Synthesis and Characterization of Covalently Linked Multilayer Films Prepared in the Absence of Solvent

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We report the preparation of multilayer organic thin films prepared by sequential vapor-phase coupling of monomers. The reactions were carried out at room temperature and atmospheric pressure. Films prepared using up to six sequential coupling reactions are reported. The following specific vapor-phase reactions were found to be viable: reactions between acid chlorides and both aliphatic and aromatic amine, hydrolysis reactions, anhydride activation, and reactions between anhydrides and primary amines. Homobifunctionalized monomers, such as hexamethylenediamine, react primarily via a single endgroup rather than cross coupling to the reactive surface via both reactive groups. The estimated coverage of the multilayer films is between 36 and 46%. The films were characterized using ellipsometric, contact angle, and spectroscopic measurements.

Introduction

Here, we report the synthesis of multilayer organic thin films prepared via multiple, sequential chemical reactions at the vapor/solid interface. Specifically, small aliphatic and aromatic molecules bifunctionalized with either primary amines or acid chloride groups were found to undergo coupling reactions at surfaces at room temperature and atmospheric pressure in the absence of solvent (Schemes1 and 2). Using this approach, it is possible to prepare partially organized thin films up to six molecular layers in thickness. This result is significant because multilayer organic thin films are normally prepared in liquids, or by vapor-phase reaction in a vacuum,[1−3] or at high temperatures.[2−4] The objectives of this study are the development of a better understanding of the types of reactions that proceed in the absence of solvents and optimization of conditions for carrying them out.

There are some potential advantages associated with synthesizing organic thin films in the absence of solvents that have motivated this research. First, vapor-phase reactions eliminate the effects of solvent and impurities (especially water) on the structure and properties of the films. Second, vapor-phase reactions are more easily automated than those requiring solvents. Third, certain types of intermolecular interactions, such as hydrogen bonding and electrostatic interactions, which are weak in many solvents, are strong in their absence. Fourth, reactions carried out at the vapor/solid interface at atmospheric pressure provide a valuable link between UHV and condensed-phase studies.[5−7]

We previously showed that several different types of intermolecular interactions can be used to prepare simple bilayer films via vapor-phase reactions. For example, when a 4-mercaptophenol-modified Au substrate is exposed to chlorodimethyloctylsilane vapor, a siloxane bond between the two layers results.[5,8] In addition to covalent bonds, noncovalent interactions, such as acid−base[7,9,10] and H-bonding interactions,[11] are also useful for preparing bilayer films in the absence of solvents. Finally, we have also shown that trilayer thin films can be prepared via vapor-phase coupling of active anhydrides, amines, and acid chlorides.[12]

Other groups have also explored the viability and scope of vapor/solid reactions, but most of these have been carried out under vacuum[1−3] and/or at high temperature.[2−4] For example, the reactivity of hydroxyl- and acid-terminated monolayers has been examined under UHV conditions,[1] hydrogen-bonded electrooptic thin films have been prepared,[2] and fluorosilane monolayer assemblies have been reported.[3] Recently, the Morris group synthesized a well-ordered bilayer film by exposing a Au substrate modified with a hydroxyl-terminated alkylthiol monolayer to a vapor-phase alkyl isocyanate at 40 °C at atmospheric pressure. These conditions resulted in the formation of a carbamate linkage.[4]

In this paper, we expand upon our previous findings by showing that multilayer films having up to six layers can be prepared by vapor-phase reactions. Two distinctly different approaches were used to demonstrate generality. Scheme 1 shows the strategy for preparing covalently linked multilayer films via sequential reaction of an aniline-modified Au surface with bifunctional acid chlo-

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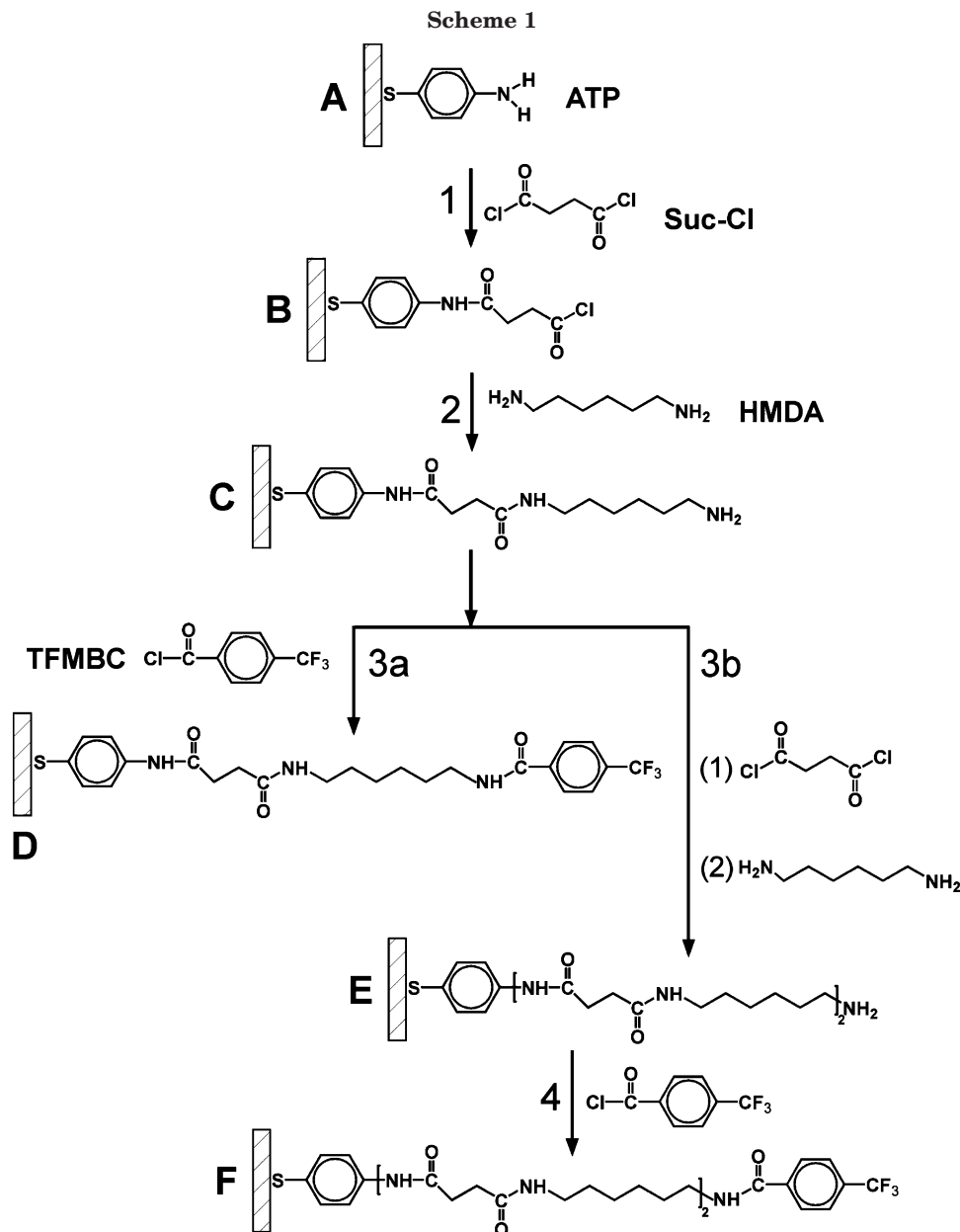
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Scheme 1

rides and amines. The method shown in Scheme 2 involves the reaction of an acid-chloride-modified Au surface with water to form the acid, activation of the acid to an anhydride, coupling with a bifunctional amine, and then capping with a second acid chloride. The results of ellipsometric, infrared spectroscopic, and contact−angle measurements indicate that these types of reactions result in partially organized thin films.

Experimental Procedures

Chemicals. Aminothiophenol (ATP, 90%), succinyl chloride (Suc-Cl, 95%), *n*-octylamine (OA, 99%), hexamethylenediamine (HMDA, 98%), trifluoroacetic anhydride (TFAA, 99+%), and 4-(trifluoromethyl)benzoyl chloride (TFMBC, 97%) were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and except for ATP were used as received. ATP was purified by vacuum sublimation. Dichloromethane (99.5+%) was purchased from EM Science (Darmstadt, Germany) and dried with molecular sieves just before use. Absolute ethanol was purchased from Aaper Alcohol & Chemical Co. (Shelbyville, KY). N_2 gas (99.995%) was used as the carrier for vapor-phase reactants. Traces of water were removed by passing it over a Drierite gas purifier (Hammond 26800, Fisher Scientific Co., Pittsburgh, PA).

Substrate Preparation. Au-coated substrates were prepared by electron-beam deposition of 200 nm of Au onto Ti primed (10 nm) Si(100) wafers (Lance Goddard Associates, Foster City, CA). Prior to use, the wafers were diced into 2.6 cm × 1.3 cm pieces. These substrates were cleaned in a low-energy ozone cleaner for 15 min (Boekel Industries, Inc., Model 135500) and rinsed with ethanol before placing them into the vapor-phase reaction chamber.

Vapor-Phase Surface Modification. The reaction chamber consisted of a borosilicate glass tube fitted at each end with caps that exposed only the PTFE/silicone liners (Alltech, Deerfield, IL) to the reactive vapors. After placing the Au substrate in this chamber, it was purged with dry N_2 for at least 30 min before dosing with reactants. N_2 gas was purified by passing it through the Drierite (W. A. Hammond Drierite CO. LTD, Xenia, OH) and activated carbon filters (Whatman, Florham Park, NJ). The reactants were stored in vials and capped with septa or in pear-shaped, two-necked flasks (ACE Glass, Vineland, NJ) fitted with Mininert syringe valves (VWR Scientific Products, Suwannee, GA). The vapor-phase reactant streams were generated by passing N_2 gas (0.5 L/min) over the headspace of a vial or pear-shaped flask containing the neat solids or liquids. The resulting vapor was passed through TFE tubing (3.2 mm o.d. and 2.5 mm

Scheme 2
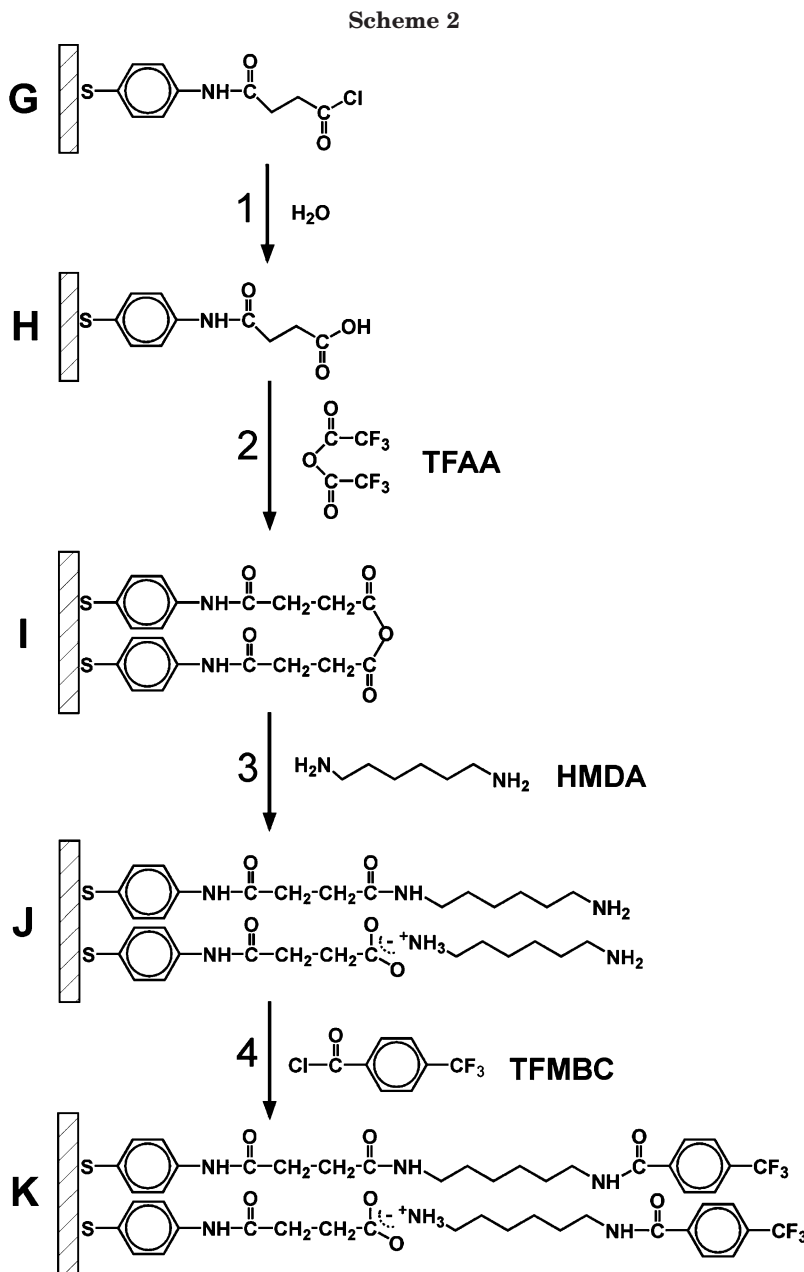
i.d.) and into the reaction chamber for 10−60 min. The chamber was purged with N_2 between each reaction step to remove excess reactants.

Liquid-Phase Surface Modification. In some cases, ATP monolayers were prepared on Au surfaces using ethanol as the solvent. In this case, the Au substrate was placed in a 1 mM ethanolic ATP solution for 24 h, sonicated for 30 s in ethanol, and rinsed with ethanol prior to characterization. An ATP-TFMBC bilayer was prepared by immersing the ATP-modified substrate in dry dichloromethane containing 1 mM TFMBC for 9 h. This film was also sonicated and thoroughly rinsed with dichloromethane prior to characterization.

Fourier Transformation Infrared-External Reflection Spectroscopy (FTIR−ERS). All FTIR−ERS measurements were performed using a N_2-purged FTS 6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid nitrogen cooled, narrow-band mercury−cadmium−telluride (MCT) detector. Spectra were obtained at 4 cm^{-1} resolution using *p*-polarized light incident on the substrate at 84° with respect to the substrate normal. The reported spectra consisted of 256−512 summed individual spectra from which a background spectrum, obtained using a freshly cleaned Au surface, was subtracted.

Ellipsometric Thickness and Contact−Angle Measurements. A Gaertner Scientific (model L2W26D, Chicago, IL) ellipsometer was used for film thickness measurements. The light source was a 632.8 nm laser incident on the substrate at an angle of 70.00 ± 0.02° relative to the surface normal. The refractive index (n_f) of the film was assumed to be 1.46.[12−14] The thickness of each film was measured at five different locations, and the average of these values is reported. The contact angle was measured using a goniometer (Rame-Hart Inc., Mountain Lake, NJ). The reported contact angles are the average of five independent measurements made on different locations on the substrate surface.

Results and Discussion

Layer-by-Layer Vapor-Phase Synthesis of Amide-Linked Multilayer Organic Thin Films. Figure 1 shows FTIR−ERS spectra of monolayer and bilayer films corresponding to structures A and B in Scheme 1. Figure

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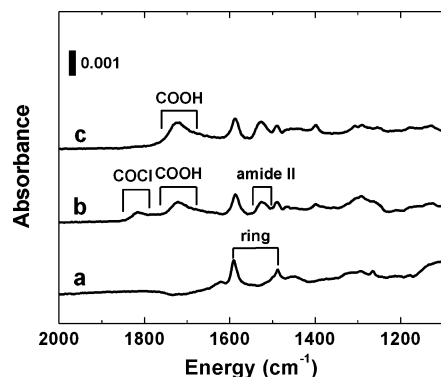
Figure 1. FTIR−ERS spectra of the thin films shown in Scheme 1. Spectra a and b correspond to structures A and B in Scheme 1. Spectrum c was obtained from a film corresponding to structure B after exposure to air for 2 weeks.

1a was obtained after vapor-phase dosing of an Au substrate with ATP. The peaks at 1590 and 1487 cm^{-1} are characteristic of the quadrant stretching and semicircle stretching modes of the ATP ring system.[15,16]

Suc-Cl was coupled to the distal amine functional group of ATP via a vapor-phase amidation reaction (step 1, Scheme 1). This results in a new IR band at 1526 cm^{-1} (amide II band, Figure 1b) that corresponds to the presence of the amide bond.[12,13,17−20] Note, however, that the amide I band, usually present in the range of 1640−1675 cm^{-1}, is absent. This is probably a consequence of the orientation of the bond relative to the substrate. The amide I band correlates most closely with the carbonyl stretch, and the amide II band corresponds to the N−H bending and C−N stretching modes. Therefore, the absence of a well-defined amide I band suggests that the C=O bond is oriented parallel to the substrate surface (as drawn in Scheme 1).[21]

The new band at 1815 cm^{-1} in Figure 1b is attributable to the carbonyl stretching mode of the acid chloride. The band at 1721 cm^{-1} probably corresponds to partial hydrolysis of the acid chloride surface, which would likely occur when the substrate is removed from the reaction chamber and transferred to the FTIR for spectral analysis.[11,14] This supposition was confirmed by exposing an acid chloride-terminated surface (structure B, Scheme 1) to air for 2 weeks and then obtaining Figure 1c. Here, the acid chloride band at 1815 cm^{-1} has been replaced with a more intense acid carbonyl stretch at 1721 cm^{-1}. As a consequence of this finding, subsequent reactions on acid chloride-terminated surfaces were carried out in the absence of air. That is, no intermediate IR spectra of acid chloride-terminated surfaces were obtained for the remainder of the films discussed herein.

The ellipsometric thickness of the ATP layer was found to be 0.7 nm, and this value increased to 1.1 nm after coupling with the acid chloride (all calculated and experimental film thicknesses are provided in Table 1). Taken together, the IR and ellipsometric data confirm

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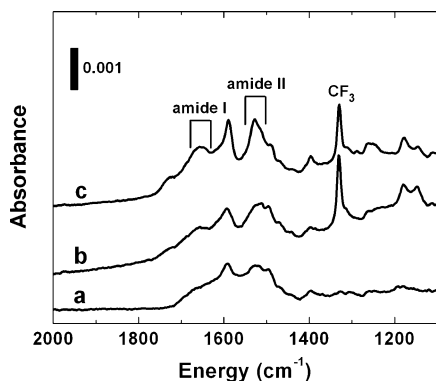(19) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: Boston, MA, 1990.
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Table 1. Ellipsometric Thickness and Contact−Angle Data for the Films Prepared by Vapor Phase Reactions

Au/monolayer	calculated thickness (nm)^a	thickness (nm)^b	contact angle (deg)^c
A	0.6	0.7 ± 0.2	51 ± 3
B	1.2	1.1 ± 0.1	d
C	2.1	1.8 ± 0.2	42 ± 4
C (OA capped)	2.2	2.0 ± 0.6	59 ± 3
D	2.7	2.4 ± 0.4	73 ± 2
E	3.6	2.8 ± 0.4	d
F	4.2	3.2 ± 0.3	70 ± 3
I	1.1	0.9 ± 0.2	d
J	2.1	2.2 ± 0.4	d
K	2.7	2.6 ± 0.4	d

^{a} Thicknesses were calculated by assuming that the films are oriented perpendicular to the substrate. Molecular dimensions were estimated using CS ChemBats3D Ultra. ^{b} Average of five ellipsometric thickness measurements made at five different locations on each of two independently prepared substrates. ^{c} Average of five static water contact−angle measurements made on each of two independently prepared substrates. ^{d} Not determined.
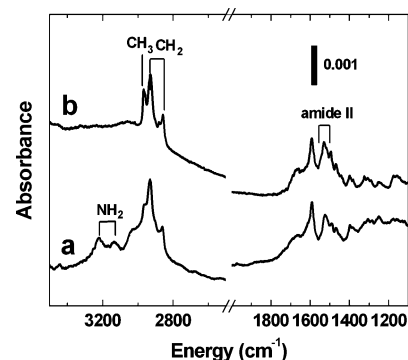
Figure 2. FTIR−ERS spectra of trilayer films corresponding to (a) structure C in Scheme 1 and (b) the corresponding film prepared by reaction of structure B with monofunctionalized octylamine rather than HMDA.

vapor-phase coupling of Suc-Cl to ATP via amide bond formation. At this point, however, it is not possible to say with certainty whether just one end of Suc-Cl couples to ATP or whether it cross couples and lays flat on the ATP surface.

This latter issue was addressed by carrying out a third coupling reaction that relies on the presence of a free acid chloride group on the surface. Specifically, a bilayer film prepared by vapor-phase reaction of ATP with Suc-Cl, but without exposing the acid chloride-functionalized surface to air, was reacted with HMDA vapor to yield a trilayer film (structure C, Scheme 1). This reaction resulted in a change in the ellipsometric thickness from 1.1 to 1.8 nm. The height of the amide II band also increased by ∼30% after reaction with HMDA (Figure 2a). New bands are present in the spectrum of the three-layer film at 3220, 3132, 2929, and 2857 cm^{-1}. The bands at 3220 and 3132 cm^{-1} are attributed to the asymmetric and symmetric N−H stretching modes, respectively, and the bands at 2929 and 2857 cm^{-1} correspond to the methylene stretching modes.[5,11,14,15,22,23] Also present in the high-frequency region are two very small shoulders at 3030 and 2961 cm^{-1}. We are not able to assign these with confidence at the present time. These spectral changes and the increase in film thickness are fully consistent with structure C in Scheme 1.

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Figure 3. FTIR−ERS spectra corresponding to (a) structure C, (b) structure D, and (c) structure F.

Figure 4. FTIR−ERS spectra of (a) structure H, (b) structure I), (c) structure J, and (d) structure K.

The just-described spectral features conclusively prove that a substantial fraction of the acid chloride groups of the two-layer film are available for further reaction with HMDA; that is, they are not cross-coupled to the original ATP surface. However, at this stage of film growth, it was necessary to address the possibility of HMDA cross coupling to the acid chloride surface by confirming that the peaks at 3220 and 3132 cm^{-1} correspond to the free amine. This issue was addressed by coupling structure B (Scheme 1) to monofunctionalized *n*-octylamine (OA) instead of to HMDA. This experiment resulted in a film having a thickness of 2.0 nm, which compares favorably to the 1.8 nm-thick HMDA-coupled film. Moreover, the OA-terminated film exhibited a significantly higher static contact angle than the HMDA-terminated trilayer (59 vs 42°, respectively).

The spectrum of the OA-capped film (Figure 2b) was similar to that of the HMDA-modified trilayer in the region from 1400 to 1600 cm^{-1}, but a new band at 2967 cm^{-1} arising from the distal methyl group is also apparent.[5,9] Importantly, however, the bands at 3220 and 3132 cm^{-1}, previously attributed to the peripheral amine group of the HMDA-capped film, are absent. Because the only difference between the two films represented by the spectra in Figure 2 is this amine group, it is reasonable to conclude that the assignment is correct and that this is a free amine ready for additional synthetic elaboration.

The amine-terminated trilayer film was exposed to vapor-phase TFMBC to yield a covalently linked, four-layer film capped with a trifluoromethyl group (structure D, Scheme 1). Evidence for the presence of TFMBC on the surface comes from the very strong absorption band at 1328 cm^{-1} (Figure 3b), which corresponds to the CF$_3$ symmetric stretching mode.[12,18,24] Other important features of Figure 3b include slight increases (10−22%) in the aromatic ring bands (1589 and 1489 cm^{-1}) and the amide II band (compare with the spectrum of the trilayer film, Figure 3a). After reaction with TFMBC, the thickness of the film increased from 1.8 to 2.4 nm. The change in contact angle from 42 to 73° is also fully consistent with the presence of CF$_3$ surface functional groups.

A six-layer film was prepared by successively dosing the three-layer film (structure C in Scheme 1) with Suc-Cl, HMDA, and TFMBC vapors (steps 3b and 4, Scheme 1). Addition of the final three layers resulted in an increase in the film thickness from 1.8 to 3.2 nm. Increases in the magnitudes of the ring modes at 1589 and 1487 cm^{-1}, and the amide II band at 1526 cm^{-1} (Figure 3c), are also consistent with formation of the thicker film (compare to
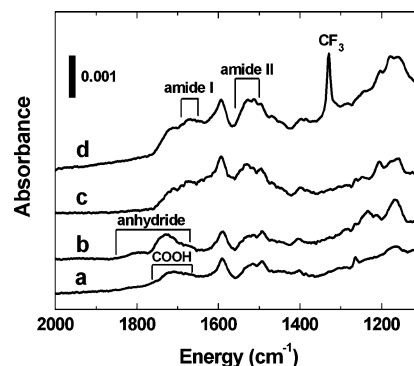
Figure 3a,b). However, the intensity of the CF$_3$ band at 1328 cm^{-1} is lower than that of the four-layer film by 22%. We attribute this finding to a gradual reduction in the density of the growing film, which is probably related to the accumulation of defects that accompanies the growth of each successive layer. However, it is also possible that this decrease is due to a thickness-dependent orientational change in the film structure; specifically, a more significant tilt of the film away from the surface normal. Evidence for this possibility comes from the appearance of an amide I band at 1656 cm^{-1}, which would be enhanced if the film cants away from the surface normal.[12,13,25,26] The main point, however, is that the spectroscopic, ellipsometric, and contact−angle measurements are all consistent with a six-layer film prepared by successive vapor-phase dosing experiments.

Vapor-Phase Synthesis of Anhydride-Based Multilayer Organic Thin Films. In this section, we describe the synthesis of multilayer films prepared using anhydride intermediates. This study commenced with the preparation of an acid chloride-terminated bilayer film (structure G in Scheme 2) prepared using the procedure described in the previous section. Figure 4a was obtained after dosing this bilayer with water (step 1, Scheme 2). The presence of the carbonyl band at 1710 cm^{-1} is consistent with conversion of the acid chloride to the corresponding acid. Note the absence of the acid chloride band at 1815 cm^{-1} observed in Figure 1b.

The acid-terminated bilayer film was activated by exposing it to TFAA vapor (step 2, Scheme 2). This results in the C=O stretching band at 1710 cm^{-1} being replaced with two bands at 1807 and 1735 cm^{-1}, which are characteristic of a carboxylic anhydride (Figure 4b).[17,27,28] No other changes are observed in the FTIR spectrum, and no change was observed in the ellipsometric thickness of the bilayer after this reaction. These results are consistent with the reaction going to completion.

Structure I (Scheme 2) was reacted with HMDA vapor to yield a trilayer film (structure J). The reaction between surface-confined anhydride groups and HMDA is more complicated than those discussed thus far because the anhydride can undergo two types of reactions with primary amines. As discussed in the previous section, and as represented in Scheme 2, HMDA should react with the surface principally via a single amine group. If this is
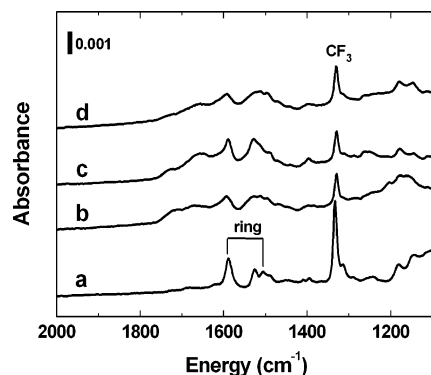
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Figure 5. FTIR–ERS spectra comparing relative magnitudes of the symmetric CF_3 stretching mode. (a) Trifluoromethyl-terminated bilayer prepared by liquid-phase reaction. (b) Structure K, (c) structure F, and (d) structure D.

true, then half of the HMDA should react with the surface anhydride to form an amide bond, and the other half should be immobilized on the surface via an electrostatic interaction with COO^-. The intensity of the amide II band at 1528 cm^{-1} (Figure 4c) increases by 25% as compared to the anhydride-terminated film (Figure 4b), and the presence of a broad amide I band can just be detected at 1670 cm^{-1}. The ellipsometric results are also consistent with reaction of the third layer with the surface: the thickness of the film increased from 0.9 to 2.2 nm after reaction with HMDA.

The HMDA-modified film was exposed to TFMBC vapor to yield a covalently attached four-layer film (structure K, Scheme 2). This reaction resulted in a change in the ellipsometric thickness from 2.2 to 2.6 nm and increases in the magnitude of aromatic ring and amide II mode by 20–25% (Figure 4d). The new band at 1329 cm^{-1} arising from the CF_3 group of TFMBC is also apparent after the coupling reaction.

Coverages of the Vapor-Phase Reactions. To determine the coverages (yield) of the four- and six-layer TFMBC-terminated films, we prepared a two-layer film capped with TFMBC using a reliable liquid-phase synthesis (details are provided in the Experimental Procedures). If we assume that this film represents 100% coverage of TFMBC, then by comparing the magnitude of the CF_3 IR bands of this film with those prepared via vapor-phase synthesis, it is possible to estimate the coverage of the films represented by structures D, F, and K.[12]

The FTIR–ERS spectrum of the bilayer film prepared by liquid-phase reaction is shown in Figure 5a. The strong band at 1332 cm^{-1} arises from the symmetric CF_3 stretching mode. The corresponding bands associated with structures D, F, and K (spectra d, c, and b of Figure 5, respectively) have relative heights of 46, 36, and 38%. These values can be correlated to the coverage of the films prepared by vapor-phase synthesis if two conditions are met. First, the orientation of the CF_3 group relative to the substrate must be the same for all four films because small differences can affect the magnitude of this band.[12] This condition is satisfied because the absorbance of the asymmetric CF_3 modes, present at 1177 and 1145 cm^{-1},[24] is very small and nearly constant. This observation is consistent with the axis of the symmetric mode being

oriented nearly normal to the substrate surface for all films.[24] Second, we must assume that reactions between the films and TFMBC take place with ~100% yield because otherwise the CF_3 IR signature will not correctly report back the yield of previous reactions.

It is also possible to estimate the extent of the surface reactions using the ellipsometric thickness data shown in Table 1. In this case, it is also necessary to make a number of assumptions. First, the individual oligomers comprising the films must have a known orientation with respect to the surface; from the IR data, we know that this condition is satisfied. Second, only the oligomers that comprise the films and void space may be present on the surface. The presence of water within the films (recall that the ellipsometric thicknesses were measured in air) will change the effective medium approximation[29] and distort the linear correlation between film thickness and extent of reaction upon which this analysis relies. Third, it is necessary to assume a single index of refraction (1.46 in this case) for all of the films. With these three caveats, the thickness data give estimated yields for films D, F, and K of 89, 76, and 96%, respectively. Clearly, these values are substantially higher than those estimated from the spectroscopic results.

There is only one reasonable situation that is consistent with both the IR and the ellipsometry data. If all of the reactions, except for the final CF_3 capping reaction, go to completion, then the film thickness will be consistent with the calculated values, but the IR data, which relies on the presence of the CF_3 group, will indicate a low yield. We view this scenario as possible but improbable given that TFMBC couples to the amine-terminated film via the same chemistry that is responsible for the other coupling reactions. On the basis of previous results,[12] therefore, we tend to have more confidence in the IR data. Clearly, however, the results reported here show that it is difficult to measure the yields of surface reactions of this type with a high degree of accuracy.

Conclusions

Here, we have shown that covalently linked films up to six monomer units in length can be prepared on a solid support using vapor-phase reactions. These films have surface coverages ranging from about one-third to one-half of full coverage, which is quite encouraging considering the number of synthetic steps that are involved and that error propagation limits the coverage of any film prepared by sequential reaction. We have also shown that a number of reactions routinely used in liquid-phase synthesis is also effective for vapor-phase reactions. These include reactions between acid chlorides and both aliphatic and aromatic amine, hydrolysis reactions, anhydride activation, and reactions between anhydrides and primary amines. Finally, we demonstrated that homobifunctionalized monomers, such as HMDA, react primarily via a single functional group rather than cross coupling on the reactive surface. This approach for preparing organic thin films may find use in some technological applications where the tradeoff between film quality and convenience is positive.

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