J. Am. Chem. Soc. **1988**, *110*, 6136–6144

Incorporation of Phenoxy Groups in Self-Assembled Monolayers of Trichlorosilane Derivatives: Effects on Film Thickness, Wettability, and Molecular Orientation

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Received November 23, 1987. Revised Manuscript Received April 8, 1988

Abstract: To evaluate the possibilities for preparing monolayer films from trichlorosilane derivatives containing aromatic functional groups, model studies of monolayer-forming trichlorosilanes which incorporate a phenoxy moiety in various positions of a long alkyl chain were undertaken. Self-assembled monolayers of several such compounds could be successfully formed. The properties of these monolayers have been evaluated by utilizing ellipsometry, wettability measurements, and FTIR and compared with analogous alkyltrichlorosilanes. Monolayers prepared from 1-(trichlorosilyl)-11-(*p*-*n*-nonylphenoxy)undecane (**1**) show that the phenoxy group can be introduced into such monolayers with no loss of oleophobicity, as compared with octadecyltrichlorosilane (OTS), and with spectral features which indicate a high level of monolayer order and close packing. Linear dichroism measurements using FTIR-ATR are used to estimate the orientation of the alkyl chains and the phenoxy group in **1**, and a model is proposed to explain the results. Shortening of the alkyl chain lengths in several examples led to more disordered, liquidlike monolayers. The orientation of the phenoxy group did not vary significantly with position in the alkyl chain.

Interest in the formation of monolayers at a liquid–solid interface by spontaneous "self-assembly" has grown considerably in recent years with the discovery of methods that result in the formation of close-packed monolayers chemically bonded to the surface. These include the use of derivatives of trichlorosilane on hydroxylated surfaces, including glass, quartz, aluminum, and silicon (pioneered by the Sagiv group[1–6]), and of thiol and disulfide monolayers on gold.[7,8] A particular advantage of the use of trichlorosilane systems is the application to the formation of ordered, cross-linked, multilayer structures. Such multilayer films can be constructed from molecules that terminate in a functional group that can be activated (e.g., a C=C bond or an ester group) to form a fresh hydroxylated surface, upon which a new monolayer can be adsorbed.[6,9–11] This technique, therefore, has great potential utility in the construction of macromolecular structures, or artificial lattices, with order at the molecular level and with electronic, electrooptic, or other "bulk" properties.

We are interested in the eventual fabrication of multilayer structures that contain useful aromatic and other functional groups for eventual optical or electronic uses. However, most of the fundamental work on self-assembled monolayers, to date, has involved the study of monolayers of octadecyltrichlorosilane (OTS) and various similar, functional-group-terminated alkyltrichlorosilanes. Many potentially useful structures that may be built into such macromolecular structures contain aromatic or heteroaromatic rings and possess symmetries different from cylindrical, long-chain alkyl groups. Hence incorporation of such groups into the alkyl chain will be accompanied by the introduction of disorder into the monolayer. The effect of this expected disorder on the packing of the monolayer, the orientation of the aromatic group and the alkyl chains, and the resultant quality of the monolayer and its surface properties are very important issues. Also important are the effects of the position in the alkyl chain of the chromophore of interest on monolayer orientation, packing, and surface properties, and the overall alkyl chain length necessary to produce good-quality monolayer formation. The chemist needs such information to be able to predict, and perhaps achieve the ability to control, details of molecular orientation and packing. Only with full understanding of the interrelationship between molecular and monolayer structures and properties will the chemist be able to construct useful structures with engineered physical properties and predicted structures.

Although dye molecules have been coadsorbed with OTS in the formation of self-assembled monolayers,[12–14] and model aromatic systems containing benzene rings at the terminus of the alkyl chain have been reported by the Sagiv group,[15] detailed investigations into the effects of benzene ring incorporation on monolayer quality, ordering, and orientation, and the effects of ring inclusion at various positions of the alkyl chain, have not been published. As a first step in our study of trichlorosilane derivatives incorporating aromatic structures, we decided to incorporate a phenoxy group into long-chain alkyltrichlorosilanes and to study the effect of its inclusion and its position in the alkyl chain on the resultant monolayer properties. Thus we synthesized molecules **1–4**, in which the chain lengths m and n and the overall chain length $m + n$ are varied, and constructed monolayers of each on various substrates. In this way we incorporated into the "interior" medium of self-assembled monolayers a phenyl group to serve in model studies useful in the design of future monolayers incorporating aromatic units. We have used analytical techniques, including ellipsometry and FTIR (in both grazing angle external specular reflection and attenuated total reflection (ATR) modes) to examine monolayer quality and group orientation in these systems. We have examined surface structure and order in these systems through the measurement of contact angles (wettability). We also prepared monolayers of several simple alkyltrichlorosilanes, including OTS, tridecyltrichlorosilane (TTS), and undecyltrichlorosilane (UTS), for comparison with monolayers of **1–4**.

Results

Characterization with Optical Ellipsometry. Optical ellipsometry provided a convenient method of verifying the monomolecular nature of the films formed and of monitoring the buildup of monolayers.[2,7,8,16] Monolayers of both OTS and **1**, which have

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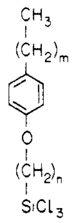

1 m = 8, n = 11
2 m = 8, n = 4
3 m = 4, n = 8
4 m = 1, n = 11

$CH_3(CH_2)_nSiCl_3$

OTS n = 17
TTS n = 12
UTS n = 10

the longest alkyl chains in the series of compounds reported here, usually formed apparently complete monolayers with a single immersion of a few minutes in the silanizing solution. However, monolayers of compounds **2–4**, TTS, and UTS required longer times and multiple immersions to reach maximum monolayer formation. Figure 1a shows a plot of film thickness vs total immersion time for a representative monolayer of **3** built on a silicon wafer. The sample was repeatedly immersed in a ca. 5 × 10^{-3} M silanizing solution, followed by a thorough rinsing with solvents and water and a cleansing with detergent, and the film thickness was checked after each immersion. Also checked at the same time were the hexadecane contact angles (see below), and these data are plotted in Figure 1b. From 30 to 60 min is required for maximal film thickness and contact angles to be achieved. We took the observation of a stable, maximal film thickness and oleophobic contact angle, which did not increase upon further immersion, as indicating the optimal formation of monolayers of each of the compounds reported on here.

Table I presents data for film thicknesses of monolayers of OTS, TTS, UTS, and compounds **1–4** on various substrates employed in this study. Generally the best substrates, as judged by the reproducibility and uniformity of film thicknesses and substrate optical constants, were polished p-doped silicon wafers, which we cleaned, after cutting to usable size, with detergent, followed by argon plasma cleaning.

We have employed a value for the film real refractive index of n_f = 1.50 in the calculation of film thicknesses from the ellipsometry data. The accurate evaluation of film thickness is dependent upon the use of a correct refractive index and assumes that the film is isotropic and homogeneous. Although, strictly speaking, this assumption is incorrect, especially where the symmetry of the alkyl chains is broken by the incorporation of aromatic groups, we employ it as a necessary approximation, with the justification that in all cases we obtain physically plausible results. The use of n_f = 1.50 has precedent[1,5,7,8,16] from previous investigations into self-assembled monolayers, where values of 1.45–1.50 have been employed.[17] The high end of this range was used, since the phenoxy group would be expected to increase the refractive index of the film (we estimate by about 0.04–0.05 for compounds **1–4**), as can be seen by a comparison of the bulk refractive indices of the C_7 compounds heptane (n_D 1.3870) and anisole (n_D 1.5160). Measurements on our instrument for a sample monolayer of OTS on a silicon wafer indicated change of −1 Å per each + 0.05 unit change in the value of n_f used.

Contact Angle and Wettability Measurements. Contact angle measurements are sensitive indicators of the surface properties of a monolayer.[1,3,16,18] Although strictly speaking the wettability of a monolayer is determined by its surface properties and not the properties of the interior medium, the medium would be expected to indirectly affect surface properties by affecting the order, packing, and tilt of surface functional groups. We have therefore used contact angles of a variety of test liquids as an indicator of the quality of monolayers formed, and, in conjunction with ellipsometry, to monitor the completion of monolayer-forming reactions.

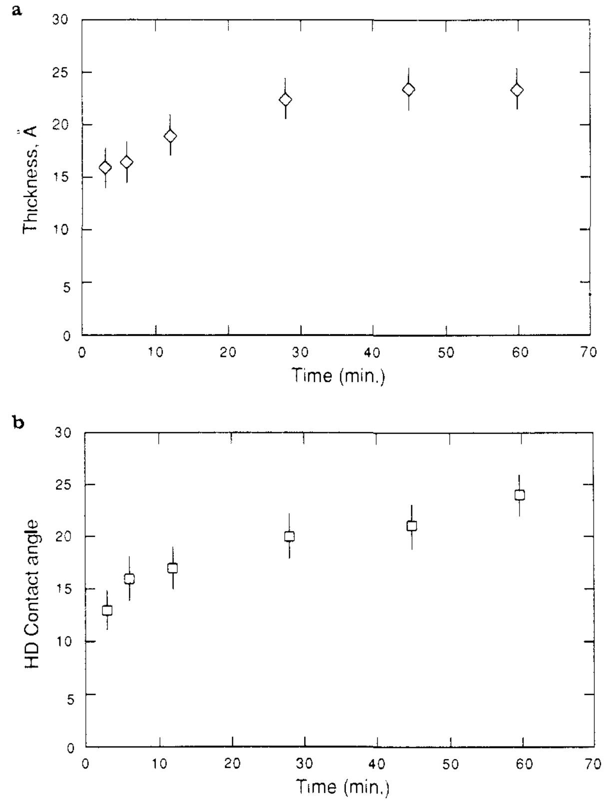

Figure 1. (a) Film thickness and (b) Hexadecane (HD) contact angle vs total immersion time for a monolayer of **3** on a silicon wafer. A silicon wafer substrate was repeatedly immersed in a silanizing solution and cleaned after each immersion as described in the text.

Table I. Film Thickness by Ellipsometry for Monolayers of Compounds **1–4**, OTS, TTS, and UTS

compd	substrate[a,b]	N^c	thickness, Å
OTS	Si wafer	2	25 (±2)
	Si ATR prism	1	25 (±3)
	Al/Si	1	26 (±4)
TTS	Si wafer	2	19 (±2)
	Si ATR prism	2	20 (±3)
UTS	Si wafer	2	15 (±2)
1	Si wafer	3	31 (±2)
	Si ATR prism	3	33 (±3)
	Al/Si	1	34 (±3)
2	Si wafer	3	23 (±2)
	Si ATR prism	2	24 (±3)
3	Si wafer	4	24 (±2)
	Si ATR prism	3	24 (±3)
4	Si wafer	1	24 (±2)
	Si ATR prism	2	25 (±3)

[a] Measurements were carried out at 5–10 spots on each substrate with optical constants predetermined for each substrate and assuming an approximate film refractive index n_f = 1.50. [b] Substrates were polished, p-doped Si wafers, silicon ATR prisms, or aluminized (1000-Å thick) silicon wafers (Al/Si). [c] N = the number of independent determinations.

The hexadecane contact angle of a monolayer of **3** on a silicon wafer continues to grow with increasing time of immersion, reaching an eventual maximum of 24° (for this example) in from 30 to 60 min total time (Figure 1b). This is characteristic of monolayer formation for the shorter chain molecules in this series, i.e., TTS, UTS, and **2–4**. We considered monolayers adequately formed only after a stable, maximal oleophobic contact angle, which does not change significantly upon further immersion, was observed. As in Figure 1b, data from contact angle measurements was found to generally parallel the results from ellipsometry.

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(16) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45.

(17) We have recently succeeded in building multilayer films by self-assembly from an alkyltrichlorosilane that are thick enough to measure the real film refractive index and find n_f = 1.50 ± 0.01. Tillman, N.; Ulman, A.; Penner, T. L., to be published.

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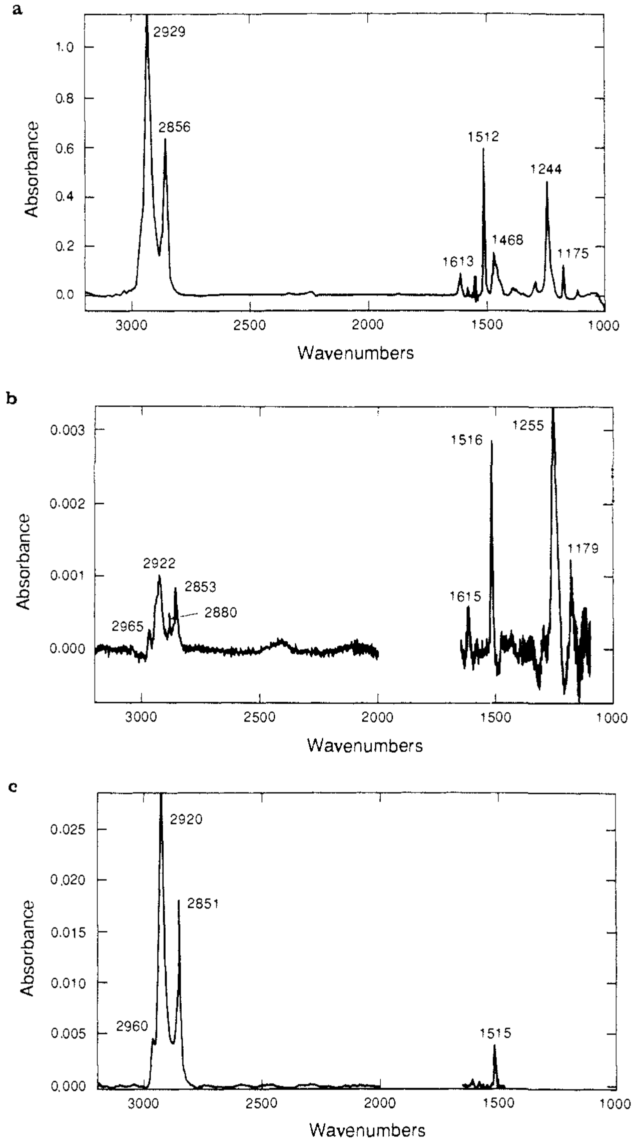

Figure 2. IR spectrum of compound **1** as (a) bulk spectrum (CCl_4 solution), (b) grazing angle (76°) external specular reflection spectrum on aluminized silicon, and (c) p-polarized ATR spectrum on silicon prism (45° incidence). Base lines have been adjusted to zero absorbance, and artifacts eliminated where necessary. The opacity of silicon prevents useful detection of IR bands below 1500 cm^{-1} in the ATR mode.

Table II presents contact angle data for four test liquids for such optimized monolayers on several substrates used in the present study. Silicon wafers gave the highest, most uniform, and most reproducible contact angles of any substrates employed. Even silicon ATR prisms failed to give monolayers as good as silicon wafers. Contact angles, particularly oleophobic contact angles, found for the silicon prisms were usually several degrees below the values obtained on the wafer silicon. Although monolayer contact angles were generally reproducible to ±2°, some monolayers showed lowered contact angles (reflecting presumably poorer quality) without there being any significant difference in the ellipsometry measurements.

Also included in Table II are critical surface tensions (γ_c) for the monolayers, derived from Zisman plots of cos θ vs γ_l (the measured liquid surface tension) for a variety of test liquids. The value of γ_l at cos θ = 1.00, estimated from the linear regression line through the data points, is equal to γ_c.[18,19]

FTIR Data. Although ellipsometry and contact angle measurements provide information on the surface properties and packing of monolayers, this information only reflects indirectly the possible orientation of alkyl chains and of substituents contained in the bulk of the film. To examine the order in self-assembled monolayers, particularly the orientation of the phenoxy group in monolayers of **1**–**4**, we have used FTIR in both grazing angle (76°) external specular reflection[20,21] and ATR (attenuated total reflection[1,3,22]) modes.

Table II. Advancing Contact Angles for Several Test Liquids and Critical Surface Tensions of Monolayers of OTS, TTS, UTS, and **1**–**4**

			θ, deg (±2)[a]				γ_c (±1.0)[b]
compd	substrate[c]	N[d]	H_2O	CH_2I_2	BCH	HD	(dyn/cm)
OTS	Si	3	111	73	48	41	20.2[e]
	SiP	1	111	72	49	40	
	Al/Si	1	107	68		42	
TTS	Si	2	110	72	45	40	20.2[e]
	SiP	2	110	70	41	37	
UTS	Si	2	109	69	41	32	21.5[e]
1	Si	2	111	74	48	41	20.1[f]
	SiP	2	111	72	48	42	
	Al/Si	1	108	66	50	42	
2	Si	3	110	70	42	32	22.0[f]
	SiP	2	110	67	39	30	
3	Si	4	107	66	36	27	23.7[f,g]
	SiP	3	107	62	32	20	
4	Si	2	100	60	30	20	26.4[f,g]
	SiP	1	97	54	27	10	

[a] θ = advancing contact angles, by sessile drop method at 24 ± 2 °C for water, methylene iodide, bicyclohexyl (BCH), and *n*-hexadecane (HD). [b] Critical surface tension γ_c at 24 ± 2 °C by Zisman method; number of determinations, N = 1. [c] Substrates were polished, p-doped test grade silicon wafers (Si), silicon ATR prisms (SiP), and aluminized silicon wafers (1000-Å thick, Al/Si). [d] N = number of independent determinations. [e] Determined from a plot of *n*-alkanes. [f] Determined from a plot of *n*-alkanes plus miscellaneous liquids. [g] Error = ±1.5 dyn/cm.

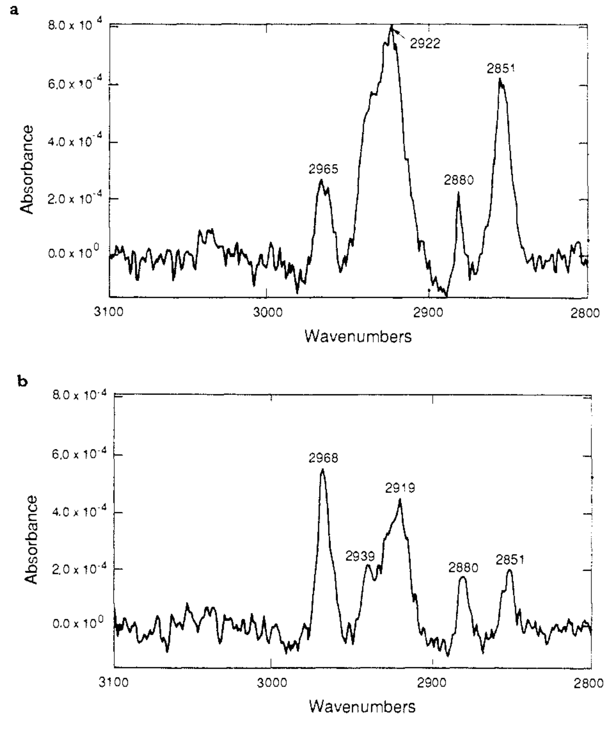

Figure 3. C–H stretch region of the grazing angle external specular reflection spectrum of a monolayer of (a) **1** and (b) OTS on aluminized silicon wafers. Spectra were recorded at 76° incidence, 1000 scans, 2-cm^{-1} resolution, and the base lines have been adjusted to zero absorbance.

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(19) Figure 1, parts a and b, in the supplementary material.

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(21) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52.

(22) (a) Harrick, N. J. In *Internal Reflection Spectroscopy*; Harrick Scientific: Ossining, New York, 1979. (b) Mirabella, F. M., Jr. *Appl. Spectrosc. Rev.* **1985**, *21*, 45.

Table III. Absorption Intensities for p- and s-Polarized Light, Dichroic Ratios, and Orientation Angle ϕ for Monolayers of OTS, TTS, and **1**–**4** on Silicon Measured by FTIR–ATR[a]

compd	ν, cm^{-1} [c]	intensity[b] p	intensity[b] s	D[d]	ϕ,[e] deg
OTS	2918	0.0356	0.0370	1.04	72
	2851	0.0227	0.0242	1.07	80
TTS	2922	0.0169	0.0162	0.96	61
	2851	0.0094	0.0091	0.97	63
1	2920	0.0287	0.0280	0.98	64
	2851	0.0181	0.0177	0.98	64
	1515	0.0042	0.0010	0.24	20
2	2923	0.0119	0.0104	0.87	53
	2853	0.0063	0.0053	0.84	52
	1514	0.0048	0.0023	0.48	32
3	2926	0.0108	0.0087	0.81	48
	2855	0.0059	0.0049	0.83	50
	1513	0.0052	0.0023	0.44	30
4	2921	0.0128	0.0119	0.93	58
	2852	0.0077	0.0078	1.01	68
	1514	0.0049	0.0024	0.49	32

[a] All spectra were recorded with the same 50 × 10 × 3 mm silicon 45° single-pass ATR prism referenced to the same s- or p-polarized background previously recorded with the uncoated prism. [b] Absorbance intensity at peak maximum. [c] Error = ± 2 cm^{-1}. [d] D = dichroic ratio = ratio of s-polarized to p-polarized intensity. Estimated error = ± 0.10. [e] Orientation angle ϕ of transition dipole moment from surface normal, estimated from Figure 5. For details, see Discussion. [f] A separate determination gave D = 1.06.

In Figure 2 are presented (a) the bulk (CCl_4 solution) spectrum of **1**, (b) the grazing angle spectrum of a monolayer of **1** on an aluminized silicon wafer, and (c) the ATR spectrum (p-polarized) of a monolayer of **1** on a silicon ATR prism (50 × 10 × 3 mm, 45° incident angle).[23] Figure 3 presents, for comparative purposes, (a) an expansion of the grazing angle spectrum of **1** in the region 3100–2800 cm^{-1} and (b) the grazing angle spectrum of OTS from 3100 to 2800 cm^{-1}.

We have recorded spectra in the ATR mode for both p- and s-polarizations for OTS, TTS, and **1**–**4**. Unfortunately, oleophobic monolayers of **2**–**4** and TTS proved impossible to obtain on aluminized surfaces, and hence grazing angle spectra for these compounds are not available. On aluminized surfaces close-packed monolayer formation was apparently not competitive with an irreversible, thick film buildup. We present here the ATR data, including the following information: (a) band absorbance intensities and peak widths; (b) peak absorption frequencies, particularly the frequency of the asymmetric CH$_2$ stretch, $\nu_a(CH_2)$, at ca. 2920 cm^{-1}; and (c) the linear dichroism of peaks, i.e., the change in peak intensity with s- or p-polarization of the incident light, expressed as the dichroic ratio $D = A_s/A_p$.

Table III compares intensities in p-polarized and s-polarized ATR spectra for the $\nu_a(CH_2)$ mode at ca. 2920 cm^{-1} and the $\nu_s(CH_2)$ mode at ca. 2850 cm^{-1} for OTS, TTS, and **1**–**4** and for the 1515 cm^{-1} band, which appears in spectra of compounds **1**–**4** (see Figure 2).[24] We assign this 1515 band as an aromatic C=C stretching vibration (vibration 19a,[25a] by comparison with assignments for similar compounds[25b]), with a transition dipole moment, assuming C_{2v} symmetry of the phenyl ring, along the C_{2v} axis (i.e., the C$_1$–C$_4$ axis).[26] Also in Table III are presented the calculated dichroic ratios D. All of the spectral studies in Table III were performed on the same ATR crystal with the same s- or p-polarized background spectra. We estimate an uncertainty of ca. ±10% in the value of D (i.e., ±0.1 at D = 1.0) in the present experimental setup.

From the ratio D it is possible to calculate the orientation of the transition dipole moment of an IR band in the ATR spectrum (see Discussion) and, provided the orientation of the dipole with respect to molecular coordinates is known, to obtain from this the orientation of molecular features in monolayers. The far right column in Table III gives the results of such a calculation in terms of an estimate of ϕ, defined as the angle of the transition dipole moment from the substrate surface normal.

Discussion

Ellipsometry and Wettability Studies. Optical ellipsometry and wettability (contact angle) studies are rapid and convenient ways to verify the monomolecular nature and quality of films formed. As a standard of quality and a check of our experimental method, we have prepared monolayers of OTS on each of the substrates employed in this study. Our results are in essential agreement with literature values of film thickness and contact angles for this well-studied system. By ellipsometry, we obtain a film thickness of 25 ± 2 Å for monolayers of OTS on silicon wafers (Table I), in comparison with a best literature value of 23 Å, determined by X-ray diffraction methods.[6] Water contact angles for OTS (111°) are close to literature values (112°), although our hexadecane contact angles (41°) are lower than those reported in the literature (45°).[1,6,27]

As a convenient way of summarizing the wettability data in a single parameter, we report here (Table II) critical surface tension values (γ_c), determined by the method of Zisman, where γ_c, defined as the surface tension of a test liquid which just completely wets the surface (0° contact angle), is found by plotting cos θ (where θ = contact angle) vs γ_l (where γ_l is the surface tension of a series of test liquids). The value of γ_c is that of γ_l at cos θ = 1.00, determined by fitting a linear regression line through the series of points.[18,19] The use of the critical surface tension parameter allows easy comparison of the surface properties of monolayers with a variety of other surfaces, including monolayer and polymeric structures, which have been previously well-characterized. Our value for OTS (γ_c = 20.2 dyn/cm at 24 °C) is lower than classical values obtained for monolayers of long-chain *n*-alkanoic acids or quaternary ammonium salts (22–24 dyn/cm[18a]), which form surfaces consisting of close-packed methyl groups. It is also somewhat lower than the value of ≈21 dyn/cm reported[28] for a crystal face of hexatriacontane (C$_{36}$) consisting of closest packed methyl groups, although this value lies within the error limits of our determination for OTS. The low value of γ_c found for OTS is suggestive of excellent monolayer quality, minimal disorder at the surface, and, as expected for a material covalently bonded to the surface, minimal dissolution or interaction of the monolayer with the test liquids. We therefore suggest 20–21 dyn/cm as a standard value of γ_c, representing an ordered monolayer of closest packed methyl groups at the surface. We also obtain γ_c = 20.2 dyn/cm for TTS (C$_{13}$). However, the contact angles are slightly lower than found for OTS, and we found that optimal monolayers of TTS are slower to form than for OTS. Monolayers of TTS usually required two or more immersions of 5–10 min in the silanizing solution (≈5×10^{-3} M), with solvent

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[23] Figure 2 in the supplementary material presents a description of the ATR prism and polarization used in these ATR experiments.

[24] Table I in the supplementary material presents the measured frequency of the $\nu_a(CH_2)$ band in solution and in monolayers of OTS, TTS, and **1**–**4**, as determined by FTIR–ATR spectroscopy on silicon prisms. Also presented are peak maximum absorption intensities and peak widths at half-height.

[25] (a) Varsanyi, G. In *Vibrational Spectra of Benzene Derivatives*; Academic: New York, 1969. (b) Varsanyi, G. In *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; Wiley: New York, 1974; Vol. 1.

[26] Figure 4 in the supplementary material presents polarized ATR spectra showing relative intensities of this 1515 band in monolayers of **1** and **2**.

[27] Since the completion of work on this project, we have found advancing contact angles for OTS monolayers on silicon wafers of 45° for hexadecane, in closer agreement with the results of other investigators[1,3,6] on both new samples, and samples employed in this study, which have been saved. Since the water and methylene iodide contact angles are quite reasonable, we do not feel the low hexadecane values reported here represent defective monolayers, but result from accidental trace contamination or batch-to-batch variation in the purity of the hexadecane employed. We note that we have used, as supplied, the best grade of hexadecane commercially available. Newer advancing *n*-hexadecane contact angles found on saved samples of other monolayers on silicon reported on here were (±2°): **1**, 44°; **2**, 36°; **4**, 26°; TTS, 45°. We note that our interpretation of contact angles relies primarily on trends, relative to OTS, rather than absolute magnitudes of individual contact angles.

[28] Fox, H. W.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 428.

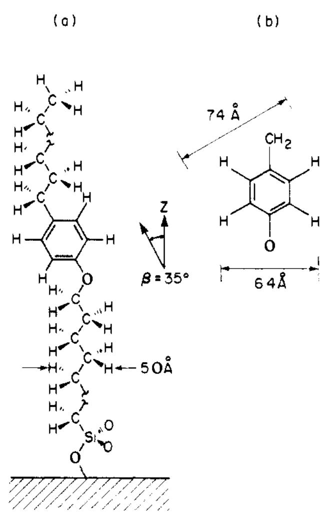

Figure 4. (a) Representation of **1** in a monolayer with fully extended alkyl chains that are perpendicular to the surface. The length of the alkyl chains has been shortened for clarity. The C_1–C_4 axis of the phenyl ring has a 35° tilt (β) from the substrate surface normal (z axis). (b) Dimensions of the phenyl ring, calculated from the usual bond lengths and van der Waals radii. Not shown is the thickness of the π-cloud, 3.4 Å.

or detergent cleaning of the surface between immersions, to optimize monolayer formation.[29] By comparison, monolayers of OTS formed at a much faster rate (~1–3 min in a single immersion). This implies a decrease in monolayer stability and quality for TTS, relative to OTS, not apparent in the γ_c value. The C_{11} molecule in the series (UTS) shows a decrease in monolayer "quality" clearly reflected in the contact angle data and γ_c, with contact angles (particularly oleophobic contact angles) significantly lower than values for OTS and TTS (by 2–9°) and a γ_c value 1.3 dyn/cm higher.

A comparison of the monolayer film thickness values in Table I for TTS (12 methylene units) and for OTS (17 methylene units) suggests an increase in film thickness of 1.2 Å per methylene unit. If we assume that the alkyl chain axis is perpendicular to the surface, then for a fully extended all-trans chain, each C–C bond is canted by 35° from the chain axis. Since the C–C bond length is 1.5 Å, each bond should add 1.5(cos 35°) = 1.2 Å to the expected film thickness. On this basis, we expect a thickness of 16.6 Å for UTS, with 10 methylene units. The observed value of 15 Å is lower than this, indicating a decrease in packing (and presumably monolayer order) or an increase in C–C chain axis tilt. This data is consistent with the increase in γ_c and wettability also observed.

Compound **1** is, like OTS, a relatively long-chain (20 alkyl carbons) material. The insertion of the phenoxy group into the alkyl chain at the C_{11}–C_{12} position breaks the alkyl chain into approximately two halves and breaks the symmetry of the system by imposing a disk-shaped benzene ring of maximum dimensions 7.4 Å across by 3.4 Å thick (the thickness of the π-cloud) into the alkyl chains, which can be considered as cylinders of ~5.0 Å diameter (known from cross-sectional areas of ~20 Å^2 determined for Langmuir–Blodgett films[30]). If the alkyl chains are represented as perpendicular to the substrate surface, then the $C_1(O)$–$C_4(C)$ phenyl ring axis would necessarily be canted at ~35° from the surface normal. These features are represented in Figure 4. In Figure 4a we arbitrarily represent the phenyl ring as lying in the plane of the paper; similar models can also be generated by rotation of the phenyl ring about the C_1–C_4 axis.

Using this value of 1.2 Å per CH_2 unit and the measured thickness of 25 Å for OTS as a reference, we estimate a contribution to the film thickness of 25 + 2(1.2) Å = 27.4 Å from the alkyl chains in **1**. The phenoxy group has a length of 2.8 Å (the distance from C_1 to C_4 along the C_{2v} axis) plus 1.4 Å (the C(aromatic)–O bond distance), or 4.2 Å. The phenoxy group would thus be expected to add a total of 4.2(cos 35°) + 1.2 Å (for the C(aliphatic)–O bond) = 4.6 Å to the film thickness. Hence we calculate an expected thickness of 27.4 + 4.6 = 32.0 Å, which is within experimental uncertainty of the 31 Å actually observed. Ellipsometry thus establishes the monomolecular nature of the films formed from **1** and qualitatively suggests that the molecules of **1** are approximately perpendicular to the substrate surface and with nearly fully extended alkyl chains.

From the wettability data for **1** (Table II), it is also apparent that the introduction of the phenoxy group into the interior of the monolayer does not perturb the critical surface tension or wettability (contact angle) characteristics of the monolayer, and a close-packed structure of surface methyl groups is essentially retained. The values for contact angles and γ_c are practically identical with those found for OTS.

When the overall chain length, $m + n$, is decreased, from 19 methylene units in **1** to 12 in compounds **2–4**, the resulting values for film thicknesses, 23–24 Å, are within experimental error of the 23 Å, which may be calculated by assuming a decrease of 1.2 Å per CH_2 unit in film thickness from the 31 Å measured for **1**. Several features of monolayers of **2–4** make clear, however, a decrease in film ordering compared with **1**. While monolayers of **1** could be formed in several minutes with a single immersion in the silanizing solution, compounds **2–4**, like TTS and UTS, required several 10–15 min immersions to optimize monolayer formation. This relatively slow buildup in monolayer film quality, as measured by film thickness and contact angles, is represented in Figure 1, parts a and b, for compound **3**. We also observe a significant decrease in contact angles and a significant increase in γ_c. Consider the data for monolayers of **2** on silicon wafers, which show oleophobic contact angles and a γ_c value (22.0 dyn/cm) very close to those observed for UTS. Since we know from compound **1** that a phenoxy group isolated from the liquid interface by nine alkyl carbons has, ipso facto, no direct effect on the monolayer surface wettability properties, it must be that inclusion of this group into the C_{13} chain results in an increase in the overall disorder equivalent to removing two alkyl carbons from the chain. This effect is masked by the appreciably longer alkyl chains in the molecule **1**.

As the phenoxy group position in the monolayer is varied in compounds **2–4**, by progressively "migrating" it toward the surface, we observe a clear increase in surface tension and wettability. Thus, γ_c changes from ~22 dyn/cm in **2** to ~26 dyn/cm in **4**. Despite the fact that each of compounds **2–4** formally terminates in a methyl group, the surface properties are progressively modified by the phenoxy group as it is placed closer to the surface. We envisage this as the result of voids and disorder introduced by the phenyl ring, which the alkyl chains compensate for by bending or tilting. Using the dimensions indicated in Figure 7b, we calculate that the cross-sectional area of the phenyl ring (its projected area on the substrate surface) may be approximated as a rectangle of dimensions of from 6.4 to 7.4 Å by 3.4 Å (the thickness of the benzene π-cloud), or from 21.8 to 25.2 Å^2. This is from 10 to 25% larger than the cross-sectional area of the alkyl chains (20 Å^2 [26]). Therefore, complete close-packing of the phenyl rings should introduce 10–25% void space into the alkyl chains of monolayers. We know from **1** that a nine-carbon chain between the phenyl ring and the solution (m = 8) is long enough to compensate for this disorder and "restore" the surface properties of the monolayer to the low values characteristic of close-packed surface methyl groups. As this chain is shortened to five carbon atoms, the effect of the phenoxy group begins to become detectable, whereas in **4**, where the chain is reduced to only two carbon atoms, the effect of the phenoxy group is quite pronounced. This effect is similar to the effect of shortening the overall chain

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[29] We preferred detergent cleaning since it afforded the cleanest surfaces in a minimal period of time, without measurably reducing monolayer quality, although substrate immersion in refluxing CCl_4 vapor for several hours gave adequate, but somewhat poorer, results. Repeat immersions, with cleaning of monolayer surfaces in chloroform in a Soxhlet extractor have also been found by Gun and Sagiv[3] to effectively "repair" incompletely formed monolayers of OTS.

[30] Kuhn, H.; Mobius, D. In *Physical Methods in Chemistry*; Weissberger, A., Rossiter, B., Eds.; Wiley: New York, 1972; Part 3B, Vol. 1, p 577.

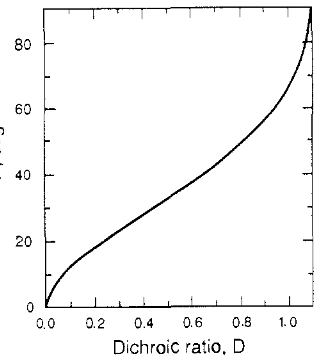

Figure 5. Plot of orientation angle ϕ vs dichroic ratio D calculated from eq 4, as described in text.

length in monolayers of *n*-alkanoic acids and thiols, where it has been found that below a certain critical length of ca. 12 carbon atoms there is a marked increase in monolayer chain tilt and disorder.[8,16,21] For this series of compounds we find that the alkyl chains lying just below the monolayer/solution interface require a length of between $m = 4$ and $m = 8$ to completely form a surface characterized by close-packed methyl groups and compensate for the disorder imposed by the phenyl ring. This value, however, may depend on the length of n.

FTIR Studies. Two types of FTIR spectroscopy have in recent years proven especially useful in the study of single monolayers: external specular grazing angle and attenuated total reflection (ATR) spectroscopy.[31] The grazing angle mode relies on the existence, where a light beam is reflected at high incident angles off a metallic, reflecting surface, of an electric field vector strongly polarized normal to the surface.[20] Consequently, vibrational modes that have transition dipole moments oriented perpendicular to the surface will show relatively strong absorbances, while transition dipoles completely parallel to the surface should approach zero.[21] In the ATR mode the incident, internally reflected beam can be polarized either perpendicular (s-polarized) or parallel (p-polarized) to the plane of incidence.[1,22,23,32]

We have recorded FTIR spectra for OTS, TTS, and **1**–**4**. The formation of monolayers of OTS and of **1** were facile enough so that monolayers could be fabricated on aluminized silicon wafers and grazing angle spectra obtained. However, TTS and **2**–**4**, which form monolayers more slowly, tended to give irreversible, bulk film buildup with poor, although noticable, monolayer features in the spectrum. Nevertheless, ATR spectra could be recorded for all these compounds.

Figure 2a presents the bulk (CCl_4 solution) spectrum of **1**. Figure 2, parts b and c, present the grazing angle and ATR spectra of **1** on aluminized silicon and a silicon ATR prism, respectively. It is apparent that each of the monolayer spectra show significant deviations from the bulk spectrum. The C–H stretching region of the grazing angle spectrum in Figure 2b is expanded in Figure 3a and compared with OTS in Figure 3b.

Figure 3a shows that the alkyl chains of **1** have an approximately perpendicular orientation, as the CH_2 stretching modes ($\nu_a(CH_2)$ at ca. 2922 cm^{-1} and $\nu_s(CH_2)$ at 2851 cm^{-1}) are greatly reduced in intensity relative to the CH_3 stretching modes ($\nu_a(CH_3$, ip) at 2965 cm^{-1} and $\nu_s(CH_3)$ at 2880 cm^{-1} [33]) as compared with the bulk spectrum (Figure 3a). For the monolayer, we find (Figure 5a) $A_{2920}/A_{2965} \approx 3.1$ and $A_{2851}/A_{2880} \approx 2.4$. By comparison, the absorbances at 2965 and 2880 cm^{-1} in the bulk spectrum are completely obscured by the intensity of the CH_2 vibrations. Note that for completely perpendicular alkyl chains, the CH_2 vibrations, which have transition dipole moments perpendicular to the alkyl chain axis[7,21,34,35] (i.e., parallel to the substrate surface), would be expected to approach zero intensity in the grazing angle experiment.[21] The alkyl chains in **1** appear to be somewhat more tilted than is the case for OTS, where we find (Figure 3b) that $A_{2919}/A_{2968} \approx 0.8$ and $A_{2851}/A_{2880} \approx 0.9$ in the monolayer grazing angle spectrum.[36] There are also interesting frequency shifts in the grazing angle spectra for the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ modes, which also appear in ATR; these will be discussed in connection with the ATR results. The other prominent features in the grazing angle spectrum of **1** are the intense bands at 1516 and 1255 cm^{-1}. The 1255-cm^{-1} band we assign as a C–O–C asymmetric stretch;[37] note that it is shifted to a higher frequency by 11 cm^{-1} from the position in the bulk spectrum. The high relative intensity of this band indicates that the transition moment for this vibration in the monolayer is roughly perpendicular to the surface. The intense band at 1516 cm^{-1} in the grazing angle spectrum we assign as an aromatic ring C=C stretch (vibration 19a). Assuming C_{2v} symmetry for the phenyl ring, this should have a transition dipole moment parallel to the phenyl C_1–C_4 ring axis.[25] Like the C–O–C asymmetric stretch, the high relative intensity of this band indicates, in a qualitative way, that the transition moment for this vibration, and hence the C_1–C_4 axis of the phenyl ring, is oriented approximately perpendicular to the substrate surface.

Figure 2c presents the p-polarized ATR spectrum of a monolayer of **1** on a silicon prism. ATR should show a reduced sensitivity to vertically oriented transition dipole moments,[1] and in fact the 1515 band, which is enhanced in the grazing angle spectrum, shows a marked diminution in intensity in the p-polarized ATR spectrum relative to the solution spectrum. In the solution spectrum, $A_{1512}/A_{2929} \approx 0.53$, whereas in the monolayer $A_{1515}/A_{2920} \approx 0.17$.

ATR affords excellent signal-to-noise ratios for the C–H stretching region of the monolayer IR spectra, and we have measured peak absorption frequencies, intensities, and peak widths for the $\nu_a(CH_2)$ band for OTS, TTS, and **1**–**4**.[24] (We used p-polarized light for these results; they would be little affected if s-polarized or unpolarized light were used instead, since the dichroic ratios for the CH_2 vibrations are close to unity.) Each of these compounds showed a liquid-phase absorption (CCl_4 solution) in the range of 2928–2930 cm^{-1}.[38] For each of the compounds studied, we observe a shift toward lower frequencies in the monolayers. In the case of OTS, the observed frequency of 2918 cm^{-1} (found also by Maoz and Sagiv[1]) is shifted by $\Delta\nu = -10$ cm^{-1} from the solution value. With TTS, the effect of shortening the alkyl chain is to reduce this frequency shift to $\Delta\nu = -7$ cm^{-1}. Thus we observe a shift in frequency $\Delta\Delta\nu = +3$ cm^{-1} for TTS (where $n = 12$ methylene units) relative to OTS ($n = 17$). This is close to a result found by Porter et al.,[8] who found $\Delta\Delta\nu = +2$ cm^{-1} for the $n = 11$ and $n = 17$ series of *n*-alkyl thiols. They have in-

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(31) Swalen, J. D. *J. Mol. Electron.* **1986**, *2*, 155.

(32) Haller, G. L.; Rice, R. W. *J. Phys. Chem.* **1970**, *74*, 4386.

(33) Band assignments follow those made by Allara and Nuzzo for monolayers of *n*-alkanoic acids and by Nuzzo et al. for alkyl thiol monolayers; ref 7, 21 and references therein. The nomenclature for CH_2 band assignments is as in ref 34 and 35.

(34) Rabolt, J. F.; Burns, F. C.; Schlotter, N. E.; Swalen, J. D. *J. Chem. Phys.* **1983**, *78*, 946 and references therein.

(35) Allara, D. L.; Swalen, J. D. *J. Phys. Chem.* **1982**, *86*, 2700.

(36) One referee has kindly suggested the result that the tilt of the CH_2 transition dipole moments in the plane of the C–C alkyl chain axis may be estimated from the $\nu_s(CH_2)/\nu_s(CH_3)$ intensity ratio, A_{2850}/A_{2880}. The $\nu_s(CH_2)$ vibration has a transition dipole moment in the plane of but perpendicular to the C–C alkyl chain axis, while the $\nu_s(CH_3)$ vibration transition dipole moment orientation is parallel to the C–CH_3 bond.[31] We assume as an approximation that the monolayers are composed of all-trans, fully-extended alkyl chains, that the films are isotropic in the plane of the substrate, that the transition dipole moments are uniaxially symmetric about the substrate normal axis, and use the simplifying assumption that the transition oscillator strengths of the methyl and methylene stretches are equal. If the tilt angle of the $\nu_s(CH_2)$ vibration with respect to the substrate surface normal is defined as ϕ ($0° \leq \phi \leq 90°$), then for an extended alkyl chain perpendicular to the surface the $\nu_s(CH_3)$ transition dipole moment has a tilt of $\sim\phi - 55°$. The tilt angle of **1** in the plane of the C–C alkyl chain axis is then given to a first approximation by $2.4 \approx (19/1)(2/3)\cos^2\phi/\cos^2(\phi - 55°)$,[31] or $\phi \approx 65°$, where the ratio 19/1 is the methylene/methyl ratio, and 2/3 is the ratio of hydrogens in a methylene group to a methyl group. A similar calculation for OTS gives $\phi \approx 75°$. Since the alkyl chain axis tilt is $90 - \phi$, the alkyl chains of **1** and OTS are seen to be tilted (on average) at ca. 25° and 15°, respectively. These values are in excellent agreement with those found by ATR (see below).

(37) Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden Day: San Francisco, 1962.

(38) The absorption for neat films, which could not always be satisfactorily obtained with the viscous, easily hydrolyzed trichlorosilanes studied here, was always within 1–2 cm^{-1} of the solution value.

terpreted this effect as the result of a more liquidlike, disordered environment for the methylene units in the shorter molecules, a shift that parallels frequency shifts observed between the liquid and solid phases of long-chain alkanes.[39] In addition to a frequency shift, we also observe a distinct band broadening in the TTS monolayers, relative to OTS. Whereas the band width of the 2920-cm^{-1} band is 25–26 cm^{-1} in solution for both OTS and TTS, it is much broader in the TTS monolayer (21 cm^{-1}) than in the OTS monolayer (16 cm^{-1}). Like the frequency shift, this is an effect of increasing liquidity and disorder in the monolayer structure. Similar band broadening occurs in long polymeric alkyl chains in the liquid state relative to the crystalline state.[40]

Similar effects are observed in the series of compounds **1–4**. The $\nu_a(CH_2)$ frequency in solution (2929 cm^{-1}) is little different from OTS. The monolayers show absorption at lower frequencies (for **1**, $\Delta\nu = -9$ cm^{-1}), and this effect diminishes with decreasing alkyl chain length (for **2–4**, $\Delta\nu = -5$ to -9 cm^{-1}). Peak widths narrow from the solution values of 30–32 cm^{-1} to 23 cm^{-1} for **1** and 26–33 cm^{-1} for **2–4**. These results indicate a relatively high degree of "crystallinity" and order in monolayers of **1**, whereas the shorter compounds **2–4** form monolayers that are in a more liquidlike, disordered state.

If the direction of transition dipole moments relative to molecular coordinates can be accurately assigned, the use of polarized ATR measurements allows the evaluation of molecular orientation from dichroic ratios of peak intensities for s- and p-polarization, since the electric field at the surface of the ATR crystal has an amplitude with both normal and tangential components.[22,31] The data for s- and p-polarized spectral intensities are collected in Table III. It should be noted that all spectra used in Table III were run on the same ATR crystal and were referenced to the same s- or p-polarized background spectra to facilitate comparison of relative trends.

For OTS, the dichroic ratio D (which we define as the ratio of s- to p-polarized intensities) for the 2920 cm^{-1} bond is 1.04 (Table III), in reasonable agreement with values of 1.03 and 1.09 found by Maoz and Sagiv[1] under comparable experimental conditions. For TTS, the ratio D drops to 0.96. For compounds **1–4**, we could measure intensities for the 1515-cm^{-1} band, in addition to the 2920 band. For **1**, we found $D_{2920} = 0.98$ and $D_{1515} = 0.24$. (We estimate the error associated with these measurements to be ca. ± 0.1.) All of the shorter molecules **2–4** show a decrease in the ratio D_{2920} (to 0.8–0.9) and an increase in the ratio D_{1515} (to ca. 0.5). As will be discussed below, this is associated with a greater degree of tilting of the molecular axis and a greater amount of disorder in the shorter molecules than for **1**.

In order to evaluate quantitatively the orientation of vibrational modes from the dichroic ratios in monolayer films, we assume a uniaxial distribution of transition dipole moments with respect to the surface normal.[23,41] We refer to the coordinate system diagrammed in Figure 2 of the supplementary material. We define ϕ as the angle between the transition dipole moment M and the surface normal (note that $0° \le \phi \le 90°$). The absorbances due to the components E_x, E_y, and E_z of the electric field of the evanescent wave[22] in the ATR experiment are given by eq 1–3.[40]

$$A_z = M^2 E_z^2 \cos^2 \phi \tag{1}$$

$$A_x = \frac{1}{2} M^2 E_x^2 \sin^2 \phi \tag{2}$$

$$A_y = \frac{1}{2} M^2 E_y^2 \sin^2 \phi \tag{3}$$

Light polarized parallel to the incident plane (p-polarized) has components in the x and z direction, while light polarized perpendicular to the incident plane (s-polarized) has only a y component. Therefore, the dichroic ratio D is given by eq 4. This

$$D = \frac{A_s}{A_p} = \frac{A_y}{A_z + A_x} \tag{4}$$

equation is written in terms of A_s and A_p, the polarized absorbances of a monolayer on the internally reflecting surfaces of the ATR crystal, omitting the contribution of the entrance and exit faces. The observed dichroic ratio D_{obsd} should, in principle, include a contribution A_T from the transmission absorption from the entrance and exit faces (eq 5).

$$D_{obsd} = \frac{A_s + A_T}{A_p + A_T} \tag{5}$$

We neglect the contribution A_T in eq 5 and set $D \simeq D_{obsd}$, since a transmission IR experiment for **1** gave only a very weak spectrum, with an absorbance at 2920 cm^{-1} of only 6% of the absorbance in the ATR mode (using p-polarized light), which would affect D by less than 0.01 at values close to $D = 1.0$, and since no significant signal could be detected for the 1515 band. The expressions for the electric field components E_x, E_y, and E_z have been evaluated by Haller and Rice,[32] based on a theory developed by Harrick.[22a] We insert these expressions into eq 1–3 and 4, calculate a plot of ϕ vs D (Figure 5), and estimate the unknown angle ϕ for a given monolayer from this plot.

The results of this procedure are included in the far right column of Table III for the methylene stretching vibrations of all monolayers and the 1515 cm^{-1} vibration in **1–4**. Since the $\nu_s(CH_2)$ and $\nu_a(CH_2)$ vibrations have transition dipole moments that are perpendicular to the alkyl chain axis,[35] the alkyl chain axis tilt (which we call α) is given, as a first approximation, by $\alpha = 90° - \phi$. Therefore we can estimate a chain axis tilt of $\alpha \approx 10$–$18°$ for OTS, 27–29° for TTS, 26° for **1**, and 22–42° for monolayers of **2–4** (with most values of 30–40°). Unfortunately, the sizable error in the dichroic ratio D (±0.10) corresponds to an uncertainty of $\sim\pm18°$ in the orientation angle ϕ for values of $D \approx 1.0$ (24° chain axis tilt, or $\phi = 66°$). For this reason, we take the values of D in Table III for the 2920-cm^{-1} vibration to indicate relative trends only (α for OTS < TTS $\sim$ **1** < **2** $\sim$ **3** $\sim$ **4**) and ascribe little significance, other than as estimates, for the absolute magnitudes of ϕ for this vibration.[42] Relative trends for this data are probably more certain, since all the spectra used in Table III were recorded from common reference, background spectra (for s- or p-polarization). The model used for calculating ϕ is strictly valid only for complete molecular ordering and uniaxial symmetry of transition dipole moments about the z axis, and as monolayers become more disordered, this presumably breaks down (for a completely isotropic film, $D = 0.897$ can be calculated[1]).

However, for values of $D \ll 1.0$, the slope of the curve decreases markedly from that at $D \approx 1.0$, and an error of ±0.1 in D at $D = 0.34$ ($\phi = 25°$) corresponds to an error in ϕ of only ca. ±5°. For the 1515-cm^{-1} band in monolayers of **1–4**, due to the aromatic ring stretching mode, vibration 19a, the dichroic ratios lie along this portion of the curve. Therefore, the measurement of linear dichroism for the 1515 band should convey more accurate and clear information about molecular orientation and monolayer quality than the CH$_2$ stretching bands. We define β as the angle between the phenyl ring C_1–C_4 axis and the z-axis. Note that $\beta = \phi$. We find that the perpendicular orientation of the phenyl ring decreases in the order **1** ($\beta \approx 20°$) < **2** ($\beta \approx 32°$) $\sim$ **3** ($\beta \approx 30°$) $\sim$ **4** ($\beta \approx 32°$).

The model in Figure 4a, with the C–C alkyl chain axis perpendicular to the surface ($\alpha = 0°$), predicts an angle of 35° for β. It is apparent from the data in Table III that monolayers of **1** are formed with β significantly less than this ($\beta \approx 20°$). At the same time, the tilt of the alkyl chains in **1** has increased by

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(39) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

(40) Zbinden, R. *Infrared Spectroscopy of High Polymers*; Academic: New York, 1964.

(41) We believe this assumption to be a reasonable one for a crystalline-like, regularly ordered monolayer assembly. An alternative, although more complex model is to assume uniaxial symmetry of transition dipole moments about a molecular axis, which itself is tilted (and uniaxially symmetric) with respect to the z axis. As monolayers become more liquidlike, this may become a progressively more valid model. For example, see: Fringeli, U. P.; Schadt, M.; Rihak, P.; Gunthardt, Hs. H. *Z. Naturforsch. A* **1974**, *31a*, 1098, and ref 40.

(42) Maoz and Sagiv report a similar conclusion (ref 1) for monolayers of OTS.

ca. 8–15°, relative to OTS. We suggest that this is the result of the mismatch of cross-sectional areas of the phenyl ring, as compared with the alkyl chains. The packing in a monolayer is undoubtedly the result of a number of different attractive and repulsive factors (head group bonding and spacing, van der Waals attractions, dipole–dipole interactions, and overlap of the phenyl ring molecular orbitals). However, the packing in a monolayer cannot be any closer than the spacing of the largest moiety in the monolayer structure. As mentioned earlier, the cross-sectional area of the phenyl ring (i.e., the projection of the benzene ring onto the substrate surface), according to the model of Figure 4a, is from 21.8 Å^2 to 25.2 Å^2, *depending upon the phenyl ring orientation.* We consider as an example a clockwise rotation of 15° in the plane of the paper of the molecule presented in Figure 4a. When the phenyl ring is oriented at 35° from the surface normal (as pictured in the figure), then this cross-sectional area (which has a maximum at 30° tilt) is 25.1 Å^2, whereas a tilt angle of 20° (after the 15° rotation) gives a cross-sectional area of 24.8 Å^2. Therefore such a tilting of the molecule allows for closer packing of the molecules in the monolayer. At the same time, the cross-sectional area of the alkyl chains increases from a spherical geometry of 19.6 Å^2 to an elliptical geometry of 20.7 Å^2. Such a tilting of the molecule creates an increase in the cohesive van der Waals interactions of the alkyl chains, relative to the unrotated molecule.

This simple model neglects many details of the monolayer organization. For example similar models to that of Figure 4a may be generated by rotation of the phenyl ring about the C_1–C_4 axis. Unfortunately, due to the opacity of silicon to IR radiation below about 1500 cm^{-1}, it is not possible to observe any aromatic vibrational bands that have transition moments orthogonal to the 1515-cm^{-1} band. This would allow both the average tilt and the rotation of the phenyl ring to be specified. It is also apparent from a comparison of the dichroic ratios of the symmetric CH_2 stretch (transition moment parallel to the substrate surface and in the plane of the C–C alkyl chain,[35] i.e., in the plane of the paper in Figure 4a) and the asymmetric CH_2 stretch (transition moment perpendicular to the symmetric stretch, parallel to the substrate surface, and out of the plane of the C–C chain axis[35]) that the molecules of **1** appear to be more or less uniformly tilted and that the alkyl chains are tilted at both an angle in the plane of the paper of Figure 4a as well as out of the plane. Nevertheless, it would appear from simple geometrical considerations that the increased tilting of the alkyl chains and the decreased tilting of the phenyl ring, relative to that expected from the simple model, is due to the difference in the cross-sectional areas of the alkyl chains and the phenyl ring and that decreased tilting of the phenyl ring would serve to increase the packing of the monolayer structure.

Considering monolayers **2–4**, it is apparent that, relative to **1**, the average tilt of both the alkyl chains and the phenyl ring has increased by ~10°. Such an increase in the tilt of all parts of the molecule would be expected with decreased packing and/or increased disorder in the monolayer, with collapse of the crystalline-like, ordered structure. This observation parallels the results for the $\nu_a(CH_2)$ frequency and band broadening discussed earlier. It is interesting that within the series **2–4** practically no difference in the orientation of the phenyl ring with its position in the alkyl chain is noted. We cannot say from this study whether such a change in orientation might occur with incorporation of the ring at either of the two interfacial positions (monolayer–substrate or monolayer–solution).

Conclusion

The development and utilization of self-assembled monolayers in a scientific or technological capacity for electronic or optical purposes requires a basic understanding of the effects of group incorporation in monolayers beyond the simple alkyltrichlorosilanes that have been to date the most thoroughly characterized materials. We have incorporated a phenoxy group into such monolayers and determined that such a modification can be made for a relatively long alkyl chain molecule (**1**) while still retaining a close-packed, ordered assembly with nearly fully extended alkyl chains and surface wettability properties identical with those of OTS. In monolayers of **1**, the phenoxy group is incorporated with an approximately vertical (≈20° tilt) arrangement of the phenyl ring C_1–C_4 axis, while the alkyl chains are somewhat more tilted (by ≈10°) than for OTS. When the alkyl chain is shorted to 13 carbons in monolayers of **2–4**, FTIR and wettability both indicate that more disordered liquidlike monolayers are formed. By comparison with the 13-carbon-atom *n*-alkyltrichlorosilane, TTS, the effect of the phenoxy group is to reduce monolayer order by a factor equivalent to shortening the alkyl chain of TTS by two methylene units. The average tilt angle of both the phenyl ring and the alkyl chains increases, an effect attributed also to increased disorder ("liquidity") and molecular tilting of the monolayers. A comparison of compounds **2–4** shows that the orientation of a phenoxy group in the interior of the monolayer is little affected by its position in the alkyl chain. However, the phenoxy group measurably affects the surface wettability when it is placed within approximately five alkyl carbon atoms from the surface.

Although the FTIR-ATR orientational measurements are subject to large uncertainties, corresponding to ±5–18° in the tilt angle of various molecular features, the results are internally consistent, and are bolstered by the evidence obtained by grazing angle FTIR studies. The orientational results are also qualitatively supported by the results from ellipsometric measurements, which are consistent with approximately vertical, extended alkyl chain axes in all monolayers studied here. In addition, trends in relative monolayer "liquidity" and disorder, which are indicated in the FTIR results by peak position and band broadening effects, are seen to be reflected in wettability measurements on the hydrophobic, methyl group functionalized surfaces by lowered contact angles and higher critical surface tension values.

The results of this study demonstrate that self-assembled monolayers can be fabricated by incorporating significant modifications to the basic alkyltrichlorosilane system. We are continuing to explore these problems, including the incorporation of other aromatic moieties and functionalized groups into monolayer assemblies.

Experimental Section

Unless otherwise specified, all solvents and reagents employed were of 98%+ grade purity. Hexadecane and CCl_4 were obtained from Aldrich (99%+ "Gold Label" grade) and used as supplied. Unless otherwise noted, ethanol was 3A ethanol (denatured with 5% methanol). Octadecyltrichlorosilane (OTS) was obtained from Aldrich and vacuum distilled prior to use. Isopar-G (Exxon) was passed through an approximately equal volume of basic alumina. Analysis by ^{1}H and ^{13}C NMR and IR indicated that the resulting solvent, a high-boiling, ligroin-type mixture of highly branched, isoparafinic hydrocarbons, was free of aromatic, olefinic, or other functional group impurities. The surface tension (γ_l) was measured in the ambient atmosphere as 22.3 dyn/cm.

Routine IR spectra were run on a Perkin-Elmer 1430 spectrometer and are accurate to ±5 cm^{-1}. FTIR spectra were run on an IBM IR44 spectrometer (see below). Solution spectra are routine spectra, unless FTIR is indicated.

Substrates. Silicon wafers were p-doped, test grade, polished silicon wafers (from Wacker Chemitronic GMBH) and were cut into smaller strips and then cleaned by brushing with detergent solution (Deconex[43] 12PA, ca. 10% in water) with a soft camel-hair brush, followed by Rf plasma cleaning (1 Torr of Ar pressure, 30-W power, 5 min) in a Harrick PDC-3XG plasma discharge cleaner. Silicon ATR prisms were 50 × 10 × 3 mm 45° single pass prisms from Harrick, and were cleaned in the same fashion as described for the silicon wafers. ATR prisms were reused but required prolonged (ca. 20 min) cleaning in argon plasma to completely remove old monolayers. Aluminized silicon wafers were prepared by vapor depositing (at 10^{-6} Torr) 1000 Å of aluminum onto cleaned silicon wafers (75 × 25 mm). The thickness was monitored with a quartz crystal thickness monitor. The chamber was back-filled with nitrogen after the deposition. The aluminized substrates were immediately coated with a protective monolayer of OTS upon receipt (thus protected, the aluminized surfaces appear to be indefinitely storable) and carefully cleaned with detergent followed by rinsing with water and argon plasma cleaning (ca. 20 min) immediately prior to use.

Monolayer Preparation. Monolayers were adsorbed from freshly prepared solutions of the silanizing agent in a solvent mixture consisting

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[43] Deconex is a trademark of Borer Chemie P. G.

of 20% (by volume) CCl_4 in Isopar-G. It was found that the rate and quality of monolayer formation was facilitated by the addition of trace amounts of water to the system by allowing the mixed solvent to stand over a few drops of water per 500 mL and decanting prior to the addition of the silanizing agent.[44]

Monolayers on silicon were prepared by immersing cleaned silicon substrates (wafers or ATR prisms) into a ca. 5×10^{-3} M solution of silanizing agent (OTS, TTS, UTS, or **1**–**4**). Monolayers of OTS or **1** could be formed rapidly (in 1–3 min) in a single immersion, but reaction for compounds **2**–**4**, TTS, or UTS proceeded more slowly, and continued immersions of 10–15 min usually resulted in a further increase of contact angles and film thickness from initially low values. After each immersion the monolayers were rinsed with, in succession, CCl_4, ethanol, water, and distilled water, and then they were cleaned with a dilute detergent solution (ca. 10% Deconex 12PA) with a soft camel-hair brush, rinsed again with distilled water, and dried in a stream of nitrogen. Immersion of the substrates was continued until a stable, maximal, limiting oleophobic contact angle and film thickness were achieved. Efforts to prepare monolayers on germanium ATR prisms proved unsuccessful.

Detergent or vigorous solvent cleaning was found to be important to remove adsorbed material on the monolayers. Prior to such cleaning, monolayers were found to have an excess thickness (by ellipsometry) of from several angstroms (in the case of OTS and **1**) to ca. 10–20 Å in the case of TTS or **2**–**4**. A sample monolayer of TTS on a Si ATR prism showed a ca. 33% reduction in the intensity of the 2920-cm^{-1} band, and a reduction in thickness of from 38 to 20 Å after a single short detergent cleaning. The spectral intensity did not change after a subsequent cleaning. The wettability of the monolayers did not appear to change significantly except that contact angle hysteresis diminished and contact angles across a given surface became more uniform. No evidence was found for any increase of film thickness (e.g., by inclusion or adsorption of impurities) for monolayers on silicon as a result of this detergent treatment.

Monolayers of **1** and of OTS on aluminized silicon wafers were prepared by immersing the clean substrate into ca. 5×10^{-3} M silanizing solutions, with use of only very short ($\leq$20 s) immersion times. Longer times resulted in thick film (greater monolayer thickness) buildup and loss of oleophobicity, for reasons that are unclear. Longer immersion times resulted also in the deterioration of monolayer features in the grazing angle IR spectrum. Monolayers on aluminum were rinsed *only* with CCl_4 (toward which monolayers of **1** and OTS are oleophobic) and dried with a stream of nitrogen. Although detergent cleaning a sample OTS monolayer did not change the grazing angle spectrum, a loss of oleophobicity (by ca. 4° hexadecane contact angle) was observed, and hence this treatment was avoided. Compounds **2**–**4** and TTS failed to give acceptable monolayers on aluminum.

Ellipsometry Measurements. Film thickness by ellipsometry was measured with a Gaertner L116B ellipsometer equipped with a 632.8-nm He–Ne laser. Optical constants were predetermined for 5–10 spots on the cleaned, uncoated substrate immediately prior to silanation of the surface. Film thickness was then measured, with an approximate value of $n_f = 1.50$ for the film refractive index, for each spot by using the optical constants determined for that spot, although in the case of silicon wafers little variation in the optical constants or final film thickness across a surface was found. For ATR prisms and aluminized silicon wafers, significant variations in the optical constants were sometimes encountered.

Contact Angle Measurements. Contact angles were measured by applying small sessile drops (<2-mm diameter) to the surface with a syringe or fine capillary tube and immediately measuring the angle visually and averaging measurements on both sides of the drop with a Rame-Hart NRL 100 goniometer. The contact angle was found by averaging the results from three independent drops. Measurements were performed in the ambient atmosphere. Advancing contact angles were taken as the maximum contact angle observed by incrementally increasing the drop size. Contact angles were generally measured within 20–30 s of liquid application. Usually, on clean, coated surfaces little difference was found between the initial contact angle and the contact angle found after increasing the drop size. Advancing contact angles were found to vary little (usually <±2°) at various positions on a given surface.

Critical Surface Tensions. Contact angle measurements for a series of test liquids were used to derive critical surface tensions of the monolayers (γ_c) from a Zisman plot of cos θ_i vs γ_l, where θ_i are advancing contact angles and γ_c are the measured liquid surface tensions of the test liquids. Linear regression was used to define the best line through the approximately linear data points (correlations were generally >0.98), and the value of γ at $\cos \theta = 1.00$ gives γ_c. The following were used as test liquids: heptane, nonane, decane, dodecane, and hexadecane (all from Aldrich, 99%+ "Gold Label" grade, used as supplied); octane (95%), tetradecane (99%), 1-bromonaphthalene (99%), methylene iodide (99%), and 2,2′-thiodiethanol (99%) (all from Kodak, passed through an equal volume of basic alumina prior to use); formamide (Kodak, polarographic and nonaqueous titration grade, used as supplied); dicyclohexyl, tridecane, and 1-methylnaphthalene (both from Aldrich, 99%, passed through an equal volume of basic alumina prior to use); and water (deionized and distilled, filtered through a Millipore Q system prior to use). The following are surface tensions measured for these liquids (at 24 ± 2 °C, ambient atmosphere) by using the Wilhelmy plate technique, with literature values[45] (at 25 °C) in parentheses (units are dyn/cm): heptane 20.1 (19.7), octane 21.4 (21.1), nonane 22.5 (22.4), decane 23.4 (23.4), dodecane 24.9 (24.9), tridecane 25.6 (25.6), tetradecane 26.2 (26.1), hexadecane 27.2 (27.0), dicyclohexyl 32.3 (32.2), 1-methylnaphthalene 39.3 (37.6), 1-bromonaphthalene 43.9 (43.9), methylene iodide 48.1 (50.8 at 20 °C[24]), 2,2′-thiodiethanol 54.8, formamide 58.9 (57.0), water (72.1, used as a standard).

FTIR Spectroscopy of Monolayers. FTIR spectra, in both grazing angle and ATR modes, were performed on an IBM IR44 spectrometer. All spectra were measured in a sample compartment purged for several hours with dry nitrogen. All polarization of the incident beam in FTIR experiments was done with a Brewster's angle germanium single-diamond polarizer (Harrick), which could be rotated through 90° to produce p-polarization (parallel to the incident plane) or s-polarization (perpendicular to the incident plane). For grazing angle external specular reflection spectra, a Harrick variable angle attachment was employed with an incident angle of 76°, and the incident light was p-polarized. Grazing angle spectra were obtained by measuring the spectrum of a monolayer on an aluminized silicon wafer, coated as described above, and subtracting a background spectrum obtained previously for an uncoated substrate and were recorded at 2-cm^{-1} resolution and 2000 scans. For the ATR spectra a Harrick variable angle sample holder was used with an angle of incidence of 45°. ATR spectra were recorded from 45°, $50 \times 10 \times 3$ mm, silicon single-pass prisms (Harrick), which had been coated with a monolayer as described above, and a predetermined background spectrum for the uncoated prism was subtracted to obtain the monolayer spectrum. ATR spectra were run at 4-cm^{-1} resolution, collecting 5000 scans. Base lines were adjusted to zero absorbance electronically for the measurement of spectral intensities and dichroic ratios.

Acknowledgment. We thank Vito DePalma of Eastman Kodak Company, Diversified Technologies Group Research Laboratories, for helpful discussions of surface properties and Jon Littman of Eastman Kodak Company Corporate Research Laboratories, for the preparation of aluminized substrates.

Registry No. 1, 115364-46-0; **2**, 115364-47-1; **3**, 115364-48-2; **4**, 115364-49-3; OTS, 112-04-9; TTS, 18406-99-0; UTS, 18052-07-8; Si, 7440-21-3.

Supplementary Material Available: Preparation of compounds **1**–**4**, Zisman plots for **1** and **2**, additional IR data for monolayers, and description of ATR experiment (17 pages). Ordering information is given on any current masthead page.

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(44) Acknowledgement is made to Prof. Jacob Sagiv for indicating the importance of trace water and suggesting the use of Isopar-G.

(45) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841.