Surface Modifications of Poly(ether ether ketone)[1]

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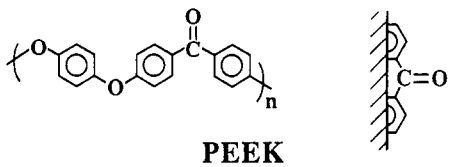
ABSTRACT: Reactions of semicrystalline poly(ether ether ketone) (PEEK) film with carbonyl-selective reagents at the film–solution interface produce modified film samples containing a thin surface layer of the reagent-induced functionality. Semicrystalline PEEK film is robust and unaffected by a variety of solvent and temperature conditions, allowing a range of standard ketone derivatizations to be carried out. In contrast, amorphous PEEK film is swollen and physically deformed by solvents that do not affect crystalline PEEK. Crystalline PEEK reacts with 2,4-dinitrophenylhydrazine to yield PEEK~C=NNHPh$(NO_2)_2$ and with hydroxylamine to yield PEEK~C=NOH. Reaction with methylenetriphenylphosphorane gives PEEK~C=CH_2. Dimsylsodium adds to the PEEK carbonyl, rendering PEEK~C(OH)CH_2S(O)CH_3. Sodium bis(2-methoxyethoxy)aluminum hydride reduces the PEEK carbonyl (PEEK~CHOH). Cyanosilylation of PEEK with trimethylsilyl cyanide yields PEEK~C(CN)OSiMe_3. PEEK~CHOH and PEEK~C=NOH react with benzenesulfonyl isocyanate to yield PEEK~CHOC(O)NHSO_2Ph and PEEK~C=NOC(O)NHSO_2Ph, respectively. PEEK~CH=CH_2 reacts with bromine to form PEEK~CHBrCH_2Br; reaction of PEEK~CHOH with thionyl chloride yields PEEK~CHCl. Reactions were monitored and products were characterized by contact angle, XPS, and ATR IR. Yields were assessed by quantitative XPS analysis of the outer 40 Å and were generally ~50% for reactions with PEEK. One non-carbonyl-selective reaction, oxidation with potassium chlorate/sulfuric acid is also reported.

Introduction

We are currently undertaking studies to correlate macroscopic polymer surface properties (adsorption, adhesion, wettability, friction) with surface chemical structure; the goal is to effect rational property control through organic surface chemistry.[2] We believe that the key to this control is to have a substrate with a chemically resistant (inert) bulk and a versatile reactive surface. Such a substrate can be converted to a range of samples differing only in surface chemical structure. We have developed the surface chemistry of fluoropolymers (poly(chlorotrifluoroethylene),[3,4] poly(tetrafluoroethylene),[5] poly(tetrafluoroethylene-*co*-hexafluoropropylene),[6] poly(vinylidene fluoride)[7,8]) to prepare such substrates. Each of the chemistries developed for these fluoropolymers involves the surface-selective introduction of a versatile functional group, which can be further reacted to prepare samples with surface-chemical differences.

Poly(ether ether ketone) (PEEK) is a thermoplastic with excellent mechanical properties and is used in various forms (fiber, matrix, coating, film) for a large variety of



PEEK

applications.[9] It is advertised as being solvent- and chemical-resistant and we have investigated its potential as a substrate for the objectives described above. It has one particularly attractive quality as a chemically resistant substrate: it contains a potentially versatile functional group (the diaryl ketone), which is present in known concentration. The extent to which this ketone reacts as a functional group at PEEK–solvent interfaces is the subject of this report. One non-ketone-selective reaction, oxidation, is also described.

Experimental Section

General Methods. PEEK film was obtained from ICI: amorphous as 1-, 2-, and 5-mil Stabar K200, 40% crystalline as 4-mil Stabar XK300. Amorphous film samples were cleaned by immersion in methanol for 30 min followed by immersion in heptane for 30 min. Semicrystalline film samples were extracted (Soxhlet) with THF for 12–24 h. All film samples were subsequently dried at reduced pressure (room temperature, 0.05 mmHg, >48 h). THF was distilled from sodium benzophenone dianion, chloroform was distilled from phosphorous pentoxide, and carbon tetrachloride was degassed by using three freeze–pump–thaw cycles. House distilled water was redistilled in a Gilmont still. Pyridine and Me_2SO were distilled from calcium hydride at reduced pressure. Methanol and ethanol were distilled from magnesium; hexane and heptane were distilled from calcium hydride. Wash solvents that were not distilled were sparged with nitrogen prior to use. Thionyl chloride, trimethylsilyl cyanide and benzenesulfonyl isocyanate (all Aldrich) were distilled (trap-to-trap) at reduced pressure. 2,4-Dinitrophenylhydrazine, methyltriphenylphosphonium bromide, and dibutyltin dilaurate (all Aldrich) were used as received. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer-Physical Electronics 5100 spectrometer with Mg Kα or Al Kα excitation (usually 300 W). Spectra were recorded at two takeoff angles, 15° and 75° from the plane of the surface. Attenuated total reflectance infrared (ATR IR) spectra were obtained by using an IBM 38 FTIR spectrometer and a germanium internal reflection element (45°). Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Water purified as described above was used as the probe fluid. Dynamic advancing and receding angles were recorded while water was added to and withdrawn from the drop. All reactions were carried out under nitrogen, unless otherwise indicated.

Reaction of PEEK[10] with 2,4-Dinitrophenylhydrazine (PEEK~C=NNHPh$(NO_2)_2$). A solution of 2,4-dinitrophenylhydrazine and four drops of concentrated HCl in 25 mL of THF was introduced via cannula to a Schlenk tube containing a PEEK film sample. After sparging with nitrogen, the tube was heated at 45 °C for 48 h. After this time the solution was removed and the film sample washed with THF (5 × 20 mL) and then methanol (5 × 20 mL). The film sample was extracted (Soxhlet) overnight with methanol and dried (room temperature, 0.05 mm, 48 h).

Reaction of PEEK with Hydroxylamine (PEEK~C=NOH).[11] A PEEK film sample, 3.0 g of hydroxylamine hydrochloride, 10 mL of ethanol, and 2 mL water were introduced to a water-jacketed (for reflux) Schlenk tube. Sodium hydroxide (5.5 g) was added in five portions, with shaking after each addition.

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The tube was sparged with nitrogen, heated at 40 °C for 24 h, and then heated at reflux for 24 h. The flask was cooled, the solution was removed, and the film sample was rinsed with 10% aqueous HCl (5 × 30 mL), water (3 × 30 mL), methanol (2 × 30 mL), and then hexane (3 × 30 mL) and dried (room temperature, 0.05 mm, 48 h).

Reaction of PEEK~C=NOH with Benzenesulfonyl Isocyanate (PEEK~C=NOC(O)NHSO$_2$Ph).[12] THF (10 mL) containing four drops of dibutyltin dilaurate was introduced via cannula to a Schlenk tube containing a PEEK~C=NOH film sample. Benzenesulfonyl isocyanate (1.2 mL) was added; the tube was shaken and allowed to sit at room temperature for 24 h. The solution was removed and the film sample was washed with THF (5 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Reaction of PEEK with Methylenetriphenylphosphorane (PEEK~C=CH$_2$).[13] Me$_2$SO (10 mL) was added to a flask containing 0.48 g of sodium hydride. The flask was heated to 75–80 °C for 40–45 min, after which time hydrogen evolution had ceased. The salt solution was introduced via cannula into a Schlenk tube containing warm (~40 °C) Me$_2$SO (10 mL), methyltriphenylphosphonium bromide (7.0 g), and a PEEK film sample. The tube was heated to 60 °C for 24 h and the solution was then removed. The film sample was rinsed with Me$_2$SO (3 × 20 mL), methanol (5 × 20 mL), and then hexane (3 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Bromination of PEEK~C=CH$_2$ (PEEK~CBrCH$_2$Br). A 0.2 M solution of bromine in carbon tetrachloride (15 mL) was prepared and introduced via cannula to a Schlenk tube containing a PEEK~C=CH$_2$ film sample. The tube was maintained at 0 °C for 24 h in the dark. After this period, the solution was removed and the film sample was washed with carbon tetrachloride (2 × 20 mL) and then THF (5 × 20 mL), extracted (Soxhlet) with THF for 24 h, and dried (room temperature, 0.05 mm, 24 h).

Reduction of PEEK (PEEK~CHOH). THF (10 mL) and sodium bis(2-methoxyethoxy)aluminum hydride (3.4 mmol) were introduced via cannula to a Schlenk tube containing a PEEK film sample. The flask was heated at 40 °C for 3 h and then the solution was removed. The film sample was washed with THF (2 × 20 mL), 15% aqueous sodium hydroxide (5 × 30 mL), water (3 × 30 mL), 10% aqueous sulfuric acid (3 × 30 mL), water (3 × 30 mL), methanol (3 × 30 mL), and hexane (2 × 30 mL) and dried (room temperature, 0.05 mm, 24 h).

Reaction of PEEK~CHOH with Thionyl Chloride (PEEK~CHCl). THF (15 mL) and thionyl chloride (1.5 mL) were introduced to a Schlenk tube containing a PEEK~CHOH film sample. After 24 h at room temperature, the solution was removed and the film sample was washed with THF (3 × 20 mL), methanol (3 × 20 mL), THF (2 × 20 mL), and hexane (2 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Reaction of PEEK~CHOH with Benzenesulfonyl Isocyanate (PEEK~CHOC(O)NHSO$_2$Ph).[12] Conditions identical with those employed for PEEK~CH=NOH (above) were used.

Reaction of PEEK with Dimsylsodium (PEEK~C(OH)CH$_2$S(O)CH$_3$).[13] A dimsylsodium solution was prepared, as described above for the PEEK~CH=CH$_2$ preparation, and introduced to a Schlenk tube containing a PEEK film sample and 10 mL of Me$_2$SO. After 24 h at 60 °C, the solution was removed and the film sample was washed with Me$_2$SO (3 × 20 mL), 10% aqueous HCl (3 × 30 mL), water (2 × 30 mL), methanol (3 × 20 mL), and then hexane (2 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Reaction of PEEK with Trimethylsilyl Cyanide (PEEK~C(CN)OSiMe$_3$).[14] Chloroform (10 mL) was introduced via cannula to a Schlenk tube containing zinc iodide (15–20 mg) and a PEEK film sample. Trimethylsilyl cyanide (1.5 mL) was added and the solution was shaken until it became bright orange-red. The tube was heated to 40 °C for 24 h. The solution was removed and the film sample was rinsed with chloroform (2 × 20 mL), methanol (5 × 20 mL), and then hexane (3 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Oxidation of PEEK with KClO$_3$/H$_2$SO$_4$/H$_2$O (PEEK(OH)CO$_2$H).[15] Potassium chlorate was dissolved in 100 mL of 50:50 (v/v) sulfuric acid/water in a flask open to the air. After the solution cooled to ~40 °C, a PEEK film sample was introduced and the solution was stirred for 30 min. The solution was removed and the film sample was rinsed with water (5 × 30 mL), methanol (5 × 30 mL), and then hexane (3 × 30 mL) and dried (room temperature, 0.05 mm, 24 h).

Table I
Advancing and Receding Contact Angles (Water) for PEEK Derivatives

film sample	side a θ_A	side a θ_r	side b θ_A	side b θ_r
PEEK	85	55	85	50
PEEK~C=NNHPh(NO$_2$)$_2$	78	47	76	40
PEEK~C=NOH	74	40	75	35
PEEK~C=NOC(O)NHSO$_2$Ph	78	38	79	34
PEEK~C=CH$_2$	78	38	77	33
PEEK~CBrCH$_2$Br	87	56	90	51
PEEK~CHOH	69	23	71	18
PEEK~CHOC(O)NHSO$_2$Ph	78	38	79	32
PEEK~CHCl	79	47	81	42
PEEK~C(OH)CH$_2$S(O)CH$_3$	70	23	72	19
PEEK~C(CN)OSiMe$_3$	79	50	79	48
PEEK(OH)CO$_2$H	69	22	67	18
PEEK(OTl)CO$_2$Tl	69	32	65	25
PEEK(OH)C(O)C$_3$H$_3$N$_2$	75	45	73	41

Reaction of PEEK(OH)CO$_2$H with Thallous Ethoxide (PEEK(OTl)CO$_2$Tl).[16] Thallous ethoxide (~20 mL) was introduced via cannula to a Schlenk tube containing a PEEK(OH)CO$_2$H film sample. After 30 s, the thallous ethoxide was removed and the film sample was washed with ethanol (5 × 20 mL) and dried (room temperature, 0.05 mm, 24 h).

Reaction of PEEK(OH)CO$_2$H with Carbonyldiimidazole PEEK(OH)C(O)C$_3$H$_3$N$_2$). A solution of 0.8 g of carbonyldiimidazole in 15 mL of THF was introduced via cannula to a Schlenk tube containing a PEEK(OH)CO$_2$H film sample. After 24 h, the solution was removed and the film sample was washed with THF (10 × 10 mL) and dried (room temperature, 0.05 mm, 24 h).

Results and Discussion

Semicrystalline (Stabar XK300) and amorphous (Stabar K200) PEEK film samples were obtained from ICI. Their potential to function as substrates for surface chemistry was initially assessed by testing their resistance to solvents that were likely to be used for surface modification reactions. Amorphous PEEK was quickly eliminated as a substrate; within 30 min at room temperature in benzene, toluene, dichloromethane, or pyridine, solvent-induced crystallization and plasticization occur, causing the films to become opaque and roll up into scroll-like tubes. The amorphous film is visibly stable to methanol, ethanol, and heptane at reflux temperatures for 24 h and acetone at room temperature. Semicrystalline film is considerably more solvent-resistant; there are no visible changes after 24 h in refluxing THF, methanol, ethanol, benzene, toluene, water, hexane, heptane, Me$_2$SO at temperatures below 65 °C, or nitrobenzene at room temperature. Dichloromethane and carbon tetrachloride at room temperature and pyridine and chloroform above 45 °C do plasticize semicrystalline PEEK. In the remainder of this article, the acronym PEEK represents semicrystalline 4-mil-thick Stabar XK300 film that has been cleaned by extraction with THF and dried to constant mass (±1 μg).

The process used to produce PEEK film causes the two sides of the film to differ to the eye. One side (called side a) is shiny and reflective, the other (side b) is dull and nonreflective. Water contact angles of the two sides differ slightly (Table I), with side b exhibiting a 5° lower receding contact angle. This difference is fairly consistent for all derivatives of PEEK and likely represents a rougher (on some scale) side b. Scanning electron micrographs of gold

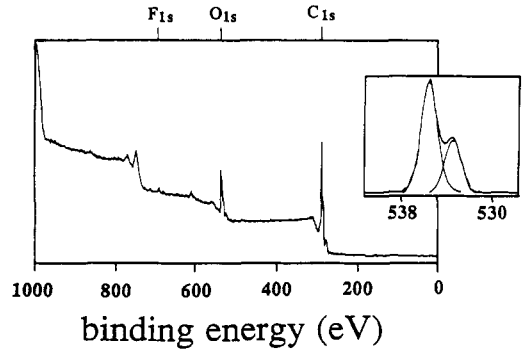
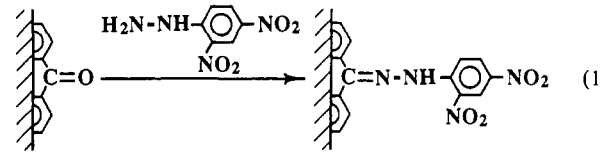


Figure 1. Survey and O_{1s} region spectra of PEEK.

sputter-coated samples show no obvious differences at any magnification, and XPS and ATR IR spectra of the two sides are indistinguishable. Figure 1 shows survey and O_{1s} region XPS spectra for PEEK recorded at a 75° takeoff angle (measured from the plane of the film to the entrance of the detector optics); quantitation (Table II) indicates a C/O ratio of 6.4. The empirical formula for the PEEK repeat unit ($C_{19}O_3$—XPS does not detect hydrogen) predicts a C/O ratio of 6.3. The O_{1s} spectrum is a composite of two partially resolved photoelectron lines. The high binding energy peak corresponds to the ether oxygen; the low binding energy peak is due to the ketone oxygen. A small F_{1s} photoelectron line, indicating 1–2% atomic composition is observed in all virgin PEEK samples. The presence of fluorine in this concentration at the surface is due to concentration of chain ends in the surface region (PEEK is prepared by condensing hydroquinone with 4,4′-difluorobenzophenone). Microanalysis of PEEK indicates 0.12% fluorine content. Exposure to Me_2SO under conditions used to prepare PEEK~CH=CH_2 and PEEK~C(OH)CH_2S(O)CH_3 (24 h at 60 °C—controls for these reactions) induces a reconstruction in PEEK that further concentrates chain ends at the surface: fluorine content measured by XPS increases to 3–5%.

A series of carbonyl-selective reactions was carried out on PEEK using modifications of literature conditions for high-yield reactions of benzophenone, when available. Reactions were monitored by contact angle, ATR IR, XPS, and SEM, and a few general comments and observations are in order. Advancing and receding contact angles of water were measured for both sides of the film and are reported in Table I. XPS spectra of side a were recorded at two takeoff angles, 15° and 75° (measured from the plane of the film). The 15° takeoff angle spectra indicate the atomic concentration of the outer 10 Å (94% of measured photoelectrons are from this region[17]); the 75° takeoff angle spectra assess the composition of the outer 40 Å (95% of the measured photoelectrons originate in this region[17]). Atomic composition data for both takeoff angles are given in Table II. The numbers are calculated without regard to the small and somewhat variable fluorine content. The data are, for the most part, independent of takeoff angle and this indicates that the outer 40 Å is homogeneous in a direction perpendicular to the film plane (not stratified). The oxygen content is slightly higher in the 15° takeoff angle data in most cases; this can, in certain cases, be rationalized by orientation of functionality. For example the nitro groups in PEEK~C=NNHPh$(NO_2)_2$ may reside in the outermost angstroms, giving rise to the takeoff-angle-dependent oxygen concentration. Slight (less than 1%) contamination by a silicon compound was observed in several spectra and oxygen associated with it is a possible source in some cases. Surface oxidation (XPS specimens are dried in room light at moderate vacuum (0.05 mm) for >24 h and are mounted in air) is the more general explanation, and regardless, the differences are small. Reaction yields are calculated by using 75° takeoff angle data. SEM and ATR IR show no changes upon reaction (except for the oxidation—discussed below): micrographs and spectra of reacted samples are indistinguishable from PEEK. We have not determined the depth of modification (thickness of the modified layer) and cannot do so with the data reported here. The XPS and ATR IR data do, however, allow a rough estimate. XPS indicates that reaction depths are, for the majority of reactions, at least 40 Å and changes in the infrared spectra would have been visible if reaction depths were greater than ~200 Å (the sampling depth[18] under the conditions employed is ~0.2–0.5 μm for 3000–1500 cm^{-1}). These facts suggest modification depths of ~100 Å. We emphasize that this is a crude estimate and may be low for some PEEK derivatives due to problems (unknown to us) in obtaining ATR IR spectra of surface-modified PEEK.[19] In two cases, reduction to the alcohol and cyanosilylation, angle-dependent XPS data were observed and the estimate of ~100 Å is likely high. The reactions are discussed in their order of appearance in Tables I and II. In each synthesis, a series of experiments was performed to maximize conversion. The conditions reported give the highest reproducible yields. Careful kinetics were not obtained for any reaction, but for all cases it was demonstrated that a "final state" had been reached—yield would not increase upon further reaction under the conditions used.

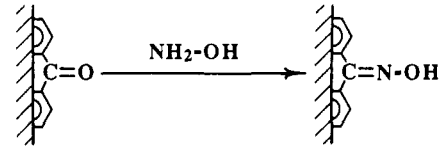
Hydrazone Synthesis. PEEK was allowed to react with 2,4-dinitrophenylhydrazine in acidic THF at 45 °C (eq 1). The resulting film product, PEEK~C=NNHPh-



(1)

$(NO_2)_2$, exhibited two N_{1s} peaks in the XPS spectrum at 406 (NO_2) and 400 eV (C=NNH). The repeat unit of the expected product predicts an XPS composition of $C_{25}O_6N_4$. The observed atomic composition is $C_{25}O_{6.4}N_{2.1}$, indicating a ~50% yield of hydrazone.[20] A small amount (<1%) of chlorine is present. Water contact angles decrease slightly, which may indicate the introduction of nitro groups.

Oxime Synthesis. PEEK reacts with hydroxylamine, under conditions[11] that convert benzophenone to benzophenone oxime in approximately quantitative yield, (eq 2) to form PEEK~C=NOH. XPS indicates a compo-



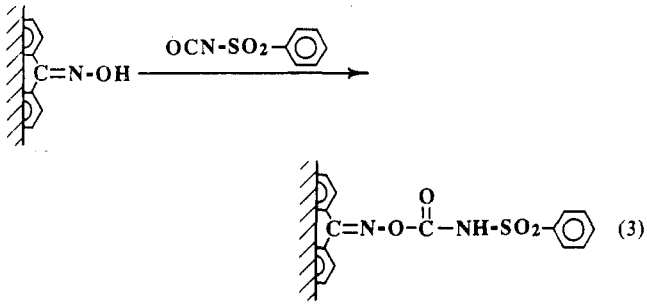
(2)

sition of $C_{19}O_{3.9}N_{0.5}$ that compares with the predicted structure, $C_{29}O_3N$, to indicate a ~50% yield of oxime. Water contact angles are lowered due to the incorporation of the polar, hydrogen-bonding oxime. The presence of oxime was verified by reaction with benzenesulfonyl isocyanate (eq 3). The predicted surface composition is $C_{45}O_9N_2S$ (based on the observed 50% yield of oxime) and the observed composition is $C_{45}O_{9.5}N_{1.8}S_{1.0}$, indicating a good yield for the urethanation reaction. A control reaction of PEEK under identical conditions showed no nitrogen or sulfur incorporation.

Table II
XPS Atomic Composition Data for PEEK Derivatives

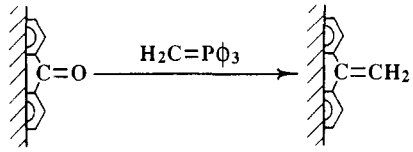
film sample	15° takeoff angle				75° takeoff angle			
	C	O	N	X[a]	C	O	N	X[a]
PEEK	86.3	13.7			86.4	13.6		
PEEK~C=NNHPh$(NO_2)_2$	72.7	21.1	6.2		74.5	19.2	6.3	
PEEK~C=NOH	80.3	17.5	2.2		81.4	16.6	2.0	
PEEK~C=NOC(O)$NHSO_2Ph$	78.0	16.3	3.8	2.1^S	78.3	16.7	3.2	1.7^S
PEEK~C=CH_2	87.0	13.0			88.7	11.3		
PEEK~C$BrCH_2Br$	82.2	14.1		3.7^{Br}	85.3	11.0		3.7^{Br}
PEEK~CHOH	84.0	16.0			85.2	14.7		
PEEK~C$HOC(O)NHSO_2Ph$	77.6	17.8	2.3	2.4^S	76.3	19.2	2.2	2.3^S
PEEK~CHCl	84.0	13.0		3.1^{Cl}	87.2	9.7		2.8^{Cl}
PEEK~C$(OH)CH_2S(O)CH_3$	80.9	16.7		2.3^S	82.7	14.9		2.4^S
PEEK~C$(CN)OSiMe_3$	82.1	13.4	2.4	2.1^{Si}	84.0	13.1	1.5	1.4^{Si}
PEEK$(OH)CO_2H$	77.2	22.7			79.8	20.2		
PEEK$(OTl)CO_2Tl$	73.6	21.3		5.0^{Tl}	73.8	21.1		5.0^{Tl}
PEEK$(OH)C(O)C_3H_3N_2$	83.1	15.0	2.1		83.6	14.5	1.9	

[a] Element is indicated by its atomic symbol as a superscript.



(3)

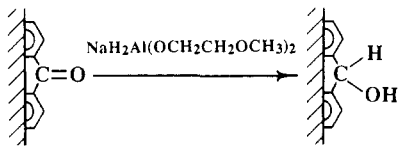
Olefination. Wittig conditions were used to convert the ketone to an olefin (eq 4). The surface composition



(4)

expected for a quantitative yield is $C_{20}O_2$; the observed XPS composition is $C_{20}O_{2.5}$, indicating a ~50% yield. A yield of 60% is calculated by a curve-fitting analysis of the O_{1s} XPS region (see below). The depressed (relative to PEEK) water contact angles are surprising. The lower receding angle can be rationalized by a dilution of the polar carbonyl groups, but we have no explanation for the lower advancing angle. Bromination of the olefin surface confirms the presence of unsaturation (PEEK is not brominated under these conditions) and renders the expectedly hydrophobic surface. The reaction proceeds in good yield, giving a surface that analyzes to be $C_{39}O_{5.0}Br_{1.7}$; the theoretical structure, based on the 50% yield olefination, is $C_{39}O_5Br_2$.

Reduction. Ketones at the PEEK surface were reduced to alcohols by use of sodium bis(2-methoxyethoxy)aluminum hydride (eq 5). The surface becomes quite wettable



(5)

(Table I) due to the presence of the polar, hydrogen-bonding hydroxyl group. The yield of this reaction cannot be determined from XPS atomic composition data as these are not expected to change (in practice the oxygen content increases slightly), but can be estimated by analysis of the

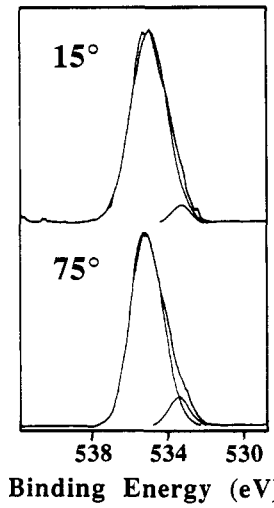
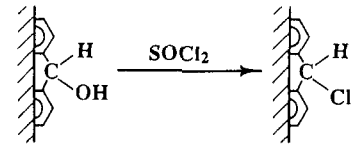


Figure 2. O_{1s} region spectra for PEEK~CHOH recorded at a 15° and 75° takeoff angles.

O_{1s} spectrum. Figure 2 shows 15° and 75° takeoff angle spectra of the O_{1s} region of the PEEK~CHOH spectra (compare with the PEEK spectrum inset in Figure 1). Curve fitting these spectra with two peaks, a low binding energy peak that represents the carbonyl and a high binding peak that represents the chain ether and PEEK~CHOH oxygen, and analysis of the relative peak areas indicate a 90% yield in the outer 10 Å and a 75% yield in the outer 40 Å. Reaction with benzenesulfonyl isocyanate produces the expected urethane and induces an increase in contact angles. The yield of the urethanation reaction is good: the expected stoichiometry (based on a 75% reduction yield) is $C_{97}O_{21}N_3S_3$, the observed composition is $C_{97}O_{24.4}N_{2.8}S_{2.9}$. The alcohol was converted to the chloride (eq 6) by reaction with thionyl chloride.

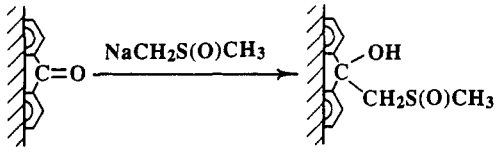


(6)

Water contact angles increase and XPS indicates a good yield: quantitative conversion of the alcohol to chloride would render a composition of $C_{76}O_9Cl_3$; $C_{76}O_{8.5}Cl_{2.4}$ is observed. This reaction (to form the chloride) is very different from the reaction of hydroxyl groups on the surface of poly(chlorotrifluoroethylene) (PCTFE-OH) with thionyl chloride.[4] PCTFE-OH reacts with thionyl chloride

to give only the sulfite; no chloride is observed. The PEEK~CHOH hydroxyl groups are present in much lower concentration and are likely much less mobile than the PCTFE-OH hydroxyl groups.

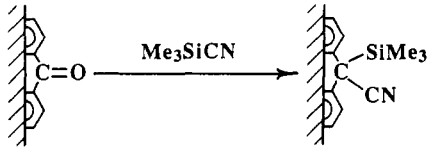
Reaction with Dimsylsodium. The addition of dimsylsodium to PEEK surface carbonyls (eq 7) proceeds to



(7)

yield a surface that exhibits low water contact angles. This is consistent with the presence of alcohols and sulfoxides. PEEK~$C(OH)CH_2S(O)CH_3$ exhibits S_{2s} and S_{2p} photoelectron lines at 230 and 167 eV, respectively. A quantitative reaction would yield a stoichiometry of $C_{21}O_4S$; the observed XPS composition is $C_{21}O_{3.8}S_{0.6}$, indicating a ~60% yield.

Cyanosilylation. Reaction of PEEK with trimethylsilyl cyanide (eq 8), using an adaptation of Evans' procedure,[14] yields a film sample that exhibits N_{1s}, Si_{2s}, and Si_{2p} photoelectron lines at 398, 152, and 102 eV, respectively. XPS atomic composition data give a reaction yield of ~40% (observed $C_{23}O_{3.6}N_{0.4}Si_{0.4}$, theoretical $C_{23}O_3NSi$) for the outer 40 Å. The yield in the outer 10 Å is higher (~60%). Water contact angles decreased slightly.



(8)

Oxidation. One non-carbonyl-specific reaction of PEEK was run: oxidation with potassium chlorate/sulfuric acid. This reagent is a very strong oxidant that is expected to cleave chains and degrade the surface; it was chosen over other oxidants (chromic acid, permanganic acid) because it leaves no insoluble metal oxides. SEM reveals the reaction to be corrosive. Circular pits with diameters of 3000–6000 Å are formed. XPS indicates an increase in oxygen content, and contact angles indicate a very hydrophilic surface. A small amount (<1%) of chlorine is present. We refer to this oxidized surface as PEEK$(OH)CO_2H$ to indicate the likely presence of phenol and a carboxylic acid functionality, but we have not carried out a detailed characterization study. The surface reacts with thallous ethoxide to form PEEK$(OTl)CO_2Tl$, indicating the presence of phenol and/or a carboxylic acid functionality, and with carbonyldiimidazole[5] to form the acyl imidazolide (PEEK$(OH)C(O)C_3H_3N_2$), indicating that carboxylic acids are present.

Conclusions and Comments

The carbonyl group in semicrystalline PEEK is a versatile reactive handle for the surface modification of PEEK film. Standard ketone transformations can be effected at the PEEK–solution interface to convert, in general, ~50% of the ketones in the outer 40 Å of the film to the desired derivative. Some derivatives can be further reacted in high yield. The consistent (with one exception) ~50% reaction yields suggest that a portion of the carbonyl groups is inaccessible to derivatizing reagents. These ketones may be in crystalline regions at the surface, but we have no proof that this is the case. One reaction, reduction with sodium bis(2-methoxyethoxy)aluminum hydride, proceeds in high (75–90%) yield; this reagent may disrupt (dissolve) crystalline regions. We estimate that the thickness of the modified layers is ~100 Å. Oxidation of PEEK is a quick and convenient method to prepare a wettable surface; acidic functionality, which we propose to be phenols and carboxylic acids, is introduced. The reaction, however, is corrosive.

Acknowledgment. We thank the Office of Naval Research for financial support.

Supplementary Material Available: 15° and 75° takeoff angle XPS spectra of reported PEEK derivatives (15 pages). Ordering information is given on any current masthead page.

References and Notes

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