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Organic Chemistry on a Polyimide Surface

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ABSTRACT: Base hydrolysis and acidification of a polyimide film resulted in a surface that resembles the poly(amic acid), which is the polyimide precursor. This modification was thoroughly characterized and found to offer an unusual opportunity to control the depth of modification. The modified surface was used as a substrate for subsequent organic reactions, including conversion of the surface to isoimide by reaction with trifluoroacetic anhydride in pyridine. The isoimidized surface was isomerized back to polyimide by heating. The reduction of the polyamic acid surface was also accomplished, resulting predominantly in a surface in which all carbonyls were reacted to give alcohol and amine functional groups. All surfaces were characterized by contact angle, XPS, and FTIR measurements and by comparison to the reaction products obtained using model compounds.

Introduction

Polyimides are a class of polymers which meet many of the requirements necessary for polymers used in the electronics industry,[1,2] as they are characterized generally by excellent thermal, electrical, and mechanical properties. These polymers are used extensively as interlayer dielectrics and as barrier layers to protect underlying circuitry from damage due to high-energy particles or corrosion. The successful fabrication of devices requires that the polyimide be made to adhere with various metals and/or cohere to other layers of polyimide. However, due to the somewhat inert surface of polyimides, it is difficult to form adhesive bonds with these materials, and the variety of surface modification schemes that have been applied to other polymers have been tried for polyimides as well. These include the use of ion beams,[3-6] photografting,[7] plasmas,[8-12] particle beams,[13] sputtering,[14] ^{60}Co γ-irradiation,[15] and wet chemical methods.[16-19]

In another category of surface modifications are the investigations involving surface-selective chemical modification of polymers and subsequent chemical reactions to prepare polymer surfaces functionalized with a wide variety of chemical groups. Two prominent examples are the surface oxidation of polyethylene and subsequent surface functionalization[20] and the lithiation of poly(chlorotrifluoroethylene) followed by a number of alternate surface reactions.[19] The present work follows that pattern with two distinguishing aspects. First, poly(pyromellitic dianhydride-*co*-oxydianiline), poly(PMDA–ODA), the substrate polymer of this work, is a significantly more challenging problem from an analytical perspective because, unlike either of the above two polymers, it has a rich spectroscopy of its own on which surface modifications are difficult to discern. For example, in general we were unable to obtain infrared spectra of the surface modifications on bulk films by surface-selective methods such as attenuated total reflectance and resorted instead to using external reflectance on very thin films on which the modification was an appreciable fraction of the total film. The second distinguishing aspect is that the surface modification studied allows an interesting degree of control in terms of the depth of modification, partly because of the physical properties of the polyimide as an engineering thermoplastic with a glass transition temperature over 400 °C and partly because of the chemistry of the imide repeat unit. The modification used is hydrolysis in dilute sodium hydroxide followed by acidification with acetic acid to produce a surface that is poly(amic acid)-like in nature. The poly(amic acid)-rich surface has been used as a precursor for subsequent chemical modifications. All modified polyimide surfaces have been characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and contact angle measurements as well as by comparison to reactions involving model compounds.

Experimental Section

Materials. Sodium hydroxide and pyridine (J. T. Baker Chemical Co., "Baker Analyzed" reagent) were used as received. Trifluoroacetic acid anhydride, borane–tetrahydrofuran complex (1.0 M), and *N*-methylpyrrolidinone (NMP) (anhydrous, 99+ %) (Aldrich Chemical Co.) were used as received. *N*-Phenylphthalimide (97%, Pfaltz & Bauer, Inc.) was recrystallized from ethanol.

Preparation of PMDA–ODA Polyimide Films. Polyimide films were made from Du Pont Pyralin 2545, a poly(amic acid) precursor polymer prepared from 1,2,4,5-benzenetetracarboxylic acid dianhydride and 4,4′-oxydianiline and dissolved in *N*-methylpyrrolidinone (NMP). Poly(amic acid) films were deposited by spin coating on single crystal silicon substrates which had been coated with a sputtered thin layer of chromium for adhesion. Film thickness is controllable by varying the spin speed and dilution of the solution with additional NMP. The spun films were dried by baking in a convection oven at 80 °C for 30 min. The poly(amic acid) to polyimide cyclodehydration reaction was accomplished by heating to 150 °C (30 min), 200 °C (30 min), 300 °C (30 min), and 400 °C (60 min) followed by slow cooling in a vacuum oven with a partial atmosphere of forming gas.

General Analytical Techniques. Melting points were recorded using a TA Instruments DSC-2910 differential scanning calorimeter. ^{1}H NMR spectra were acquired on an IBM Instruments Inc. AF 250 spectrometer. Manipulations involving air-sensitive reagents were performed in a Vacuum Atmospheres drybox with MO-40-2 dri-train under an argon atmosphere.

Contact Angle Measurements. Contact angle measurements were performed using a Ramé-Hart Model 100-00 goniometer using the sessile drop method.[21] The probe fluid was dispensed with a Gilmont microliter syringe (glass body and Teflon plunger) through disposable 23 gauge needles (Assemblyionics Inc.). The probe liquids were prepared from Hydrion Dry Buffers (Aldrich Chemical Co.) of the appropriate pH using deionized water. The volume of the probe liquid used was 10–30 μL for advancing angles and half of that for receding angles. In this range, the volume of the drop had little effect on the measured

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contact angle. During the contact angle titration experiments, the angle was observed to change from its initial value especially at intermediate pH's, so a 1–2-min equilibration period was used before all measurements. Averages from six measurements (3 drops) across the sample surface are reported. Although the effects of storage did not appear to alter the observed contact angles, measurements were generally made immediately after the preparation of the surface. If storage of the films was required, it was done in a container flushed with nitrogen.

X-ray Photoelectron Spectroscopy (XPS). XPS data were obtained with a SSX 100-05 spectrometer from Surface Science Laboratories using monochromatized Al Kα radiation. Elemental binding energies (BE) are referred to C 1s at 285.0 eV. Data collection on thicker samples required the use of a flood gun due to the insulating nature of the polymer. Data reduction was done using a nonlinear least-squares curve fitting program monitoring the goodness of fit with χ^2 and peak area error, keeping the latter as small as possible.[22]

Ellipsometry. Thickness measurements on polymer films were made on a Gaertner Scientific Corp. Waferscan L11B ellipsometer employing a He–Ne laser. The refractive index of PMDA–ODA (633 nm) was set at 1.73.[23] Thicknesses were determined from the average of 10 measurements across the sample.

FTIR Spectroscopy. FTIR spectra were recorded on a Nicolet 730 FTIR spectrometer equipped with a MCT-A detector. The spectra of model compounds were recorded as KBr pellets. The samples of polymer film on Si wafers were mounted on an external reflection (ER) accessory equipped with a polarizer (Harrick Scientific, Inc.). The polarizer is oriented to transmit radiation polarized parallel to the plane of incidence of the sample. The IR beam was incident on the sample at 78° with respect to the sample normal. Typical scan conditions were 200 scans and a resolution of 4 cm^{-1}. The acid–base equilibrium study involving the interconversion of carboxylic acid groups and amate groups of 2 was accomplished starting with 500-Å films of cured polyimide 1 on a silicon wafer which was coated with chromium serving as an adhesion layer and as a reflection element for the ER experiments. The films were hydrolyzed in an aqueous 1 M NaOH solution for 1 h. These conditions were chosen to ensure complete modification of the film which was verified by FTIR. The samples were rinsed with deionized water for <1 s and dried by blowing with clean nitrogen. The pH of the film was adjusted by dipping the hydrolyzed sample in the appropriate buffer solution for 2 h, followed by rinsing with deionized water for <1 s and drying in a stream of clean nitrogen. Peak deconvolution and area determinations were made using Spectra Calc TM (Galactic Industries, Inc.). A shift of 10–20 cm^{-1} is common when the sample is examined in the KBr pellet form vs external reflection. For polyimide samples, the carbonyl stretch of the imide ring is at 1732–1742 cm^{-1} (ER), depending on film thickness vs 1725 cm^{-1} (KBr). A small shift in peak positions is also noted when going from monomer to polymer.

Conversion of Polyimide 1 to Poly(amic acid) 2. The initial precursor poly(amic acid) surface was prepared typically by hydrolysis in an aqueous 0.25 M NaOH solution for a specified period. At this stage, a portion of the polyimide film has been converted to the sodium salt of the poly(amic acid). The salt was transformed to the amic acid form by treatment of the film with an aqueous 0.25 M acetic acid solution for an equal period of time followed by rinsing extensively with deionized water.

Base Hydrolysis of *N*-Phenylphthalimide. A water/ethanol (300 mL/150 mL) solution of *N*-phenylphthalimide (5 g) and NaOH (23 g) was stirred and refluxed for 15 min and then chilled in an ice-water bath. Concentrated HCl (55 mL) was added with a pipet, and the white precipitate was collected on a Buchner funnel and washed with a large amount of deionized water. The white crystalline solid was dried overnight, giving 4 g (75%) of *N*-phenylphthalamic acid, mp 169 °C (lit.[24] mp 169 °C).

Conversion of Poly(amic acid) 2 to Poly(isoimide) 4. The reagent solution was prepared by adding slowly an equal volume of trifluoroacetic anhydride to pyridine under an argon atmosphere. A base-hydrolyzed/acidified PMDA–ODA polyimide film 2 was immersed into the reagent for 12–24 h. The sample was then rinsed extensively with pyridine prior to removal from the drybox. It was further rinsed with acetone and deionized water and then allowed to dry. IR (ER): 1822, 1731, 1697, 1498, 1252, 927 cm^{-1}. The IR spectrum of 4 is in good agreement with that reported for a poly(pyromellitisoimide) film.[25]

Isoimidization of *N*-Phenylphthalamic Acid. *N*-Phenylphthalisoimide was synthesized by refluxing *N*-phenylphthalamic acid with acetyl chloride. After recrystallization from ether, a pale yellow solid was isolated and characterized as *N*-phenylphthalisoimide by its mp (116–117 °C; lit.[24] mp 115–116 °C) and ^{13}C NMR and IR spectra. The IR spectrum has two intense peaks at 1705 and 1787 cm^{-1}, characteristic of the lactone ring.

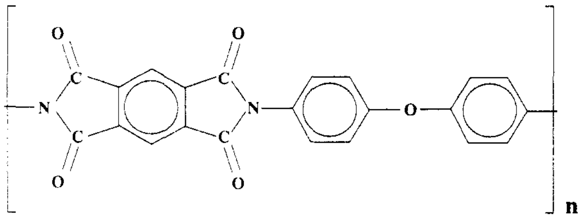
Reduction of Poly(amic acid). A poly(amic acid) 2 sample was immersed into a 1.0 M borane–tetrahydrofuran solution, under an argon atmosphere, for 22 h. The sample was rinsed thoroughly with acetone and deionized water and then allowed to dry.

Reduction of *N*-Phenylphthalamic Acid. *N*-Phenylphthalamic acid (1.02 g) was dissolved in 20 mL of 1.0 M borane solution in tetrahydrofuran. The effervescence subsided after about 15 min of stirring at room temperature, and the solution was left unstirred and stoppered for 2 days. Excess borane was destroyed by adding 1 mL of aqueous acetic acid (1/1, v/v). The solvent was evaporated from this turbid mixture, leaving a semisolid residue which was stirred with 12 mL of saturated aqueous sodium bicarbonate. The product was then extracted into methylene chloride (three 100-mL portions) using a separatory funnel. After drying over magnesium sulfate, the solvent was evaporated to give 1.05 g of semisolid crude product. All but ca. 50 mg of this residue was soluble in 25 mL of anhydrous ether. The insoluble fraction (mp 138–139 °C) was identified as *o*-(hydroxymethyl)-*N*-phenylbenzamide (lit.[26] mp 135–137 °C) and IR (amide carbonyl at 1642 cm^{-1}). The ether solution was treated with 5 mL of 1.3 M ethereal HCl to precipitate the amine hydrochloride. The precipitated amine hydrochloride was dissolved in 15 mL of anhydrous ethanol and reprecipitated with 100 mL ether to give 0.5 g of white crystalline *N*-phenyl-*o*-(aminomethyl)benzyl alcohol hydrochloride salt mp (dec) 145–151 °C (lit.[26] mp 156–157 °C (dec)). IR (KBr): 3120, 2860, 2708, 2662, 2570, 2440, 1595, 1561, 1440, 1395, 1295, 1225, 1198, 1075, 1035, 1002, 972, 949, 762, 698 cm^{-1}. ^{1}H NMR (CD$_3$OD): δ 7.5–7.3 (m, 10 H), 4.9 (br), 4.8 (s, 2 H), 4.7 (s, 2 H).

Etching of Polyimide during Base Hydrolysis. A thin (420 ● 9 Å) polyimide film was prepared on a chromium-covered silicon wafer. The wafer was then fractured to provide several samples of equal thickness. Samples of the film were treated for 1, 2, 3.5, and 4.5 h with 0.25 M NaOH and then immersed into a 0.25 M acetic acid solution for an equal period of time. After extensive rinsing with deionized water, the samples were recured to 400 °C in a vacuum oven with forming gas ambient. The thicknesses of the films were then remeasured.

Results and Discussion

Surface Hydrolysis of Polyimide to Poly(amic acid). The polyimide chosen for investigation was PMDA–ODA 1 which was modified by exposure to dilute NaOH at room temperature followed by acidification with acetic acid. The characterization of the hydrolyzed polyimide surface has been the subject of several recent studies,[27,28] which suggest that the surface of 1 has been converted into a surface that resembles that of 2. The carboxylic acid and amide functional groups should then impart to



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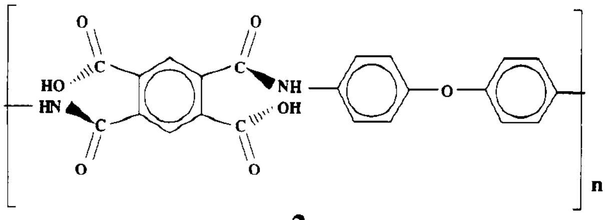

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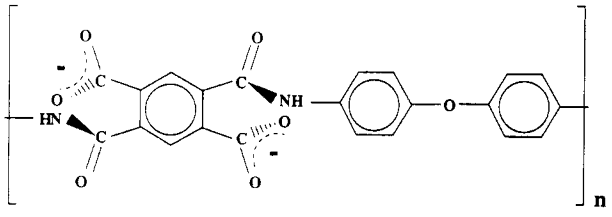
the modified polyimide different surface properties while retaining those properties representative of the bulk. Note that the hydrolyzed region has the structure of the poly(amic acid) precursor film, but because it previously was subjected to the 400 °C thermal excursion necessary to imidize the poly(amic acid), it is free of any NMP solvent which plays an important role in the thermal processing of PMDA–ODA films.[29]

Extensive modification of 1 might be expected to impart appreciable solubility to the polymer at the interface and to affect subsequent analyses. Etching of the polyimide during modification was examined by comparing film thickness measurements on untreated films of 1 with those that had been surface-modified to 2 followed by reimidization (400 °C) to 1. The results of the film thickness measurements are shown in Figure 1. The film is seen to decrease ~25 Å in thickness in the first hour of treatment and does not change dramatically after, at least not in the time frame of observation. It is not clear if the initial drop in thickness is a result of the actual etching of the polymer or some artifact. The absence of any substantial thickness change after 60 min, however, implies that under the conditions of surface hydrolysis, etching of the film does not play a significant role. The lack of etching of the film is consistent with the fact that in the more aggressive conditions of the hydrolysis of the *N*-phenylphthalimide model compound, little or no cleavage of the amide bond accompanies the ring-opening reaction. As will be shown, the absence of etching allows the depth of modification to be controlled to a significant degree.

The extent of hydrolysis of 1, i.e., the conversion of imide groups to the amide–amate salt groups of 3, was monitored via external reflection (ER) FTIR spectroscopy by following the relative peak intensity of the imide C═O stretching vibration (1740 cm^{-1}). Examined in the amate salt form, polyimide films of 1100-Å thickness were hydrolyzed in 0.25 NaOH solution for the specified periods of time and then rinsed with deionized water for 5 min. The experimental results are shown in Table I.



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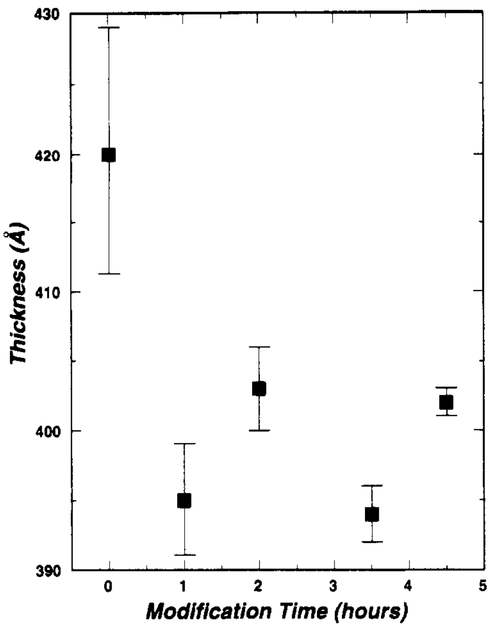


Figure 1. Ellipsometry data. Polyimide films were measured after hydrolysis (various times), acidification, and thermal reimidization.

Table I
Extent of Polyimide Hydrolysis

hydrolysis time (h)[a]	IR (1740 cm^{-1})[b]	fraction of 1 hydrolyzed (%)[c]	nominal depth of hydrolysis (Å)[d]
0	0.315	0	0
1	0.269	14.6	160
2	0.231	26.7	294
3.5	0.195	38.1	419

[a] Using 0.25 M NaOH and 1100-Å-thick polyimide films. [b] Absorbance of the imide carbonyl stretch not corrected for the minor amount of amic acid (1727 cm^{-1}) introduced by 5 min of rinsing in deionized water. [c] Based on the ratio of the 1740-cm^{-1} absorbances. [d] Assuming no etching during hydrolysis and a sharp boundary between 1 and 2.

Based upon the IR data, the initial rate of hydrolysis was estimated to be ≈160 Å/h with the 0.25 M NaOH solution. This estimate assumes that the hydrolysis occurs to give a sharp boundary between hydrolyzed and virgin polymer, an assumption which we will show to be incorrect. The "nominal depth of hydrolysis" term is used here, however, to approximate within an order of magnitude the extent of polyimide hydrolysis. The data suggest that the rate of hydrolysis is not constant with time. The modification of 1 must involve a sequence of mechanistic steps in which the reactant must diffuse into the film and then react with the polymer. This type of reaction with diffusion often follows rate laws which have an exponential time dependence.[30,31] Therefore, it is not surprising that the rate decreases as a function of time. The measured rate of hydrolysis appears reasonable based on contact angle measurements. As will be discussed in detail later, hydrolysis times as short as ~5 min, corresponding to about 10–15 Å based on crude extrapolation of the FTIR data, are sufficient to show the characteristic contact angle vs pH behavior of 2 (see Figure 3).

The exact state of the modified polyimide is particularly sensitive to processing conditions. In controlling the number of amate versus amic acid groups on the film, special attention must be paid to the acid–base equilibrium of these two groups. By treating the hydrolyzed film samples (500-Å thickness) with pH-buffered solutions ranging from pH 2 to 8, the extent of interconversion of the two functionalities as a function of pH can be followed by the relative IR band intensities (see Figure 2). Since there are a number of peaks present in the region 1500–1740 cm^{-1}, including 1727 cm^{-1} (C═O stretch of the CO_2H group), 1670 cm^{-1} (C═O stretch of the CONH group), 1606 cm^{-1} (C═O stretch of the CO_2^- group and the phenyl ring (of the PMDA moiety) stretch), 1583 cm^{-1} (NH bend of the CONH group), 1501 and 1513 cm^{-1} (crystalline and amorphous phenyl ring (of the ODA moiety) stretches), the peaks are resolved by curve fitting assuming Gaussian–

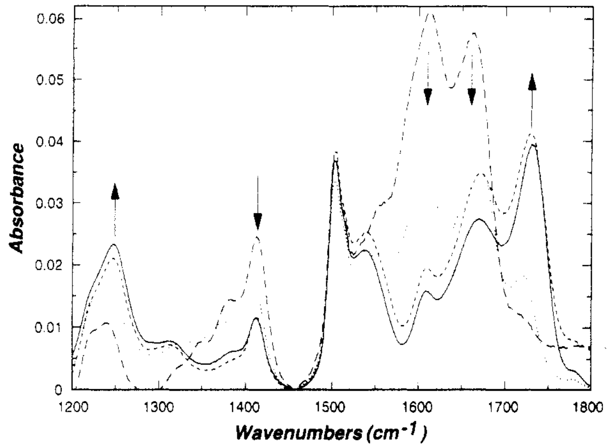


Figure 2. External reflection FTIR spectra. Spectra are for completely hydrolyzed 500-Å films as a function of pH; (- -) pH 8; (···) pH 6; (- - -) pH 4; (—) pH 2. Arrows indicate spectral changes which occur as pH is decreased.

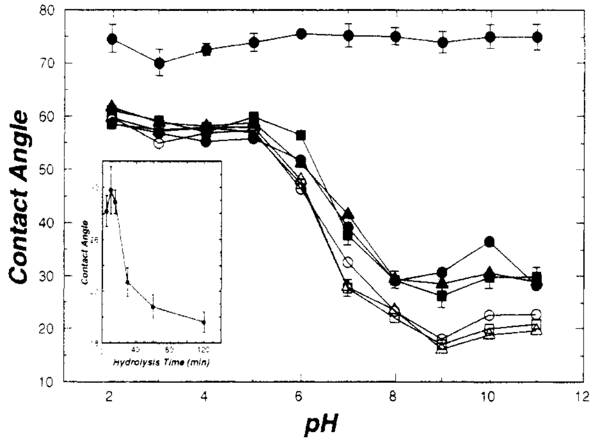


Figure 3. Advancing contact angles vs pH as a function of hydrolysis time of polyimide. Shown are data for (●) 5, (■) 10, (▲) 15, (○) 30, (□) 60, and (△) 120 min of hydrolysis and equal times for acidification. The trace at the top (●) shows the data obtained for the unmodified polyimide 1. For clarity, error bars are shown only for values of pH ≥ 7, for data collected after 10 and 60 min of modification, and if error bars are larger than the symbol. The inset shows the effects of modification times on contact angles for data gathered on the surface of 2 at pH 11.

Lorentzian mixed-type band shapes. Peak areas are then used to find the relative amounts of acid vs amate in the film. The combined peak areas under the narrow and more well-defined peaks at 1501 and 1513 cm^{-1} are used as the internal standard for absorbance calculations. Since the peaks at 1606 and 1670 cm^{-1} overlap extensively, the absorbance due to the amate group at 1606 cm^{-1} is found by subtracting the absorbance of the combined peak areas at 1606 and 1670 cm^{-1} at pH 2 (assuming no amate is present) from that at the pH of interest. The ratio of the absorbance at 1727 cm^{-1} for the sample at pH 2 to the absorbance due to the amate group at 1606 cm^{-1} at pH 14 is then used to convert the relative absorbance to concentration for the acid–base pair.

The conversion of the surface of polyimide to poly(amic acid) was examined by contact angle measurements as a function of pH. This type of measurement, termed "contact angle titration", has been exploited by Whitesides et al.[20] Shown in Figure 3 are the contact angle data for PMDA–ODA polyimide 1 as a function of pH. The advancing contact angle, θ_{adv}, was measured to be $\approx 70°$ while the receding contact angle, θ_{rec} (data not shown), was determined to be $\approx 55°$. As anticipated from the type of functional groups present on the surface of 1, both angles are invariant with pH.

Shown in Figure 3 are the advancing contact angle data as a function of pH obtained for surfaces of 1 which had been hydrolyzed (0.25 M NaOH, then acidified with 0.1 M CH_3CO_2H for an equal period of time) for 5, 10, 15, 30, 60, and 120 min. Several observations are worth noting. Under the current experimental conditions, it is seen that the surface of 1 is quickly enriched in carboxylic acid groups due to hydrolysis. As one would expect, the poly(amic acid) surface is more hydrophilic than that of the precursor polyimide 1. The inflection of the contact angle data with changes in pH indicates clearly the conversion of 2 to the poly(amate salt) 3 as the solution is made increasingly alkaline.

Some hydrolysis-time dependence of the data in Figure 3 is evident. Although all of the surfaces in acid form (pH ≤ 5) are of equal hydrophilicity of $\theta_{adv} \approx 60°$, as the pH of the probe liquid is increased and acid groups are converted to amate salts, there is a clearly discernible dependence of the contact angle on hydrolysis time. All of the samples exhibit an inflection of the wetting curve, but the surfaces which had been hydrolyzed for longer times ultimately show $\theta_{adv} \approx 20°$ compared to $\sim 30°$ for shorter hydrolysis times. The differences between these values exceed experimental error ($\delta \approx \pm 2°$).

Assuming that the relative contribution to wetting behavior of a given functional group is additive,[32] the lower contact angles at high pH obtained on the samples subjected to longer hydrolysis times imply that the sessile drop is exposed to a greater number of carboxylate anions as a result of the longer hydrolysis time. Two factors may contribute to an explanation for why hydrolysis-time dependence of the contact angles is observed at high pH and not low pH: (i) the difference between the low-pH contact angles of the virgin and hydrolyzed surfaces is only 10–15°, so small increases in the density of carboxylic acid groups may not lead to observable differences in the contact angles; and (ii) the differences in amate group density with hydrolysis time at high pH are magnified by surface reconstruction, exposing more amate groups at the interface. Reversible ambient-induced reconstruction has been noted previously on plasma-modified polyimide surfaces.[8]

The inset to Figure 3 (hydrolysis time vs contact angle at pH 11) displays the hydrolysis-time dependence of the contact angle more dramatically. Within the scatter in the data, the contact angles appear to be concentrated into two different regimes. We believe that the break in the data reflects the progression of the hydrolysis beyond the region sampled by the contact angle measurement. Previous studies have shown that the wettability of an organic surface is determined by the outermost region of the material.[33] Using self-assembled monolayers of alkanethiols on gold, Whitesides and Bain established a depth sensitivity of wetting of ~2–5 Å.[34] The possibility of surface reconstruction would likely increase the depth sensitivity significantly.

Using the method of Whitesides et al,[20] the data from contact angle titrations can provide additional information regarding the nature of the modified polyimide surface. The hydrolyzed surface 2 is rich in carboxylic acid groups. Contact angle titrations and FTIR experiments have demonstrated clearly the dissociation of acid groups as the environment about the acid groups is increased in alkalinity. From these experiments, information regarding the dissociation behavior of acid groups on the surface of 2 can be gathered.

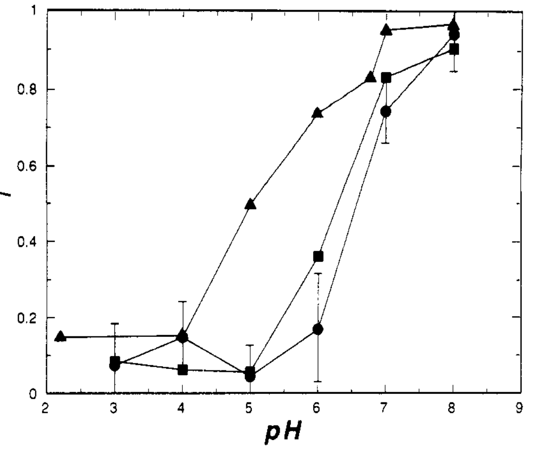


Figure 4. Extent of ionization vs pH. Contact angle data for the poly(amic acid) surface **2** after 120 (●) and 10 min of hydrolysis (■) and FTIR data for complete hydrolysis of a 500-Å film (▲) are shown.

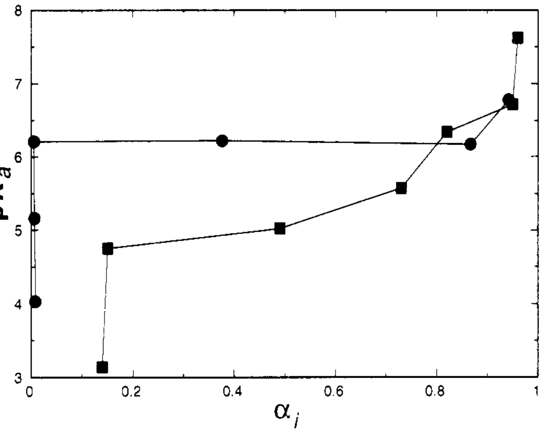


Figure 5. Effective acid dissociation constant vs extent of ionization. Data shown are for modified polyimide surface **2** from Figure 3 using contact angle titration (●) (120-min hydrolysis and acidification) and FTIR experiments (■).

In a global sense, the dissociation behavior of polyelectrolytes can be related directly to electrostatic interactions between a dissociating proton and ionized groups on the polymer chain. Specifically, the dissociation behavior of poly(amic acid) groups of **2** can be related to the behavior of other polyelectrolyte systems.

The effective dissociation constant, pK_a^{eff}, can be related to the extent of ionization, α_i, in the following fashion:[35]

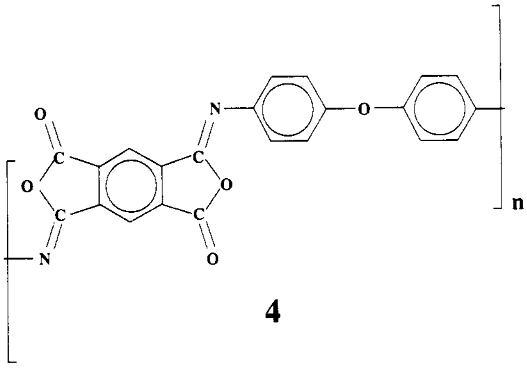
$$pK_a^{eff} = pH - \log[(\alpha_i)/(1 - \alpha_i)]$$

For a monobasic acid, pK_a^{eff} is independent of α_i, while polybasic acids show an informative dependence on α_i. This effect is due to the electrostatic interaction of CO_2^- on neighboring CO_2H groups as the functional groups are interconverted during ionization. Several examples of this behavior have been forwarded.[35-37] The previous studies highlighted the fact that inductive effects, between acid groups, decrease sharply with increasing distance of separation.

Using data from contact angle titrations on **2**, along with data from FTIR experiments on this surface, the change in α_i with pH can be observed and is shown in Figure 4. The data from hydrolysis times of 10 and 120 min show a sharp inflection during the course of ionization, whereas the FTIR data exhibit a broadened transition region. More informative is the display of the data, Figure 5, as pK_a^{eff} vs α_i. Shown only are the data from the FTIR experiments and the titration using the surface which had been hydrolyzed for 120 min. The other data were found to behave similarly within experimental error. Determined from contact angle data, the intrinsic dissociation constant, pK_0 (pK_a^{eff} extrapolated to $\alpha_i = 0$), was determined to be ≈6.5. This is comparable to the value of ~6 estimated for oxidized polyethylene.[20] Both of these values are several pK units higher than that measured for poly(acrylic acid) derivatives,[35] a reasonable solution-phase model for the oxidized polyethylene, and that reported for *N*-phenylphthalamic acid ($pK_a = 3.6^{38}$), serving as a model for the hydrolyzed polyimide surface. Considering the dissimilarity in structure, the similar shift of the pK_0 values for the modified polyimide and oxidized polyethylene from that of suitable solution model systems may not be coincidental but a reflection of the difficulty in generating charged groups at the polymer–water interface, as alluded to by Whitesides et al.[32]

Perhaps consistent with such a surface effect, the data gathered from the FTIR experiment exhibit some variation of effective pK_a with extent of ionization, increasing from ~4.75, at low α_i, to ~7.5, at large α_i. To the extent that it is different from that obtained from the contact angle data, the shape of the curve (Figure 5) more closely resembles that of a polybasic acid in solution. The carboxylic acid groups on the surface of **2** should have a fixed orientation on the polymer chain, and the nearest-neighbor acid-to-acid distances, within a polymer chain, are fixed at ~6 Å (based upon the experimentally-determined molecular structure of benzene-1,2,4,5-tetracarboxylic acid).[39] It would be expected that the acid groups on **2** would represent a rather homogeneous community. While the contact angle data are representative of the surface, the FTIR data, collected on a 500-Å film which was hydrolyzed completely, reflect the bulk film behavior. Intermolecular contacts, if sufficiently close in proximity, between carboxylic acid groups might influence the acid dissociation behavior during ionization. In addition, the dielectric constant, in the bulk film, is likely to be influenced by the interconversion of carboxylic acid and amate groups through the depth of the film. These two effects, perhaps in addition to others, may be responsible for the difference between surface and bulk acid–base behavior for films of **2**.

Conversion of Poly(amic acid) to Poly(isoimide). The conversion of **2** to the poly(isoimide) **4** is effected easily by reaction with trifluoroacetic anhydride in pyridine (1/1, v/v).[40] The course of this reaction was followed by XPS, and the data are shown in Figure 6. Shown also in Table II are the results obtained by applying the trifluoroacetic anhydride treatment to a poly(amic acid) film that was dried to remove solvent but not cured thermally. The spectral changes which occur on this surface are similar to those obtained on surfaces of **2**, but the results are more pronounced. The results and assignments are compiled



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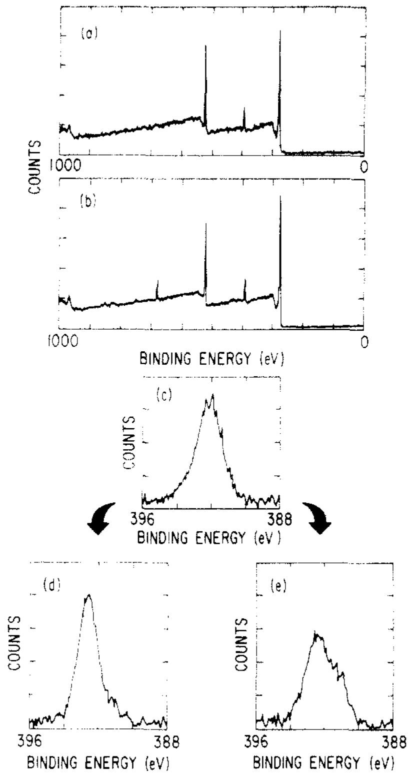


Figure 6. XPS data. Conversion of poly(amic acid) 2 to poly(isoimide) 4 with trifluoroacetic anhydride (TFAA): (a) Survey scan of film after 115 min of hydrolysis and acidification; (b) (a) after treatment with TFAA; (c) N 1s spectrum of (a); (d) N 1s spectrum after 8 min of hydrolysis/TFAA; (e) same as (d) except 115 min of hydrolysis.

in Table II. Figure 6a shows the survey scan obtained on a surface of **2**. The survey scan (Figure 6b) for the isoimidized surface **4** exhibits the characteristic C 1s, N 1s, and O 1s peaks in addition to a F 1s peak at ∼686 eV due to contamination with excess reagent. This contamination is also seen in C 1s data as a higher BE peak associated with CF_x species; it and the $\pi \rightarrow \pi^*$ transition are not listed in Table II. The poly(isoimide) possesses two types of functional groups that are not present on either **1** or **2**. These are ester-like OC═O and imine-like N═CO structures from the isoimide ring. The C 1s signal at ∼286.1 eV is assigned to CO, CN, and PMDA carbons while the peak at ∼288.1 eV may be assigned to OC═N[42] and the peak at ∼289.6 eV may account for OC═O. The N 1s peak obtained for **4** and occurring at ∼399.6 eV can be assigned to isoimide N 1s due to a relatively electron-rich nitrogen atom which is doubly bonded to carbon (compared to the relatively electron-deficient imide N 1s signal at ∼401 eV).[42] The largest O 1s peak appears at ∼534.1 eV and is assigned to O, as in ether or ester species. The lower binding energy O 1s signal at ∼532.6 eV is due to carbonyl O 1s electrons.

The isomerization of **4** back to the polyimide **1** can be effected thermally with the reaction having an equilibrium constant of ∼55 when heated to 400 °C.[40] A polyimide sample which had been derivatized to **4** was heated to 300 °C using the same conditions employed to cure samples of **1**. The XPS data obtained for this surface were only indistinguishable from that of **1** by the small concentration of fluorine retained.

The isoimidization reaction of **2** to **4** is useful in determining the extent of hydrolysis by XPS. Shown in Table III are the elemental composition data for films of **2** which had been hydrolyzed for the indicated times and then converted to the amic acid form by acidification. The XPS spectra for hydrolyzed and unmodified polyimide are quite similar and not of much use in discerning between the two possible surfaces. The conversion **2** → **4** alters the surface, and hence XPS spectroscopic properties, by isoimidization. Table III shows that the N 1s signal of **4** is shifted to lower binding energy vs the N 1s signal of **1**, allowing the portion of the film which had been hydrolyzed to be differentiated from that which is unhydrolyzed. The trifluoroacetic anhydride treatment does not affect the unmodified polyimide. The reaction is not quantitative, however. As shown in Table II, a portion of the amic acid is imidized. Figure 6d shows the N 1s data which were obtained from the surface of **4** (8 min of hydrolysis time). The ratio of isoimide N 1s to imide N 1s signals is ∼0.18. Contrast this with a surface of **4** which was obtained by isoimidization after 115 min of hydrolysis (Figure 6e). The ratio of isoimide N 1s to imide N 1s has increased to ∼0.58, indicating that longer hydrolysis times lead to increased extent of conversion from polyimide to poly(amic acid). In neither case is the conversion of **1** → **2** complete within the XPS sampling volume.

The results from the XPS study of the isoimidization reaction along with the FTIR and contact angle data on films of **2** can be used to obtain a picture of the spatial shape of the boundary between polyimide and hydrolyzed polyimide. The XPS sampling depth for polyimide under our experimental conditions is about 50–100 Å. XPS experiments measuring, indirectly, the extent of conversion of **1** to **2** through the conversion **2** to **4** demonstrated that **2** is not formed to completion for hydrolysis times up to 115 min. The nominal depth of hydrolysis from the FTIR experiments (Table I) for 2 h was ca. 300 Å. If the boundary between hydrolyzed and unhydrolyzed polyimide were sharp, then the XPS data would have to show complete conversion of **1** to **2**, as analyzed by the conversion to **4**, since 300 Å is well beyond the XPS sampling depth. This analysis is complicated by the fact that the conversion of amic acid to isoimide is known to be less than quantitative (see Table II), but the 15% of imidization that accompanies isoimidization is not sufficient to explain the amount of imide seen by XPS on the surfaces of films that have undergone the **1** to **2** to **4** conversion. On the basis of both the XPS and FTIR results for the films hydrolyzed for 2 h, it can be estimated that the boundary region between hydrolyzed and unhydrolyzed polyimide must be on the order of ca. 500 Å. This number is derived by assuming that the 300-Å nominal depth from FTIR is the midpoint of the boundary region and that a significant amount of unhydrolyzed polyimide must still be present about 250 Å closer to the surface in order for XPS to detect it. Obviously, this picture of the hydrolyzed surface only applies to the 2-h hydrolysis time, as one might expect diffusion processes to cause a dramatic increase in the boundary region from short hydrolysis times to long.

Another "snapshot" of the hydrolyzed surface can be derived from consideration of the contact angle behavior. It is clear from Figure 3 that the outermost surface of **1** is converted substantially to **2** after only 5 min of exposure. As discussed previously, however, full development of the contact angle behavior is not seen until 30 min of exposure. Based on the FTIR data, the nominal depth of hydrolysis for 15 min is about 40 Å. Thus, using the same sort of derivation as for the XPS data, one can estimate that the boundary region after 15 min is about 60 Å, assuming that some fraction of unhydrolyzed polyimide must still exist within 10 Å of the surface in order for the contact angle behavior to be less than fully developed. This information about the surface, while certainly approxi-

Table II
XPS Results for Isoimidized Film

	C 1s				N 1s		O 1s	
BE (±0.2 eV)	285.0	286.1	288.1	289.6	399.6	400.9	532.6	534.1
atom %	38	42	10	9	85	15	37	63
assignment[a,b]	CH_n	COC, CN, PMDA	C(=N)O	C(=O)O	N=C<	imide N	>C=O	O=COC or COC
fwhm[c] (eV)	1.1	1.2	1.3	1.4	1.1	1.3	1.6	1.7

[a] Reference 41. [b] Reference 42. [c] Full width at half-maximum.

Table III
XPS Study of Isoimidization of Hydrolyzed Surface

	results after hydrolysis				results after hydrolysis and TFAA treatment	
hydrolysis time (min)	C %	O %	N %	% N 1s at 400.8 eV	% N 1s at 401.0 eV	% N 1s at 399.6 eV
8	75	18	7	100	87	13
115	75	18	7	100	63	37
calc PI	75.9	17.2	6.9			

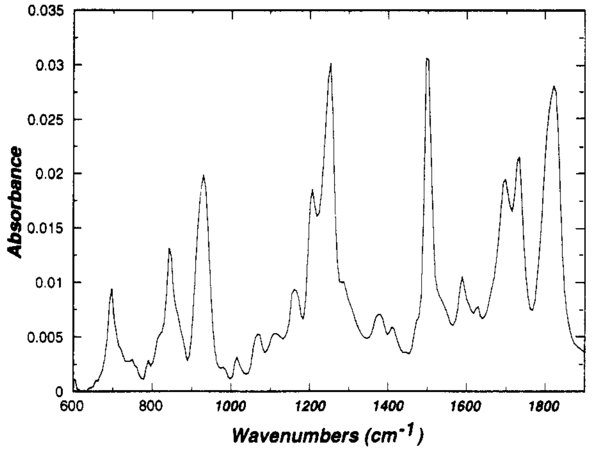


Figure 7. FTIR spectrum of isoimidized polyimide. Film 4 was produced by isoimidization of 2 with TFAA.

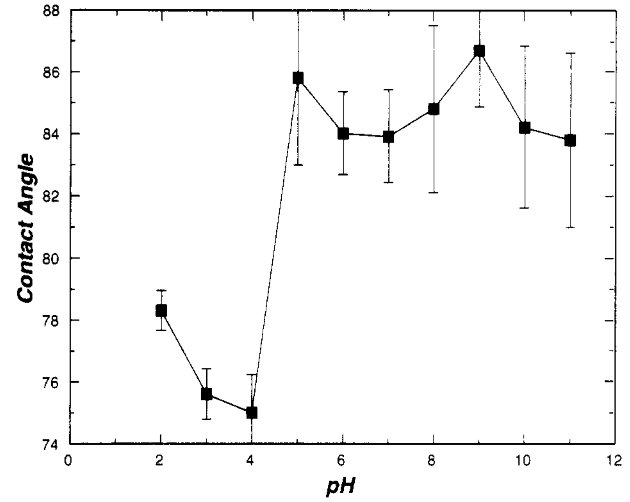
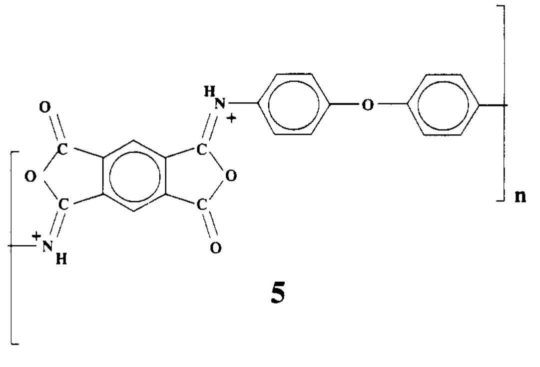


Figure 8. Advancing contact angle data. Shown is isoimidized surface 4 produced by isoimidization of surface 2.

mate, does indicate that the surface hydrolysis reaction allows a high degree of control and flexibility for surface modification.

The conversion of poly(amic acid) 2 to the poly(isoimide) 4 was also examined by FTIR spectroscopy. The external reflection FTIR spectrum, depicted in Figure 7, is characterized by strong peaks at 1822 cm^{-1} (C=O), 1697 cm^{-1} (C=N), and 927 cm^{-1} (CO), which is in good agreement with the reported transmission spectrum of a poly(pyromellitisoimide) film,[25] except the intensity patterns, as anticipated, are different.[43]

Examination of 4 by contact angle measurements reveals that it too possesses an ionizable functional group. Contact angle data as a function of pH for this modified polyimide are shown in Figure 8. At low pH, the isoimide nitrogen would be expected to be protonated to the isoimidinium salt 5. The basicity of isoimides, relative to the parent imide, has been noted previously.[44] At higher pH, the poly(isoimide) structure should dominate. The data shown in Figure 8 indeed indicate that the expected transformation, 4 → 5, is occurring. In contrast to the poly(amic acid) 2 the surface of 5 is made to be more hydrophobic as the pH of the probe liquid is increased.



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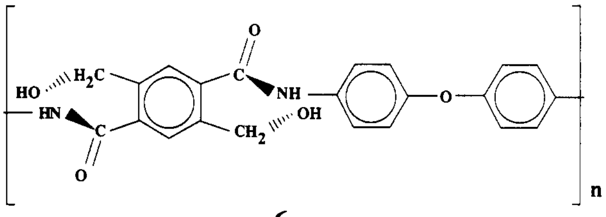
Reduction of Poly(amic acid). The molecular structure of 2 contains several functional groups which are capable of being reduced with a variety of agents. Both functional groups on the surface of 2 (acid and amide) are capable of being reduced to give three possible products. They are, namely, the poly(alcohol–amide) 6, the poly(acid–amine) 7, and the poly(alcohol–amine) 8.



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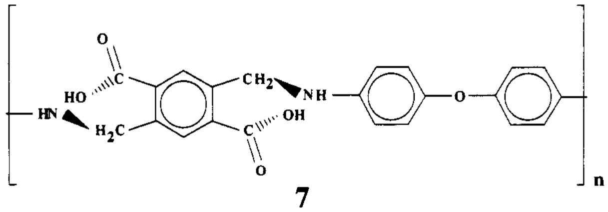

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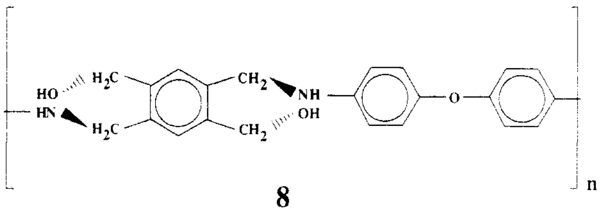
As a first check on the probable course of this reduction, the reaction of the model compound, *N*-phenylphthalamic acid, with borane was investigated. The product obtained in major (ca. 95%) yield is the fully-reduced species *N*-phenyl-*o*-(aminomethyl)benzyl alcohol. The other product, obtained in small amount, is the partially-reduced compound *o*-(hydroxymethyl)-*N*-phenylbenzamide. These



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results for the model compound suggest that the favored course of reduction of the polyamic acid surface 2 will be to give structure 8.

FTIR was used to follow the reduction of 2 on fully hydrolyzed thin films. Several reducing agents, including catecholborane, lithium aluminum hydride, and borane, were examined for their effectiveness. Of the three, borane gave the cleanest reaction, resulting in a film largely depleted of carbonyl groups (see Figure 9). The IR peak intensity in the C=O stretching region is reduced to ~$^1/_4$ of the original value, and there is a broad peak (3200–3600 cm^{-1}) centered at ~3390 cm^{-1} which can be attributed to the hydrogen-bonded NH and OH groups of the reduced amine and alcohol units. This broad peak is not present in the reflectance spectrum of 1. In the spectrum of 2, a similar broad peak is present but the maxima are at 3056 and 3270 cm^{-1} and are probably due to the acid OH and amide NH vibrations. A band at ~1238 cm^{-1} is observed, and it may contain, as a component, the CO stretch of an alcohol; however, the ether COC stretch is also observed in this region, and it may serve to obscure the presence of the alcohol absorption. The strongest peak in the spectrum of 1, the C=O stretch at 1742 cm^{-1}, is also absent, indicating no ring closure has occurred. It can be concluded, based upon IR data, that borane has reduced nearly all the carbonyl groups of the amic acid functionalities present on 2. The residual carbonyl peak intensities suggest that there are some amic acid groups remaining which were not accessible to the reducing agent even at long reaction times. These groups may be well beneath the surface of the film, as the FTIR external reflectance method used is not surface selective.

The reduction of 2 has also been followed by XPS. Shown in Table IV are the elemental composition data obtained for the borane-reduced surface compared to the theoretical values for 2 and 8. Figure 10 shows the experimental spectra; results of curve fitting are shown in Table V. The data for the borane-reduced polyimide surface most closely match the theoretical values for the poly(alcohol–amine) 8, although uncertainties in the accuracy of elemental composition determination by XPS preclude a definitive choice of reaction products based on this information. Listed in Table V are the XPS peak binding energies and functional group assignments. The survey spectrum (Figure 10a) shows the usual C 1s, N 1s, and O 1s signals in addition to a Si 1s signal at ~100 eV due to contamination from the wafer used as the substrate. The C 1s spectrum exhibits peaks which are attributable to phenyl ring carbons and/or carbon singly-bonded to oxygen or nitrogen at 285.0–287 eV. A smaller peak is visible at ~289 eV (3% of C 1s total) and attributed to a carbonyl carbon species. The O 1s spectrum shows two broad peaks centered at ~532.1 and ~533.4 eV. These peaks are assigned to carbonyl oxygen and oxygen singly-bonded to carbon, respectively.

The XPS data indicate that the fully-reduced species 8 is the major component produced by borane reduction of 2. The C 1s composition data indicate that 50% or more of the carbonyls have been reacted. This conclusion rests not only on the depletion of the carbonyl C 1s peak but also on the relative area of the 285.0 and 286.4 eV C 1s peaks. The PMDA ring carbons are normally shifted to 286.1 eV by the presence of four carbonyls on the ring,[41] causing that peak to be the largest area peak in the C 1s spectrum of PMDA–ODA. Such a shift is not evident in the reduced film, which has the low binding energy peak as the dominant peak. The N 1s spectrum is also consistent with extensive reduction, but the correct assignment for the minor high binding energy peak is unclear. The 401.0-eV peak actually corresponds to that of an imide nitrogen,[42] but because the FTIR on this same sample shows no evidence for imide, we prefer to assign this peak to structure 6 and postulate that the amide nitrogen may be shifted from its usual position at 400.2 eV[42] perhaps by hydrogen bonding with the alcohol group.

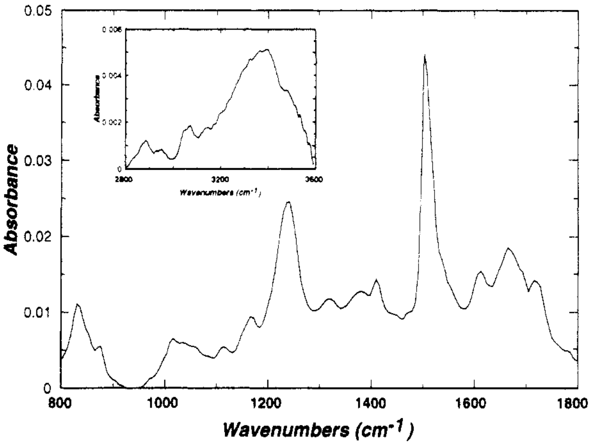

Figure 9. FTIR spectrum for a borane-reduced poly(amic acid) surface. The inset shows a high-frequency region of the spectrum.

Table IV
XPS and Calculated Elemental Composition Data for a Reduced PI Surface

surface	C %	N %	O %
borane-reduced surface[a,b]	78	6	16
poly(amic acid) 2[c]	71.0	6.5	22.6
poly(alcohol–amide) 6[c]	75.9	6.9	17.2
poly(acid–amine) 7[c]	75.9	6.9	17.2
poly(alcohol–amine) 8[c]	81.5	7.4	11.1

[a] ≈1 atom % Si contamination detected (from wafer). [b] XPS data. [c] Calculated.

The reduced film was also characterized by contact angle titration (Figure 11). The data are obviously different from those of 1 or 2. There appears to be an increase in hydrophilicity as the pH is increased from ~5 to ~11. Note that the magnitude of this effect is small relative to that observed during the contact angle titration of 2, but it is a reproducible effect which is just larger than the experimental error in the measurements. Residual carboxylic acid groups from unreacted 2 or acid groups from 7 might explain the change at higher pH, but it is difficult to base any conclusions on this limited evidence. Contact angle evidence for any amine groups at the surface is even more equivocal. While the amine group should be ionizable and hence exhibit changes in wetting within the pH range examined,[32] the downturn in contact angle from pH 5 to pH 2, while reproducible, is within the scatter of the data. The only explanation we can offer is that the conformation of 8 does not favor exposure of a sufficient number of amine groups to the contacting liquid to give a significant effect on the wetting behavior at low pH. In sum, despite the lack of corroboration from contact angles, the weight of evidence from the model reaction, FTIR on fully modified thin films, and XPS favors the formation of structure 8 from borane reduction of 2.

Table V
XPS Results for Borane-Reduced Surface

	C 1s			N 1s		O 1s	
BE (±0.2 eV)	285.0	286.4	288.7	399.8	401.0	532.1	533.4
atom %	73	24	3	77 ± 10[a]	23 ± 30[a]	43 ± 15[a]	57 ± 10[a]
assignment[a,b]	CH_n	COC or CN	>C═O	amine N	see text	>C═O	CO
fwhm (eV)	1.6	1.6	2.3	1.7	1.5	1.5	1.5

[a] Actual atom % difficult to determine because peaks are broad and not well separated.

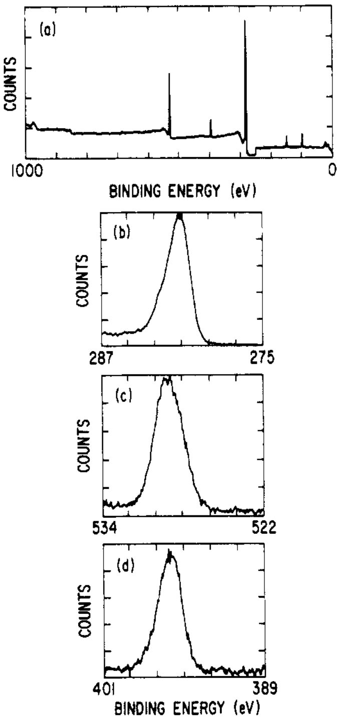

Figure 10. XPS data. Poly(amic acid) surface 2 after borane reduction: (a) survey scan; (b) C 1s region; (c) O 1s region; (d) N 1s region.

Contact Angle Correlation. Whitesides et al.[32] have correlated extensive data on contact angles of modified polyethylene films vs Hansch hydrophilicity parameters.[45,46] Because these parameters are derived from the partition coefficients for substituted benzenes, it is of interest to do a similar correlation with our contact angle data on modified polyimides despite the limited number of data points presently available. On the basis of the equation derived by Whitesides et al.[32]

$$\cos\theta_{\mathrm{adv}} = \sum_i A_i C \pi_i$$

where A_i is the normalized area that functional group i occupies at the solid–liquid–vapor interface, C is a combination of constants (for experiments at constant temperature), and π_i is the Hansch parameter for functional group i, the Hansch parameter was correlated with the observed θ_{adv} for a variety of surfaces examined. The Hansch parameters were estimated for the combination of functional groups present in each case by assuming that each of the two occupies a normalized area fraction of 0.5, which is certainly an oversimplification since it neglects, for example, any exposure at the surface of the ODA portion of the polymer. Figure 12, however, shows there to be a reasonable correlation between the estimated Hansch parameters and the observed contact angles for those groups for which parameters were available. Note that the parameters for 6–8 do not differ sufficiently to give weight to any choice among those three possible reduction products. The correlation is limited by the small number of data points, but it does suggest that the correlation is as valid for modified polyimide as it is for modified polyethylene.[47]

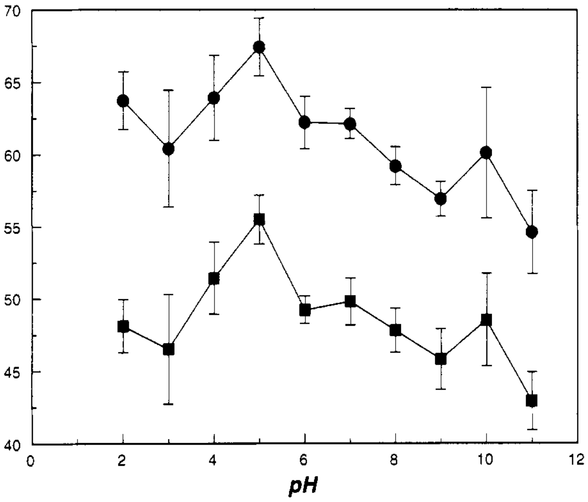

Figure 11. Variation of advancing (●) and receding (■) contact angles with pH for the borane-reduced poly(amic acid) surface.

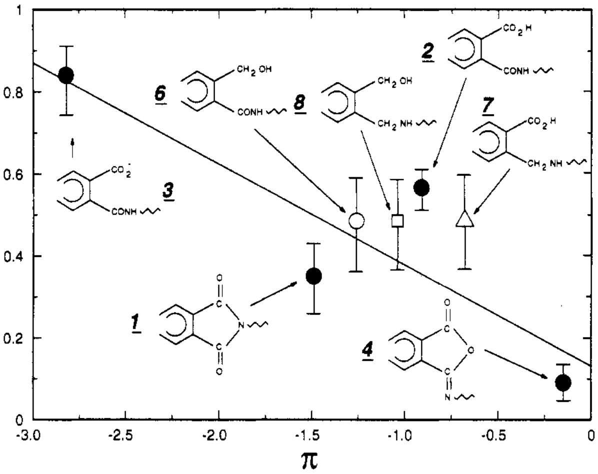

Figure 12. Advancing contact angles obtained for the various polyimide derivatives vs estimated Hansch hydrophobic parameters, π. The π values were numerical averages using the closest substituent value. θ_{adv} for 3 was averaged from pH 8–11 using $\pi = -4.36$ for CO_2^- and -1.49 for $CONH_2$. θ_{adv} for 2 was averaged from pH 2–5 using $\pi = -0.32$ for CO_2H. θ_{adv} for 4 was averaged from pH 5–11 using $\pi = -0.01$ for CO_2CH_3 and -0.29 for $CH{=}NC_6H_5$. θ_{adv} for 1 was averaged from pH 4–10 using $\pi = -1.49$ for $CONH_2$. θ_{adv} for 6–8 was measured at pH 7. π for 6 was estimated using -1.03 for CH_2OH. π for 7 was approximated using -1.04 for CH_2NH_2.

Conclusions

The surface of PMDA-ODA polyimide is modified easily by reaction with dilute aqueous base followed by acidification. Little or no etching accompanies this modification, and a high degree of control over the depth of hydrolysis is possible simply by varying the hydrolysis time. The surface poly(amic acid) serves as a useful precursor for subsequent chemical reactions, as shown by two preliminary examples: isoimidization and reduction.

The potential for further chemistry on this surface is large, providing some attractive possibilities for engineering the surface while maintaining the desirable bulk properties of polyimide.

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Registry No. 1 (copolymer), 25038-81-7; 1 (SRU), 25036-53-7; 2 (SRU), 9043-05-4; *N*-phenylphthalimide, 520-03-6; *N*-phenylphthalamic acid, 4727-29-1; *N*-phenylphthalisoimide, 487-42-3; *o*-(hydroxymethyl)-*N*-phenylbenzamide, 33966-11-9.