Ni- and Pd-catalyzed reactions of the corresponding halide, stannane, or Grignard derivatives.[27] The cyclic voltammetry and chronocoulometry of the oligomers (10^{-4} M) in 0.1 M $Bu_4N\ BF_4/CH_2Cl_2$ solutions were recorded using a 0.5-cm Pt electrode and an SCE double junction electrode and with a PAR Model 273. The electrochemical data are summarized in Table I. The heptamer VII (Chart I), pentamer V, and tetramer IV all show two one-electron redox waves which can be cycled

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