

Deposition and Characterization of Polyimide Langmuir-Blodgett Films

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Langmuir-Blodgett films have been prepared from three polyamic acids and subsequently converted to the corresponding polyimides. Some of these polymers contain trifluoromethyl groups chosen for their enhanced moisture resistance and low dielectric constant. Infrared and ultraviolet spectroscopy confirmed transfer of the film and conversion by chemical or thermal means to the polyimide in multilayers at least up to 80 layers. Transmission electron microscopy and reflection-high energy electron diffraction characterization showed spacings of 5.3-5.6 Å in the plane of the film. In the case of the polyimide containing no trifluoromethyl groups, a spacing of approximately 5 Å was observed between layers of the imidized film.

Introduction

Polyimides have several attractive characteristics, including good thermal stability, simple preparation, and excellent dielectric properties. By using the Langmuir-Blodgett (LB) technique, we sought to prepare very uniform films with well-controlled thickness less than 1000 Å. Examples of polyimide LB films are known in the literature,^{1-4,7,8} but in this work, the objective was to extend the range of polyimide LB films to include fluorinated polymers, which are expected to have improved moisture resistance and reduced dielectric constant. Films have been prepared from three polyamic acids (1-3). In

acids was first reported by Kakimoto et al.¹ This procedure converts the polyamic acid to the polyimide by reaction with acetic anhydride in a benzene-pyridine solution, but we found that films of the fluorinated materials (2 and 3) dissolved in this solution.

Uekita et al. have reported imidization of LB films of polyamide diesters by heat treatment.² An octadecyl diester of 2 was prepared and LB films successfully imidized thermally.

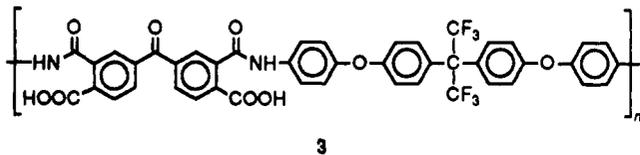
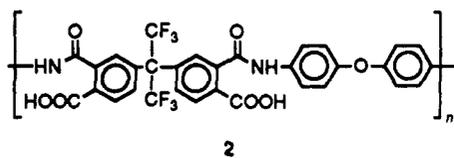
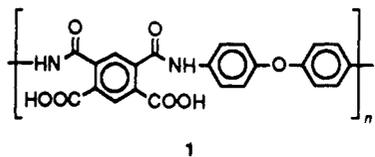
This paper describes the material preparation, effects of various experimental parameters on LB film forming and film transfer characteristics, and IR, UV, TEM, and RHEED characterization of the multilayers produced.

Experimental Section

A. Polymer Synthesis. Polyamic acids 1 (DuPont Electronic Materials Division, Wilmington, DE, PI-2545) and 3 (Ethyl Commercial Development Division, Baton Rouge, LA, HP-2222) were used as supplied. Octadecylamine complexes of these polymers were prepared by mixing a 1 mM solution of polyamic acid in 3/2 (v/v) benzene/dimethylacetamide with a 1 or 2 mM solution of octadecylamine (Aldrich, 99%, as supplied) in 1/1 (v/v) benzene/dimethylacetamide at room temperature. Benzene and dimethylacetamide (DMAC) solvents (Fisher, spectrophotometric grade) were distilled prior to use. The LB films were prepared from the resulting solution.

Polyamic acid 2 was prepared by reaction of 10.0 g (0.023 mol) of hexafluoroisopropylidene-4,4'-bis(phthalic anhydride), 4 (Hoechst-Celanese, Specialty Chemicals Division, Sommerville, NJ, Sixef), with 4.5 g (0.023 mol) of diaminodiphenyl ether (DAPE, Chriskev Co., Inc., 99.5%) in 100 mL of DMAC under rigorously dry conditions. The polyamic acid was formed after reacting for 5 h at room temperature. The product was stored at -3 °C in a dry, sealed bottle.

Poly(diamide dioctadecyl ester), 7, was prepared in several steps from 4 according to reaction Scheme I. The half ester, 5, was prepared by dissolving 27.05 g (0.1 M) of *n*-octadecyl alcohol (Aldrich, 99%) in 100 g of methyl isobutyl ketone (Fisher ACS certified, dried over MgSO₄) at 60 °C, and then adding 22.20 g (0.05 M) of 4. The mixture was heated to reflux (123 °C) and held for 1.5 h. The solvent was removed and 48.89 g of 5 collected (99% yield). The composition of 5 was confirmed by titration with 0.1 N KOH in methanol. Formation of acid chloride 6 was performed by reaction of 39.40 g (0.04 mol) of 5 with 10 mL (0.14 mol) of thionyl chloride (Aldrich, 99%) at reflux for 3 h and then permitted to cool overnight. Reaction was resumed the following day for another 4 h at reflux until there was no more HCl released. The reaction mixture was evacuated to remove excess SOCl₂ then back filled with N₂ and permitted to stand overnight. The polyamide diester 7 was prepared by reacting 30.82 g (0.034 mol) of 6 with 4.90 g (0.025 mol) of DAPE in 71.92 g of DMAC (distilled from P₂O₅). The reaction mixture was cooled to 5 °C in an ice



solution, these polyamic acids form complexes with amines via proton exchange between the carboxylic acid moieties and amine nitrogen. By using an amine with a long aliphatic chain, such as *n*-octadecylamine (ODA), it is possible to form LB films of the complexes on a water surface. This method of preparing LB films from polyamic

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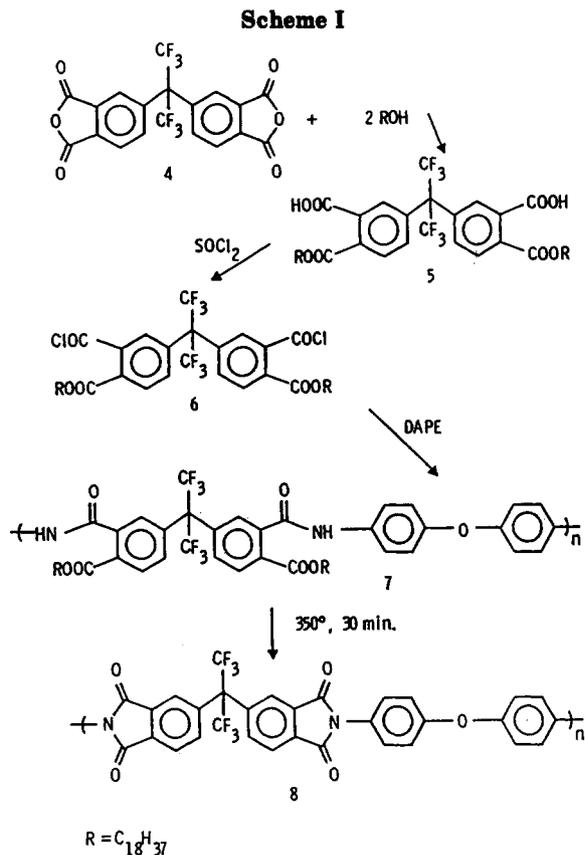
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bath and DAPE added slowly over 10 min. The temperature was maintained below 15 °C. Reaction was terminated by precipitating in deionized water after 90 min. Polymer 7 was converted to polyimide 8 by heating at 350 °C for 30 min.

B. LB Film Preparation. Films were prepared using a Joyce-Loebl Langmuir Trough IV using >18 MΩ water. The subphase was maintained at 10, 15, or 20 °C. The polyamic acid-ODA complexes were transferred at a subphase pH of 4–5. Films of the polyamide diester 7 were deposited at a pH of 9 obtained using 10⁻⁴ M borax buffer in the subphase. Pressure-area isotherms were recorded after films had been compressed at 25 mN/m for 1 h and then relaxed and compressed at a rate of 144 cm²/min.

Films were transferred to several types of substrates: quartz slides, single crystal silicon web, electropolished aluminum, and glass cover slips. Substrates were typically cleaned with No-chromix (Godax Laboratories, Inc.) and rinsed. Substrates were treated with (α -aminopropyl)triethoxysilane (DuPont, VM651) in order to improve adhesion between the substrate and the polyimide film. The polyamic acid/ODA complexes were transferred at 37.5 mN/m after the film had been compressed at that pressure overnight. The polyamide diester 7 materials were transferred at 35 mN/m after the film had been compressed at that pressure for 8 h.

C. Imidization. Films of 1/ODA were imidized by reaction with a 1:1:3 (by volume) acetic anhydride/pyridine/benzene solution overnight. The polyimide film was then dried completely at 140 °C for 2 min.

Films of polyamide diester 7 were imidized by heat at 350 °C for 30 min.

D. Characterization. Film preparation was monitored by IR and UV spectroscopy. Morphological characterization of selected films was performed using a Philips EM 400T analytical electron microscope operated at 120 kV. Planar specimens were prepared by mechanically thinning the substrate, dimple grinding to approximately 50 μ m, and then Ar-ion-milling the substrate to perforation. The technique of ultramicrotomy was employed in the preparation of cross-sectional films which had been deposited on electropolished Al substrates. After being sectioned with a diamond knife, the cross-sectional samples were floated onto grids and dried. For films deposited on glass substrates,

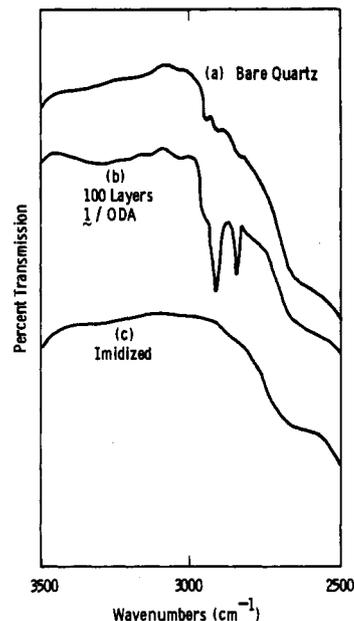


Figure 1. Infrared spectra of (a) bare quartz substrate, (b) 100 layers of 1/ODA on quartz, and (c) 100 layers of 1 following imidization.

small fractured film/substrate segments were examined in the AEM by employing high tilt angles. A thin carbon film was deposited on the substrate surface prior to TEM examination in order to reduce charging in the electron microscope. With this type of specimen, no subsequent preparation was necessary for TEM examination. The specimens were examined by transmission electron microscopy and high-resolution scanning electron microscopy.

RHEED patterns were recorded using a JOEL JEM-7 electron microscope with 80-kV electrons directed at the sample for 2 min at an angle of less than 1°. Samples were films deposited on quartz slides as described above.

Results and Discussion

A. Imidization Reaction. The effectiveness of the acetic anhydride solution for imidization of 1 was confirmed by IR spectroscopy. The aliphatic C–H stretches of the *n*-octadecyl chains provide a convenient indication of unreacted polyamide rings. Figure 1 shows the disappearance of those absorptions at 2920 and at 2860 cm⁻¹.

The intermediates in the synthesis of 7 were identified by IR spectroscopy, as shown in Figure 2. Half ester 5 showed C=O stretches at 1710 cm⁻¹ (acid) and 1740 cm⁻¹ (ester). Conversion to the acid chloride resulted in loss of the acid carbonyl and appearance of an acid chloride carbonyl stretch at 1805 cm⁻¹. Polymerization of this material with diaminodiphenyl ether produced an amide (1660 cm⁻¹) and N–H stretch (3320 cm⁻¹) in the IR spectrum. Finally, thermal imidization converted this polymer to the polyimide with a C=O stretch at 1720 cm⁻¹. Note the loss of N–H (3320 cm⁻¹) and much of the aliphatic C–H (2860 and 2920 cm⁻¹) during this reaction. We are thus confident of the effectiveness of this scheme for producing the desired material.

B. LB Film Preparation. Pressure-area isotherms have been recorded under a variety of conditions in order to explore the roles of ODA content, compression rate, subphase temperature, and subphase pH in the film forming characteristics of these materials. First we shall discuss results with polyamic acid/ODA films. Addition of ODA causes the films to spread more on the trough surface with the extrapolated area per monomer increasing

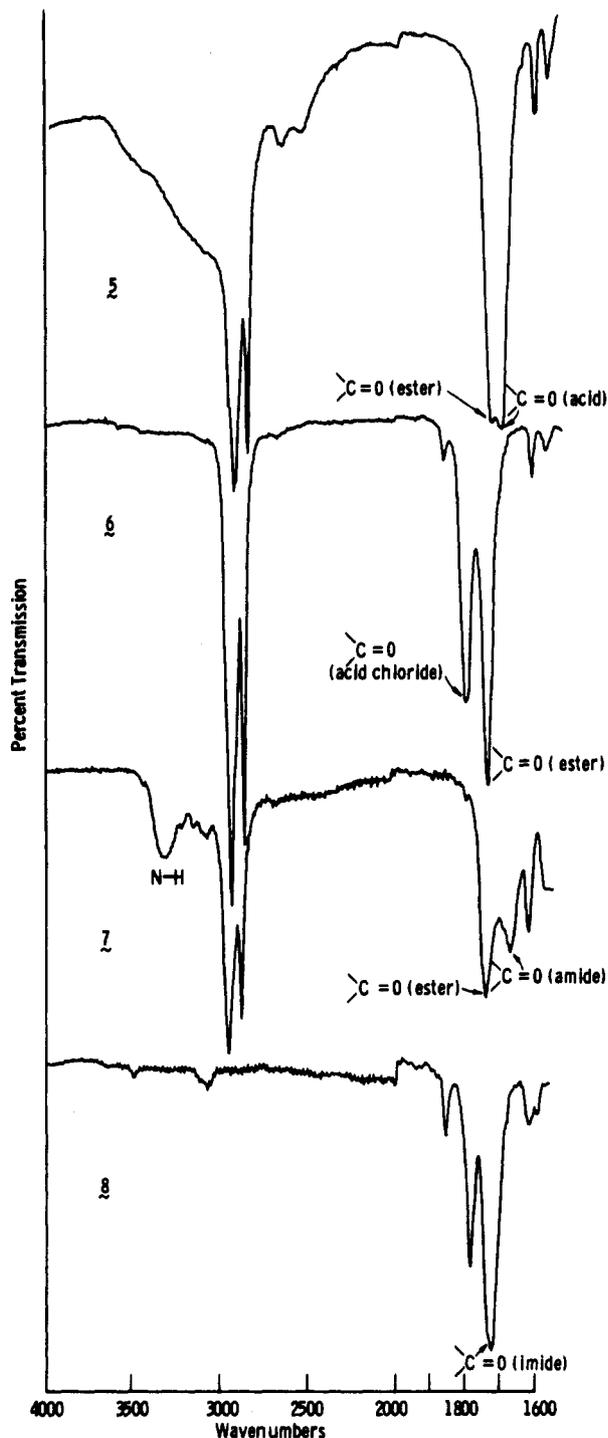


Figure 2. Infrared spectra of intermediates in the preparation of 8.

Table I. Extrapolated Area per Monomer from Pressure-Area Isotherms of LB Films (20 °C) (\AA^2)

amine/polyamic acid ratio	1/ODA	2/ODA	3/ODA
0	19	15	12
1	70	64	60
2	104	122	147

from 19 to 70 to 104 \AA^2 with increasing ODA content. A similar trend was observed with 2/ODA and 3/ODA LB films (Table I) and has been reported by other workers.^{1,3} Subphase temperature over the range of 10–20 °C did not have a significant effect on the isotherms.

Isotherms of 2/ODA, 3/ODA, and 7 are shown in Figure 3. With the ODA complexes, increasing size of the repeat unit of the polymer from 1 to 2 to 3 caused an increase in

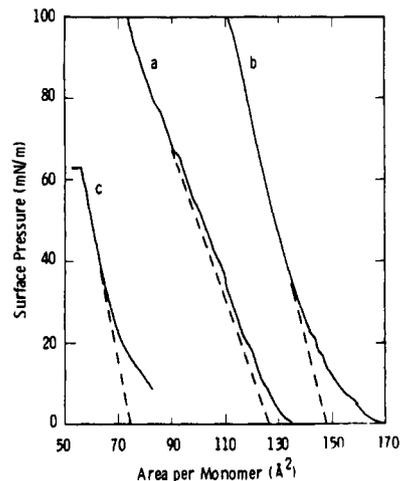


Figure 3. Pressure-area isotherms of (a) 2/ODA, (b) 3/ODA, and (c) 7 LB films at 15 °C.

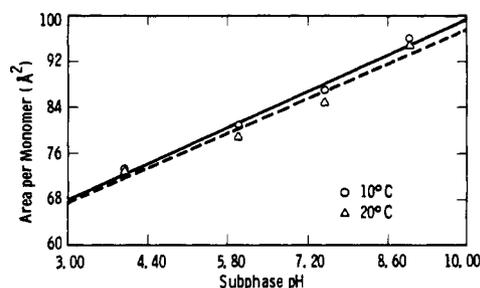


Figure 4. Dependence of extrapolated area per monomer on pH of the subphase in LB films of 7: recorded at 10 °C (O) and 20 °C (Δ).

the extrapolated area per monomer unit from 104 to 122 to 147 \AA^2 , respectively (see Table I). Comparing the extrapolated areas per monomer for 2/ODA and 7, the diester, which has the octadecyl chains covalently bonded to the polymer, occupied much less area than the complex. The differences may be due to Coulombic repulsion expected between ions in nearby ODA complexes and/or the shorter bond distance in the ester group of 7 compared to the 2/ODA complex.

The influence of subphase pH was examined with the polyamide diester 7 films. The repeat units were found to occupy more area as the pH increased from 4 to 9 (Figure 4). This phenomenon occurred at 10 and 20 °C. There was no evidence of hydrolysis of the film as the area occupied by the film was stable over 8 h when held compressed at 35 mN/m.

C. Film Transfer Characteristics. The films of all these materials were very stable and transferred to quartz substrates with Y-type deposition. For example, the film area of 1/ODA decreased by just 1% at a surface pressure of 27 mN/m overnight. The subphase temperature was 15 °C during transfer and pH between 4 and 5 for transfer of polyamic acid/ODA films. The coverage was somewhat rate-dependent, however, as illustrated in Figure 5. That figure shows the change in area occupied by the film of 1/ODA during transfer at two dipping rates: 1.6 and 6.4 mm/min. During each pass through the film, slightly less material was transferred at the higher rate. This also occurred with the other materials, so multilayers were routinely prepared at 1.6 mm/min to ensure maximum coverage.

The polyamide diester 7 did not transfer at low pH, so the pH of the subphase was raised in steps by addition of borax buffer to the subphase. The films were observed to

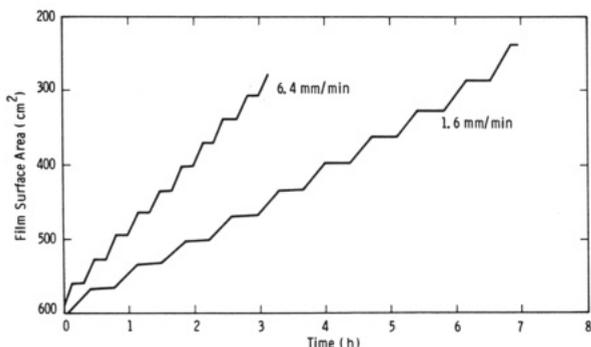


Figure 5. Barrier movement during deposition of 1/ODA at 15 °C, pH = 4, 37.5 mN/m.

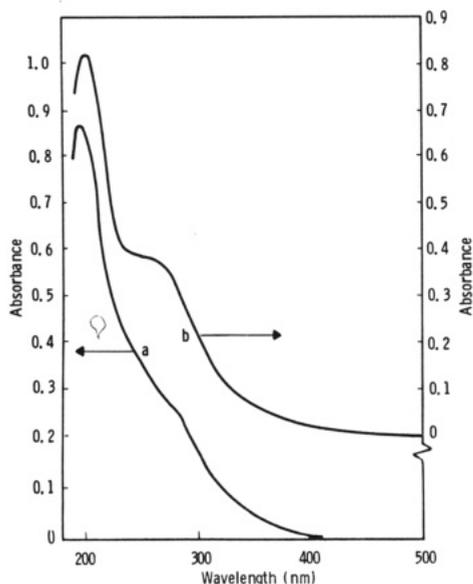


Figure 6. UV absorption spectra of (a) 2/ODA and (b) 3/ODA LB films.

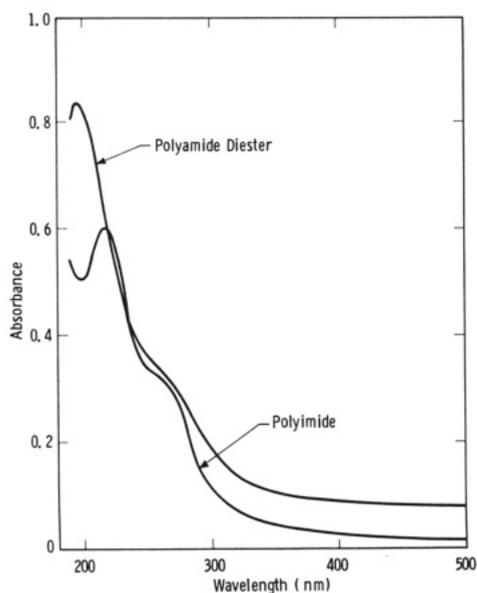


Figure 7. UV absorption spectra of 7 (diester) and 8 (polyimide) LB films.

transfer well at pH = 9 in Y-type deposition. Temperature and substrate surface treatment did not have an effect. These multilayers were transferred at 15 °C onto hydrophobic substrates.

D. UV Spectroscopy. All three materials have intense absorptions in the UV range before and after imidization.

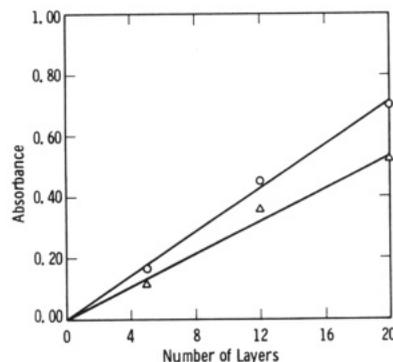


Figure 8. UV absorbance of 7 (diester) and 8 (polyimide) LB films.

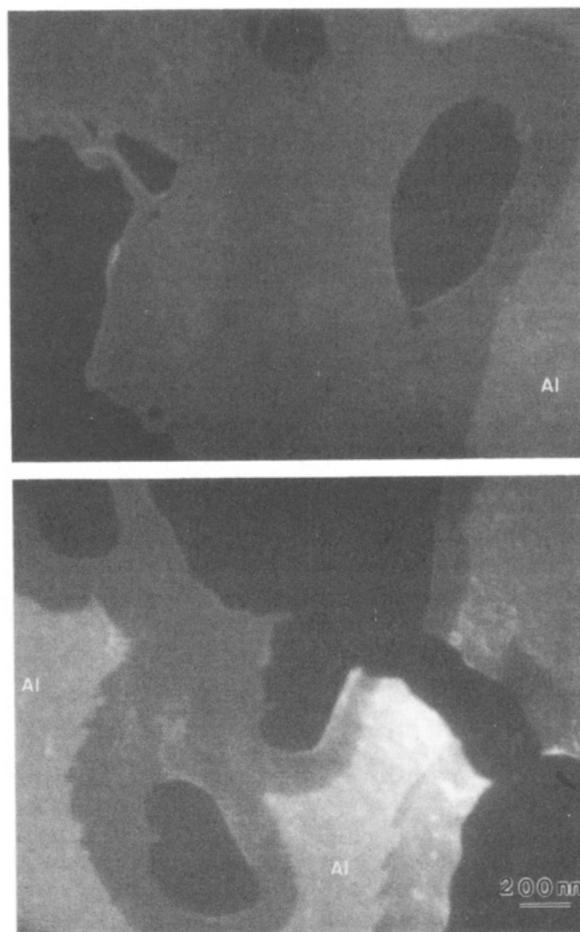


Figure 9. Scanning electron micrographs of imidized 1 LB films.

These absorptions make it possible to monitor multilayer depositions and confirm that the multilayers are intact following imidization. Spectra of 1/ODA LB films before and after imidization have been reported previously.¹ Spectra of 2/ODA and 3/ODA are given in Figure 6. Cyclic amides, such as maleimide, typically show strong absorption at 200–230 nm with a shoulder between 250 and 300 nm, as observed in both spectra in Figure 6.⁵ The absorption maxima followed Beer's law at multilayer thicknesses of 20–80 layers that we investigated. The spectra for polyamide diester 7 are shown in Figure 7. The spectrum of the polyamide diester is similar to the other amide spectra. Following imidization, the lower wavelength absorption was shifted by approximately 20 nm to longer wavelength, possibly due to the conversion of the chromophore to a polyimide. The variation in absorbance with film thickness obeys Beer's law, as shown in Figure

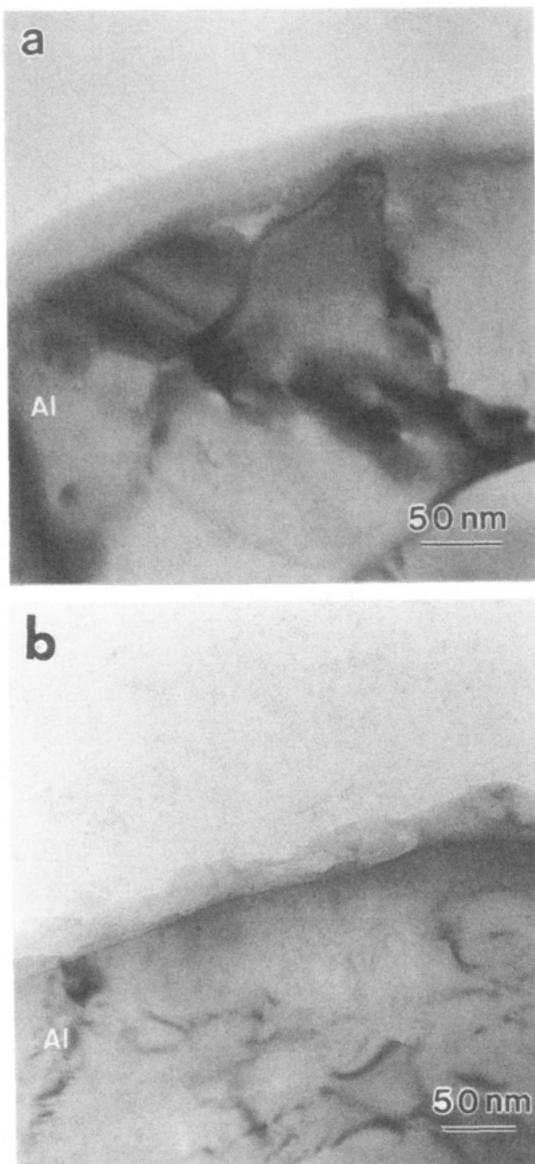


Figure 10. Transmission electron micrographs of (a) 1/ODA and (b) 1 films deposited on Al substrates, ultramicrotomed cross-section specimens.

8, thus confirming the integrity of the multilayers before and after thermal imidization.

E. Electron Microscopy. An important issue in the preparation of LB films from preformed polymers is the orientation and packing of the polymer chains in the film. The *n*-octadecyl chains were expected to orient away from the water surface, with the rest of the polymer chain on the surface, based on published STM results on similar polyimides.^{4,8} That expectation is consistent with the isotherm results shown in Figure 3, in which the increasing size of polymer repeat unit is accompanied by increasing extrapolated area per monomer. With the *n*-octadecyl chains oriented away from the surface, the spacing between layers would be on the order of 20 Å, corresponding to a linear aliphatic hydrocarbon chain. There is a report of 18–20 Å per layer in an LB film of 1/ODA, reducing to 9–12 Å per layer after imidization, based on ellipsometry.⁶ Following imidization and loss of the alkyl groups, much smaller spacing between layers is expected. In fact, there are reports of spacings of 4–6 Å following imidization in the same material, measured by X-ray interference or profilometry.^{1,7} Given the uncertainties in these thickness measurement methods for thickness in this range, the

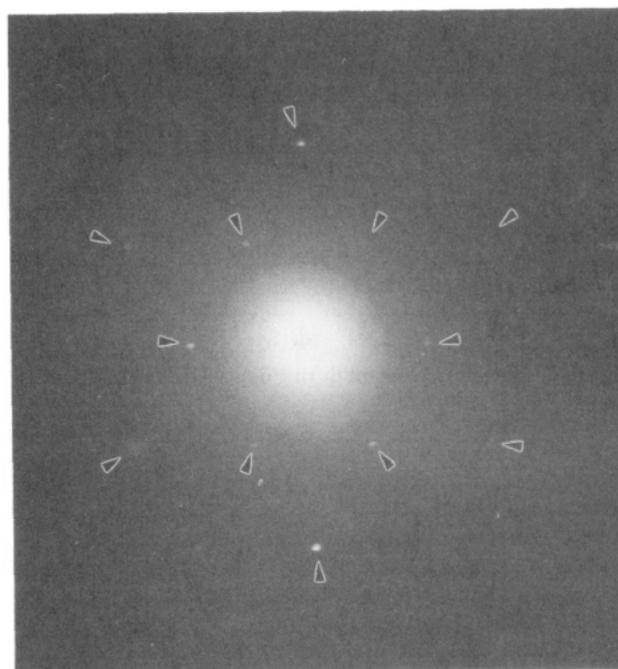


Figure 11. Selected area electron diffraction pattern obtained from 8.

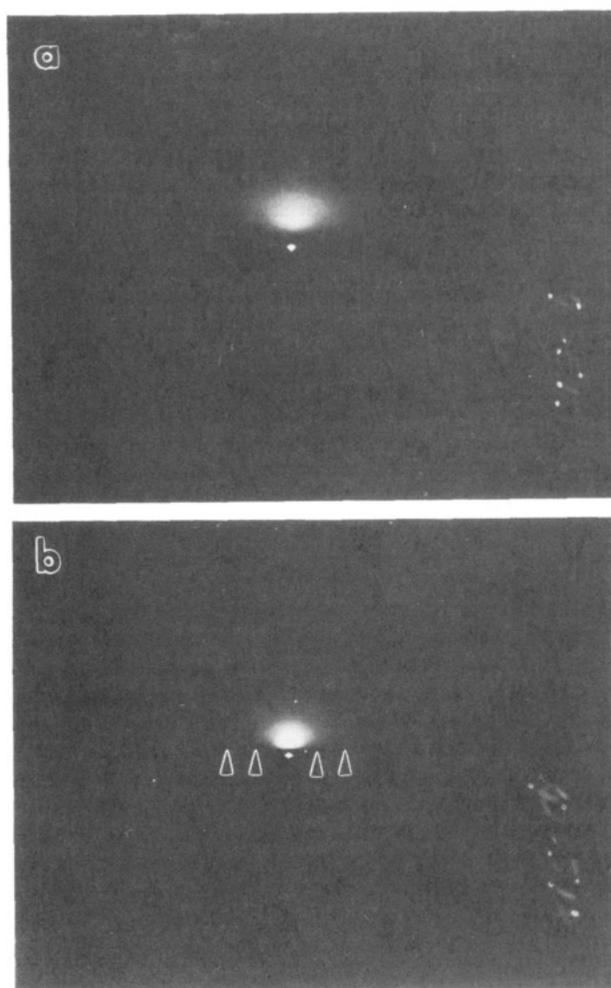


Figure 12. RHEED patterns obtained from (a) 1 imidized after spin coating and (b) 1 imidized after 12 layers deposited.

difference between these reports may not be significant. The objective of our electron microscopy studies was to determine the spacing between layers in the various

systems studied and the structural effects of the imidization process.

Films of 1 and 7 (before and after imidization) have been examined by SEM and TEM following deposition on single crystal Si web, electropolished aluminum and glass cover slips. Sample preparation has been difficult and different techniques were used with the two materials, as discussed below. Samples of 1 for RHEED analysis were deposited on quartz slides by spin coating and LB transfer.

Films of 1/ODA deposited on aluminum were mechanically thinned from one side to approximately 50 μm in the center of the sample. The specimen was then ion milled (Ar^+) from the back to remove the remaining aluminum in the thinned region. This procedure left areas of free standing film, which was perforated in places during ion milling. Figure 9 contains secondary electron images of the planar sample which had been prepared by mechanical thinning and ion-milling from the substrate side. In these micrographs, the brighter (lighter) regions are the Al substrate, whereas the gray areas are portions of the free-standing LB film. The perforations in the sample appear dark in these images. TEM examination of the planar specimens revealed a relatively featureless, smooth film.

Samples of 1/ODA and imidized 1 deposited on aluminum were encapsulated and ultramicrotomed for cross-sectional views (Figure 10). The film appeared to be relatively smooth before imidization, whereas some regions of surface roughness were observed in the imidized films. The film thickness observed in those photographs of 40-layer samples corresponds to approximately 9 \AA per layer before imidization and 5 \AA per layer after imidization. Individual layers were not evident in these TEM micrographs. These results compare to a previous report of 18–20 \AA before imidization and 9–12 \AA after imidization determined by ellipsometry.⁶ In both cases the film thickness is reduced by half during imidization. The differences in absolute magnitude of the thickness may be due to different substrates or film transfer conditions.

With respect to ordering of the polymer within the film, we were unable to observe any electron diffraction from films deposited on Si substrates. SEM micrographs of

our films show a featureless surface.⁹ However there did appear to be ordering in the plane of a film of 8, as selected area electron diffraction patterns revealed the presence of some discrete reflections, corresponding to an in-plane spacing of 5 \AA (Figure 11). That finding is consistent with the distance between adjacent 1 polyimide chains (5–7 \AA) determined by Fujiwara, et al. using STM on a LB monolayer deposited on highly oriented pyrolytic graphite.^{4b} They deposited the film as a complex of 1 and *N,N*-dimethylhexadecylamine and then imidized it using the acetic anhydride solution described above. They reported that the STM image showed a zigzag arrangement of polymer chains with 15–20 \AA between O atoms in a single chain. The distance between adjacent polymer chains was 5 \AA .

A broad diffuse ring pattern was observed in the RHEED pattern obtained from a 12-layer film of 1 (Figure 12b). This ring was associated with a spacing of approximately 5.3–5.6 \AA . No such diffraction was observed with a spin-coated sample of comparable thickness, as shown in the Figure 12a.

Conclusions

Preparation of polyamic acid LB films by complexation with aliphatic amines has been extended to fluorinated materials 2 and 3 complexed with *n*-octadecylamine. The film area occupied by each repeat unit in the polymer increased from 104 to 147 \AA^2 as the size of the repeat unit increased. While multilayers of 1/amine can be imidized using acetic anhydride, the others (2/ODA and 3/ODA) were dissolved in the solution. Multilayers of 7 have been prepared for the first time and imidized thermally. Spacings of 5 \AA between layers and 5.3–5.6 \AA between polymer chains within a layer were determined by TEM and RHEED of imidized 1.

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(9) Burke, M. G. Unpublished results.