Phosphonic Acid Derivatized Polythiophene: A Building Block for Metal Phosphonate and Polyelectrolyte Multilayers

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A water-soluble polythiophene with pendant phosphonic acid groups, poly(3-(3′-thienyloxy)propane-phosphonate) (P3TOPP), has been synthesized. Matrix-assisted laser desorption ionization (MALDI) measurements showed that P3TOPP is an oligomer with an average chain length of 10 monomer units. In aqueous solutions it could be electrochemically oxidized and displayed self-acid doping at pH below 13. P3TOPP was used to prepare polyelectrolyte multilayers with poly(diallyldimethylammonium chloride) (PDADMA) and metal phosphonate multilayers with Zr^{4+} ions by the sequential layer-by-layer technique. The films were characterized by electrochemistry, atomic force microscopy (AFM), UV−vis, IR, and X-ray photoelectron (XPS) spectroscopy. A regular layer-by-layer growth was observed with both types of multilayers. The nature of the films was probed with XPS, which showed that the observed binding energies were characteristic for metal phosphonates and polyelectrolyte multilayers in Zr/P3TOPP and P3TOPP/PDADMA films, respectively. In the former, the Zr:P ratio showed deviation from the theoretical stoichiometry, and the reasons for the nonstoichiometry are discussed. In the latter, the N:P ratio was consistent with the partial deprotonation of the phosphonate groups. The multilayers exhibited both electrochromism and pH-induced halochromism.

Introduction

The use of molecular and polymeric materials to modify various surfaces and the subsequent characterization of the constructed structures have been very popular during the past decades,[1] and the beneficial properties of these films are used in various applications, e.g., in sensors, electrooptics, and LED technology.[2] For successful application designs, it is important to find robust and easy methods to bind materials on interfaces. The modification of interfaces first started with the Langmuir−Blodgett technique (LB),[3] a method originally developed in the 1930s, but unfortunately it suffers several drawbacks that reduce the film stability and limit the shape and dimensions of the substrate. To circumvent the shortcomings of the LB technique but still preserving the good structural order, many approaches have been developed for the preparation of layered structures, in which the interaction between the individual layers may be ionic, covalent, or electrostatic. The self-assembly of thiols on gold surfaces, phosphonic acids on oxide surfaces, and alternate adsorption of polyelectrolytes on charged surfaces have been the most popular methods of modification.

In 1988, Mallouk et al.[4] developed a convenient method to form multilayer assemblies on oxide surfaces by the alternate adsorption of α,ω-bis(phosphonate)s and Zr^{4+} ions. The self-assembly of layers proceeds simply by dipping the substrate alternately in solutions of bis-(phosphonate)s and zirconium ion. The spontaneous adsorption yields sparingly soluble metal−bis(phosphonate) multilayers, which are bonded via ionic coordination chemistry and are mechanically and chemically robust, compact, and well-ordered. A scheme in which the LB films were used to form multilayers by the zirconium phosphonate chemistry was introduced in 1993.[5,6] The thickness of the film could be controlled to angstrom resolution by choosing the appropriate phosphonic acid chain length and the number of layers. Hybrid layers containing different bis(phosphonate)s or metal ions can also be formed. Several types of phosphonate group containing molecules and metal ions have been used, and recently, the use of polymers with pendant phosphonate groups for the preparation of monomolecular polymer layers has been reported.[7] The use of the pendant anionic phosphonate group in the polymer backbone opens up an alternative way for the multilayer formation, too. Decher[8] has devised a method where multilayers are formed on charged substrates by alternate adsorption of polycations and polyanions. Individual layers are held together by multiple electrostatic interactions between the oppositely charged groups, and the layer-by-layer growth is based on the surface charge reversal after every adsorption step. The thickness of individual layers is easily controlled by the ionic strength of the adsorption solution, higher concentrations of small electrolytes yielding thicker poly-

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electrolyte layers.[9] The films exhibit only long-range order due to strong interpenetration of the adjacent layers, contrary to metal phosphonate layers where the short-range order is achieved by strong coordination to a metal lattice.[10]

Polythiophenes and its derivatives are a well-known class of conductive polymers, which have been studied extensively, and our recent studies concerning thin films of poly(alkoxythiophene)s with pendant sulfonate groups have proven their usability in polyelectrolyte multi-layers.[11–13] Tripathy et al. were the first to successfully devise layer structures in which polythiophenes with pendant carboxylic acid groups were coordinated to Eu^{3+} ions.[14] Although oligothiophenes[15,16] with pendant phosphonic acid groups have been used to construct thin metal phosphonate films, so far the studies concerning poly-thiophenes have been sparse, limited only to synthesis[17] and solution studies.[18] The unique optical and electrical properties of polythiophenes, combined with the robust-ness and structural uniformity of the metal phosphonate approach, could yield supramolecular structures with short-range order usable in various applications. In this paper, we report the synthesis and characterization of a poly(alkoxythiophene) with pendant phosphonate groups, poly(3-(3′-thienyloxy)propanephosphonate) (P3TOPP). Two types of multilayers were fabricated, using either the metal phosphonate or polyelectrolyte techniques, and the films were characterized by electrochemistry, atomic force microscopy (AFM), UV/vis, IR, and X-ray photoelectron (XPS) spectroscopy.

Experimental Section

Materials. Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, Merck), 2,4,6-trimethylpyridine (Merck), phosphorus oxychloride ($POCl_3$, Merck), (3-aminopropyl)triethoxysilane (ICN Biochemicals), 2-mercaptoethylamine hydrochloride (MEA, Aldrich), *N*-(tri-methoxysilylpropyl)-*N,N,N*-trimethylammonium chloride (ABCR, Germany), poly(diallyldimethylammonium chloride) (PDADMA), $M_w = 400-500$ kDa (Aldrich), and polyethylenimine (PEI), $M_w = 25$ kDa (Aldrich), were used as received. All solvents were of analytical grade. 3-Mercaptopropylphosphonic acid (MPPA) was synthesized analogously as described in ref 19.

3-(3′-Thienyloxy)propanephosphonic Acid Diethyl Ester (3TOPPEt). 3-(3-Bromopropoxy)thiophene was synthesized from 3-methoxythiophene and 3-bromopropanol analogously as described in ref 20. Product (4.72 g, 21.3 mmol) was dissolved in triethyl phosphite (4.2 mL, 25.5 mmol). The solution was heated overnight at 150 °C, and the product was obtained by purification with silica gel (5% MeOH/CH_2Cl_2) with 62.5% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): 7.18 (1H, dd, Ar−H), 6.75 (1H, dd, Ar−H), 6.25 (1H, dd, Ar−H), 4.12 (6H, m), 2.00 (4H, m), 1.33 (6H, t). ^{13}C NMR ($CDCl_3$, 400 MHz): 157.5, 124.7, 119.3, 97.3, 69.4, 61.6, 22.6, 16.4. Anal. Calcd: C, 47.47; H, 6.88; S, 11.52. Found: C,

45.45; H, 7.1; S, 10.78. MS (EI+, 70 eV): Calcd for $C_{11}H_{19}O_4PS$: 278.074 430. Found: 278.074 170 (see Supporting Information for the ^{1}H and ^{13}C NMR and MS spectra).

Poly-3-(3′-thienyloxy)propanephosphonic Acid Diethyl Ester (P3TOPPEt). Attempts to polymerize the phosphonic acid or its sodium salt failed. Therefore, the corresponding ethyl ester (3TOPPEt) (1.24 g) was electropolymerized in 0.1 M $LiClO_4$/acetonitrile:CH_2Cl_2 (1:1, analytical grade) at 1.8 V vs SSCE (sodium saturated calomel electrode) using a three-compartment electrochemical cell equipped with a Pt sheet working electrode and a carbon rod auxiliary electrode. The shift in the visible $\pi \rightarrow \pi^*$ transition was used to follow the progress of polymer-ization. The supporting electrolyte was extracted with H_2O, and the product was precipitated with diethyl ether. Yield: 0.50 g (40.5%). MALDI−TOF spectra (Voyager DE PRO mass spec-trometer) were measured using a terthiophene matrix. Solutions of P3TOPPEt (1 mM) and terthiophene (0.1 M) in THF were mixed in a ratio of 1:9 and crystallized on the target immediately before the measurement. The spectra were analyzed as described in ref 21: $M_n = 2630$ g/mol, $M_w = 3680$ g/mol, PD index = 1.40, repeat unit mass = 277 g/mol (see Supporting Information for the MALDI−TOF-spectrum).

Poly(3-(3′-thienyloxy)propanephosphonate) (P3TOPP). Silyl dealkylation of poly(3-(3′-thienyloxy)propanephosphonic acid diethyl ester) (100 mg, 0.36 mmol, with reference to monomer) in CH_2Cl_2 was done with addition of bromotrimethylsilane (0.38 mL, 2.9 mmol) in a drybox as previously reported.[22] Subsequent hydrolysis with quartz distilled water yielded the polymer in the acid form. The reaction was monitored with ^{31}P NMR spectros-copy, and the final product contained two types of phosphorus: fully hydrolyzed (86%) at 24.6 ppm and partly hydrolyzed (14%) at 30.0 ppm. Yield: 47.6 mg (47.6%). This product was used without any further purification (see Supporting Information for the ^{31}P NMR spectrum).

Pretreatment of the Substrates. Microscope slides, SnO_2-coated glass slides (20 Ω/□), and Si(100) wafers (Okmetic, Finland) were first cleaned in a fresh piranha solution (concen-trated H_2SO_4/30% H_2O_2 (3:1)−*warning*! piranha solution is very corrosive and must be treated with extreme caution; it reacts violently with organic material and must not be stored in tightly closed vessels), rinsed thoroughly with quartz distilled water, and dried. SnO_2 substrates were additionally cleaned with O_2 plasma (3 min, Harrick PDC-3XG plasma cleaner).[23] Microscope slides were silanized[24] with (3-aminopropyl)triethoxysilane in dry toluene solution (1% v/v) for 4 min at 60 °C, and a thin gold layer (ca. 100 nm) was evaporated using the Edwards E306A coating system. Silicon substrates for metal phosphonate films were silanized in a similar fashion and subsequently phospho-rylated in 0.2 M $POCl_3$/0.2 M 2,4,6-trimethylpyridine in dry acetonitrile for 1 h in drybox under an argon atmosphere.[15] Positive charge on SnO_2 substrates, required for the polyelec-trolyte adsorption at pH 12 and 3, was accomplished by silanization with *N*-trimethoxysilylpropyl-*N,N,N*-trimethylam-monium (TMSPA) chloride (5% v/v in MeOH) in a drybox[25] or by treatment with 10 mM poly(ethylenimine) (PEI) in 0.1 M acetic acid buffer (pH 4, ionic strength adjusted to 0.6 M with Na_2SO_4), respectively. Silicon substrates were silanized in a similar manner.

Polymer Characterization in Solution. The UV−vis spectra were recorded using a Hewlett-Packard 8453 spectro-photometer and the IR spectra (in KBr) obtained with a Nexus 870 FT-IR instrument (see Supporting Information for the IR spectra). The spectroelectrochemical measurements of P3TOPP in aqueous solutions were carried out in a homemade Au-minigrid optical thin layer cell.

Preparation of Multilayers. Multilayers on silicon and SnO_2 substrates were made using both the metal phosphonate and

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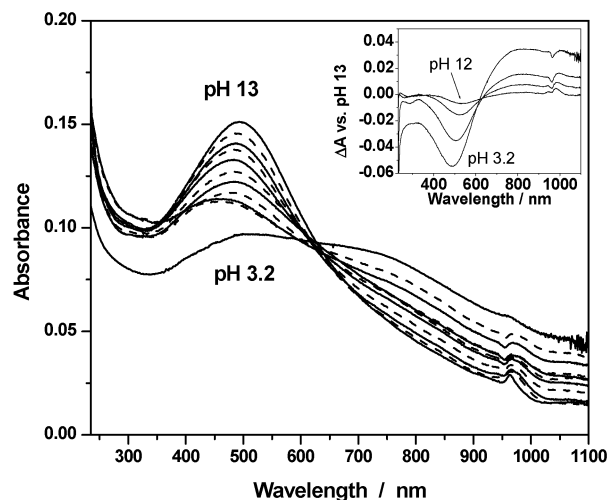(25) Szentirmay, M. N.; Campbell, L. F.; Martin, C. R. *Anal. Chem.* **1986**, *58*, 661.

the polyelectrolyte approaches. For these purposes a 1 mM (with reference to the monomer) P3TOPP solution was made by diluting the polymer with 10 mM NaOH(aq) and subsequently adjusting the pH at 3 with H_2SO_4.[15] Also, a 5 mM solution of $ZrOCl_2 \cdot 8H_2O$ and a 10 mM solution of PDADMA in quartz distilled water were prepared. No additional electrolyte was used in the preparation of the metal phosphonate layers. Natural oxide layer on SnO_2 provided a convenient surface to bind P3TOPP layer directly on SnO_2 substrates. The substrates were immersed in 1 mM P3TOPP (pH 3, 50 °C) for 16–18 h, washed with 10 mM NaOH and quartz-distilled water (for 3 times 1 min), and finally dried in air.[7] They were then immersed in a 5 mM $ZrOCl_2$ solution for 1 h at room temperature. Washing with quartz-distilled water (3×1 min) and drying in air completed the sequence. The silanized and phosphorylated silicon wafers (vide supra) were immersed in a $ZrOCl_2$ solution for 1 h, and the layers were then formed as described for SnO_2. The alternate adsorption of 1 mM P3TOPP (30 min) and 10 mM PDADMA (15 min) on positively charged silicon and SnO_2 substrates was used to form polyelectrolyte layers. In this case the ionic strength of the solutions was adjusted to 0.6 M with Na_2SO_4. The substrates were washed with quartz-distilled water and dried in air after the deposition of each layer. Gold-coated glass slides were primed with 2-mercaptoethylamine or 3-mercaptopropylphosphonic acid to yield polyelectrolyte or metal phosphonate multilayers, respectively.

Layer Characterization. UV–vis and IR spectra of multilayers on SnO_2 and silicon substrates, respectively, were measured with the spectrometers described above. Monolayers on gold surface were studied by polarization modulation infrared reflection–absorption spectroscopy (PM-IRRAS). The X-ray photoelectron spectra (XPS; see Supporting Information for the spectra) were recorded with a Perkin-Elmer PHI 5400 spectrometer using an electron takeoff angle of 45° and analyzer pass energy of 35.75 or 89.45 eV (for narrow scan spectra or wide scan survey spectra, respectively). For all samples unmonochromatized Mg Kα radiation (1253.6 eV) was used. The thickness of the dry multilayers on silicon wafers was measured with atomic force microscopy (AFM, AutoProbe CP from TM microscopes; see Supporting Information for the AFM images).

Results and Discussion

Polymer Properties in Solution. Poly(3-(3-thienyloxy)propanephosphonate) (P3TOPP) belongs to the class of self-dopable conducting polymers. The pK values of the phosphonic acid group in the monomer are close to 2.5 and 8.2 (for *n*-propylphosphonic acid pK_1 = 2.49 and pK_2 = 8.18),[26] suggesting that in the medium pH range the pendant phosphonic acid group exists mainly in the form of a monoanion. The polymer displayed good solubility in alkaline aqueous solutions giving purple color but precipitated from the solution when the pH was lowered below ca. 2.6. The MALDI–TOF measurements revealed that P3TOPP consists of oligomers with an average chain length of 10 monomer units, which is less than reported for other poly(alkoxythiophene)s using size exclusion chromatography (SEC).[11,12,20] However, SEC has been shown to exaggerate polythiophene molecular weights in highly disperse systems.[27] Higher mass components tend to be underrepresented with respect to lower mass components in MALDI–TOF experiments,[28] which was here taken into account by the correction procedure presented by Montaudo et al.[21]

In alkaline aqueous solutions, the absorption maximum of the undoped form (Figure 1) is at 496 nm, lower than or comparable to several alkoxythiophene-based polyelectrolytes or poly(alkoxythiophene)s in aprotic sol-
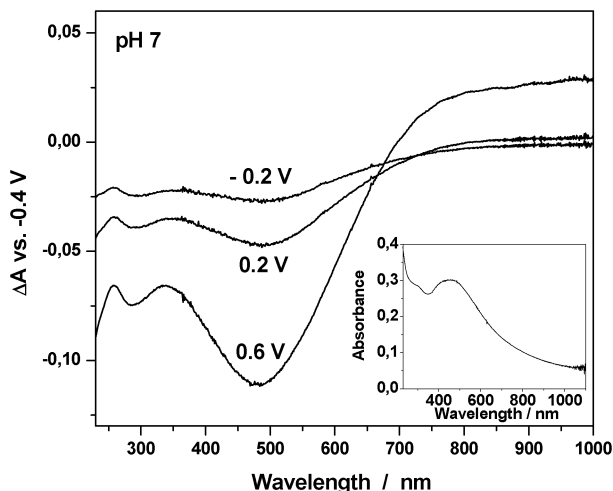
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Figure 1. Absorption spectra of P3TOPP solutions (40 μM) at different pH: 13.0, 12.1, 11.0, 10.0, 9.0, 8.1, 7.1, 6.1, 5.0, 4.0, and 3.2. Inset shows the difference spectra at selected pH (12.1, 10.0, 6.1, and 3.2) vs pH 13.0.

vents.[13,20,29,30] The band at 496 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the conjugated backbone and characterizes of the effective conjugation length of the polymer. The spectra in alkaline solutions exhibited noticeable absorbance also at longer wavelengths, which has generally been attributed to the presence of oxidized polymer segments or aggregation. In DMSO, the $\pi \rightarrow \pi^*$ transition was slightly blue-shifted to 490 nm, and the absorption at longer wavelengths decreased, similar to the case of sulfonic acid bearing poly(alkoxythiophene)s.[13]

In aprotic solvents ($CHCl_3$ and CH_2Cl_2), the corresponding alkoxyphosphonic acid diester (P3TOPPEt) exhibited a maximum at 520 nm, which is higher than reported for the nearly regioregular alkylphosphonate ester polythiophene under similar conditions, in which the intermolecular interactions are small.[18] Although the alkoxy substitution induces a red shift in the spectrum, this indicates that the electronic structure and conjugation length of P3TOPP are comparable to those of higher poly(alkoxythiophene)s. However, addition of acid to alkaline aqueous solutions of P3TOPP decreases the absorption at 496 nm, and a new absorption band appears at around 750 nm (Figure 1). The observed changes upon decreasing pH resemble the spectral behavior during oxidation of the polymer in the thin layer cell (Figure 2).

No clear isosbestic point can be observed in either case, which implies that more than two kinds of chromophoric species are involved. The apparent doping of ionically substituted polythiophenes with Brönstedt acids represents the so-called self-acid-doping,[20] and the addition of NaOH to the acidic polymer solution induces the reverse color change, making it chemically reversible. Upon addition of acid in the alkaline solution the spectrum of P3TOPP began to change already at pH 12 and cannot result from the protonation of the polythiophene backbone. In polyacids, compared to the corresponding monomeric forms, the effective pKs are shifted to higher values, and the width of the dissociation regime is increased due to the electrostatic interactions of the ionic groups with their neighbors. Titrations of polythiophene carboxylic acids indicate that the pK value may be increased by 1–2 units, and the transition may extend over 5 pH units.[31] Therefore,

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Figure 2. Difference absorbance spectra of a 10 mM P3TOPP solution (pH 7) at potentials indicated. Spectrum at -0.4 V vs Ag/AgCl reference electrode taken as reference. Inset shows the spectrum at -0.4 V.

the second pK value of the phosphonic acid group in P3TOPP is shifted upward, and the group may be partially protonated already at pH 12. We attribute the gradual changes in the spectrum down to ca. pH 6 to the slow formation of the monoanionic form of P3TOPP. At high pH counterion condensation takes place around these highly charged polyanions, but the countercations are mainly sodium ions and the only effective process to bring protons into a close vicinity of the polythiophene chain is side group protonation. A tentative mechanism can, therefore, be presented for the self-acid-doping as shown in Scheme 1.

We suggest that the protonation of a phosphonate dianion may lead to the formation of a tautomeric form, in which the proton has been transferred to a backbone carbon. Various mesomeric forms can be drawn for the resulting structure. It should be pointed out that although we show protonation at the α-carbon of the thiophene ring, we cannot rule out protonation at the 4-position. It is also possible that only the end positions of the relatively short oligomers are protonated.[32] However, not depending

on the site of protonation in the chain or the regularity of the monomer coupling, the conjugation is broken at the site of protonation. This can explain the blue shift and decrease of the $\pi \rightarrow \pi^*$ transition. On the other hand, a new type of conjugated segment is formed adjacent to the protonation site, and its structure bears similarity with the radical cation (polaron) structure caused by oxidation, explaining the appearance of a new band above 600 nm. Below pH 6 and, especially, on going from pH 4 to 3, other processes come into play. The second protonation step probably starts below pH 6, and in acidic solutions the direct protonation of the polymer backbone itself (classic Brönstedt acid doping) has to be considered, too. As mentioned above, the electrochemical oxidation of P3TOPP in a thin layer cell brings about similar spectral changes than the addition of acid and the spectral changes are larger in neutral (pH 7) than acidic (pH 3) solutions.

Formation and Properties of Multilayers. Both the metal phosphonate and polyelectrolyte approaches can be used to form multilayers with P3TOPP. Metal phosphonate multilayers were formed on SnO$_2$ and silicon substrates by sequential adsorption of P3TOPP (at pH 3) and Zr^{4+} ion. Under these conditions P3TOPP is in an acid-doped state as evidenced by the UV–vis spectrum. Polyelectrolyte layers on positively charged SnO$_2$ and silicon substrates were formed by the alternate adsorption of P3TOPP (at pH 3 and 12, the latter only on SnO$_2$) and PDADMA at ionic strength 0.6 M. The layer growth is regular in both cases as indicated by the linear increase of absorbance as a function of layers (Figure 3).

The amount of P3TOPP deposited is the same in the polyelectrolyte and metal phosphonate layer-by-layer assembly method, indicating similar polythiophene layer thickness and linear growth in both cases. Oxidation of multilayers on SnO$_2$ electrodes revealed subtle differences between the two types of layers (Figure 4a).

Upon oxidation, the film absorbance decreased at 530 nm and increased above 730 nm in polyelectrolyte multilayers. In metal phosphonate layers the corresponding changes took place at 490 nm and above 680 nm, respectively. However, the changes were small compared to the total absorbance of the films, especially with metal phosphonate multilayers. In analogous polyelectrolyte multilayers containing a sulfonic acid derivatized poly-

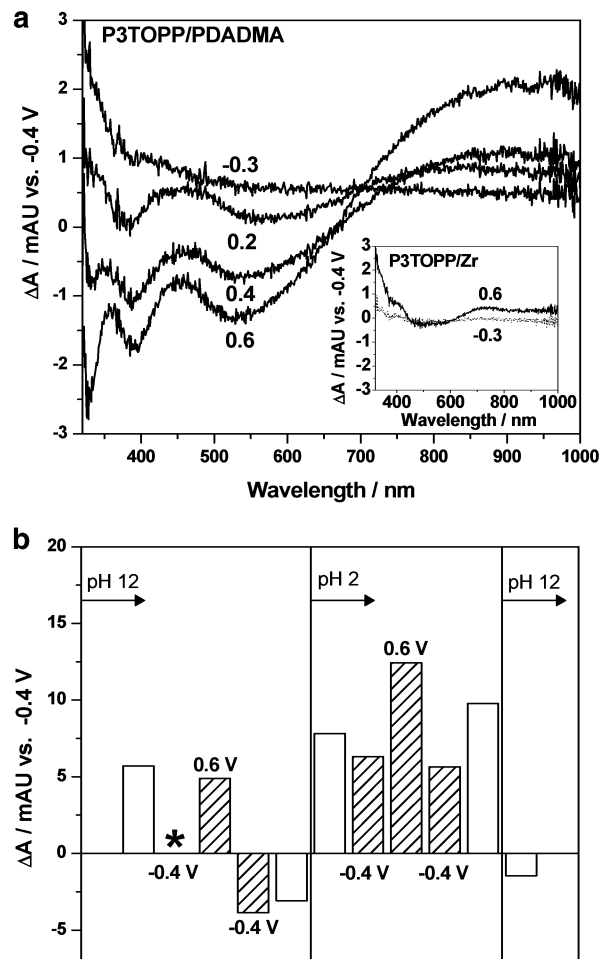**Scheme 1. A Tentative Mechanism for the Self-Acid-Doping of P3TOPP**
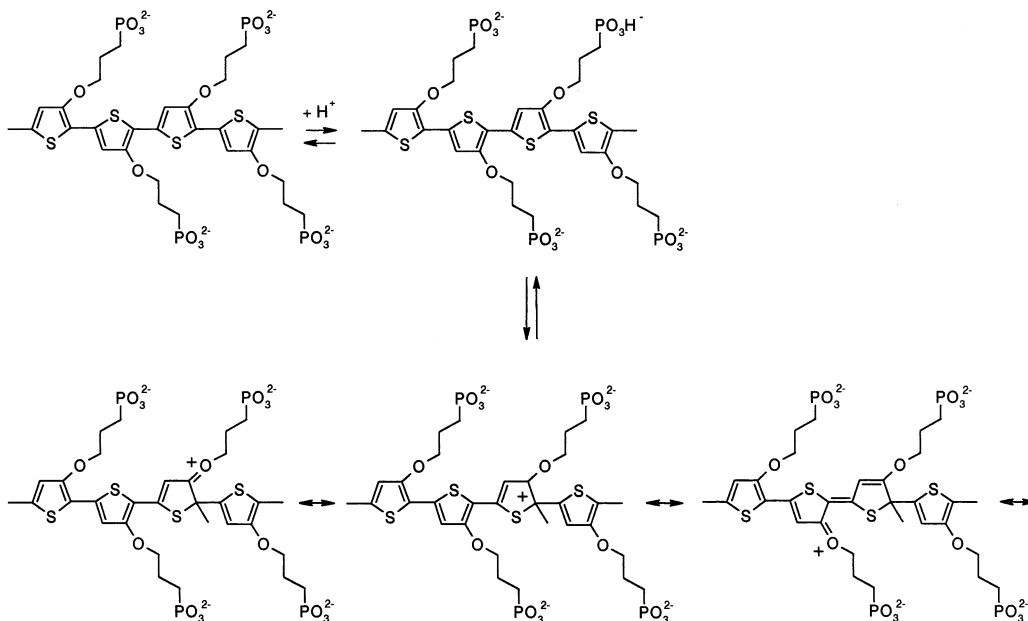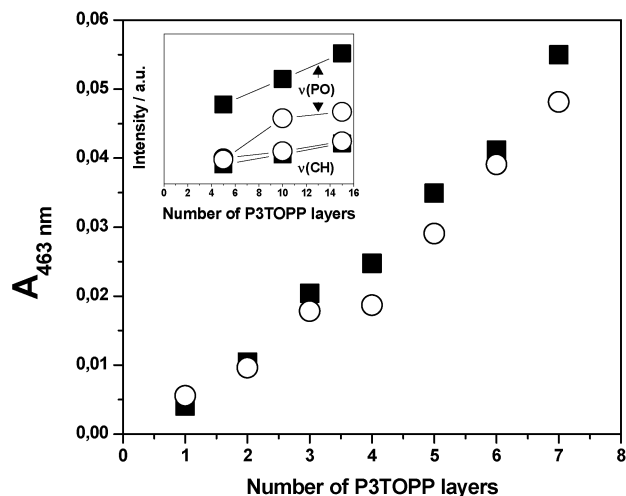
Figure 3. Increase of absorbance at 463 nm with metal phosphonate (P3TOPP/Zr)$_n$ (■) and polyelectrolyte (pH 3) PEI/(P3TOPP/PDADMA)$_n$ (○) multilayers on SnO$_2$. Inset shows the dependence of the integrated intensity of the C−H and P−O stretching vibrations (2830−3000 and 900−1250 cm^{-1}, respectively) on the number of layers (on Si).

thiophene the changes due to oxidation have been shown to be ca. 30 times greater.[11] The spectral response of a P3TOPP/PDADMA multilayer to changes in pH and the oxidation state is shown in Figure 4b. The changes due to pH are comparable to or larger than changes induced by oxidation and reduction. However, some material is lost, especially during the first redox cycle as clearly seen from the decrease of absorbance at 530 nm (data not shown). This may stem from the low molecular weight of P3TOPP.[33] The low electroactivity of the P3TOPP multilayers, especially in the P3TOPP/Zr films, is surprising. In solution, the relative absorbance change during the oxidation of P3TOPP was larger, and we tentatively attribute the behavior in thin films to steric restraints caused, e.g., by the Zr−phosphonate bonds. However, both in thin films and in solution, the color of P3TOPP is responsive to electrochemical oxidation and reduction (electrochromism) and changes in the solution pH (halochromism).

Transmission IR spectroscopy (on silicon substrates) was also used to follow the multilayer formation. The integrated intensity of the C−H stretching vibrations between 2830 and 3000 cm^{-1} displayed a linear increase with the number of layers for both P3TOPP/Zr and P3TOPP/PDADMA films (inset of Figure 3). As expected, the latter film shows higher C−H stretching intensity due to the methylene and methyl groups of PDADMA although the amount of P3TOPP is similar in both films according to UV−vis spectroscopy. The P−O stretching vibrations displayed a wide peak at ca. 1060 cm^{-1} with no discernible details in either case, but the intensity of the peak increased with the film thickness. All the peaks in the transmission IR spectra of the multilayers were rather wide, which is indicative of variation in the conformation and chemical environment. The molecular order in metal phosphonate multilayers has been shown to deteriorate with the film thickness, and on the other hand, polyelectrolyte multilayers are inherently disordered at the

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Figure 4. (a) Difference absorbance spectra (mAU = milliabsorbance units) of SnO$_2$/PEI/(P3TOPP/PDADMA)$_7$ multilayers at potentials indicated (0.2 M Na$_2$SO$_4$). Spectrum at −0.40 V vs Ag/AgCl taken as reference. Inset shows the difference spectra of SnO$_2$/(P3TOPP/Zr)$_7$. (b) Absorbance of SnO$_2$/TMSPA/(P3TOPP/PDADMA)$_7$ multilayers at 900 nm when both the pH of the solution and the potential of the electrode were varied. Open and dashed bars measured at open circuit conditions and under potentiostatic control, respectively. The solution pH and applied potentials are indicated in the figure. (*): Absorbance at −0.4 V vs Ag/AgCl (undoped form, pH 12) taken as reference.

molecular scale.[8,34] Therefore, we used the PM-IRRAS technique to obtain information about the molecular order in monolayers of P3TOPP. The spectra of the CH stretching region are shown in Figure 5 for Au/MPPA/Zr/P3TOPP and Au/MEA/P3TOPP monolayers. Vibrations originating from the priming layer (MPPA or MEA) on gold were negligible. The asymmetric ν_a(CH$_2$) vibration gives information about the quality of the layer structure. For ordered "all-trans" structures in long alkyl chain thiols on gold the ν_a(CH$_2$) stretching vibration should appear at 2918 cm^{-1} with a line width of 15 cm^{-1}.[35] When more disordered "liquidlike" layers are formed, the vibration shifts to larger wavenumbers and the peak broadens (>30 cm^{-1}).

PM-IRRAS results from samples deposited on primed gold surface showed that the ν_a(CH$_2$) vibration appeared at 2927 with a half-width of 31 cm^{-1} in both cases. This indicates that the propoxy side chains are completely

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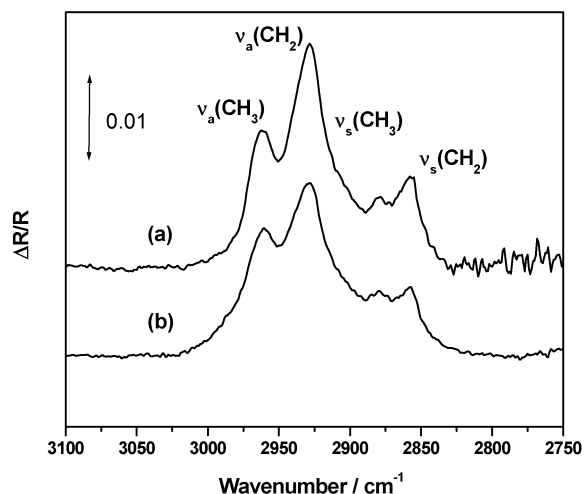
Figure 5. PM-IRRAS spectra of MEA/P3TOPP (a) and MPPA/Zr/P3TOPP (b) monolayers on gold.
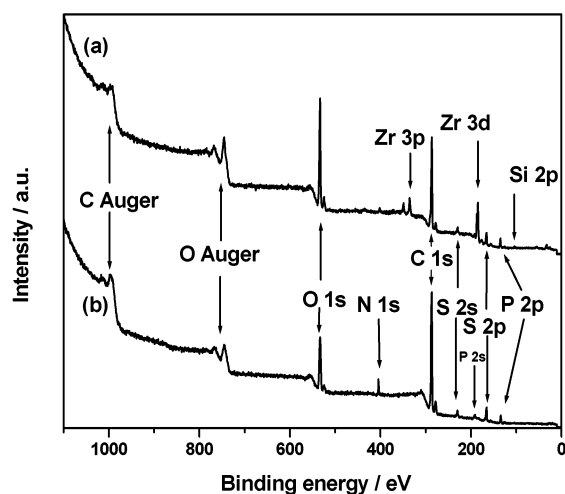
Figure 6. XPS survey scans of (a) (P3TOPP/Zr)$_{15}$ and (b) (P3TOPP/PDADMA)$_{15}$ multilayers on silicon indicating the elements present.

disordered in both monolayers. The modes attributable to the CH$_3$ stretching vibrations (asymmetric ν_a(CH$_3$) and symmetric ν_s(CH$_3$) at 2960 and 2879 cm^{-1}, respectively) are in good agreement with the results from ^{31}P NMR, which showed that a small amount of phosphonate ester was still present in the final product. The presence of unhydrolyzed side chains did not seem to cause problems in the layer-by-layer assembly. However, the most noteworthy fact in the PM-IRRAS spectra was the absence of the modes attributed to the thiophene ring stretching vibrations (around 1300−1500 cm^{-1}). This implies a nearly planar orientation of the thiophene rings in both types of layers with respect to the substrate surface. Unfortunately, instrumental limitations prevented us from analyzing the P−O stretching region with necessary accuracy.

XPS Measurements. XPS is a useful tool for analyzing the interlayer chemistry in both multilayer structures. The survey spectra of 15 bilayers of P3TOPP/Zr and P3TOPP/PDADMA on silicon are shown in Figure 6, and a summary of the observed binding energies (BEs) is given in Table 1.

Charging of the substrate was observed, and for all the values reported the C 1s line at 285.0 eV (adventitious impurity or aliphatic carbon) was used as a reference. The emission from the substrate, typical for SiO$_x$, was observed only in P3TOPP/Zr samples because the

Table 1. XPS Binding Energies, Peak Areas, and Assignment of the Peaks for 15-Layer P3TOPP Metal−Phosphonate and Polyelectrolyte Films on Silicon[a]

element	(P3TOPP/Zr)$_{15}$		(P3TOPP/PDADMA)$_{15}$		assignment
	energy/eV	area/ASF	energy/eV	area/ASF	
C 1s	285.0	13128	285.0	24507	**C**−H, **C**−C
	285.8	15757	286.3	12220	**C**−O
	289.0	2328	288.0	2710	**C**=O contam
N 1s	400.5	742	399.8	444	N contam
			402.4	1860	**N**$^+$
O 1s			530.4	3095	PO$_3$$^{2-}$, PO$_3H^-$
			531.8	3063	
			532.9	2146	
	532.1	14196			P−**O**−Zr
	533.8	1356	533.4	986	Th−**O**−C[b]
P 2p			132.2	854	**P**O$_3$$^{2-}$
			132.8	376	**P**O$_3$H$^-$
	133.4	1899			**P**−O−Zr
S 2p	164.0	2202	164.0	2098	C$_4$H$_4$**S** (=Th)[b]
Si 2p	102.6	469			**Si**O$_x$
Zr 3d	183.2	1916			P−O−**Zr**

[a] ASF stands for atomic sensitivity factor. [b] Th = thiophene.
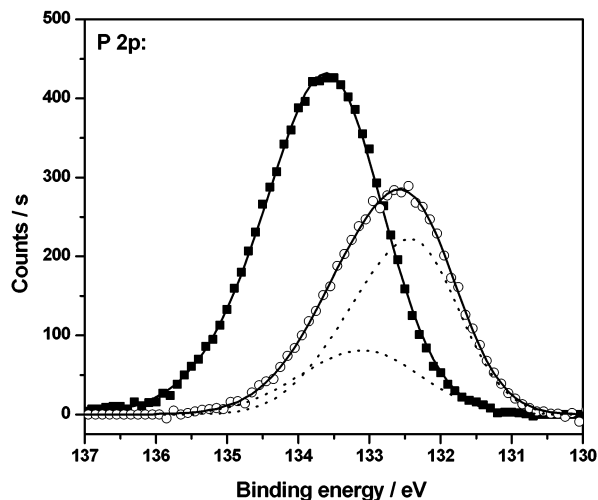
Figure 7. P 2p emission (with Shirley background correction) from (P3TOPP/Zr)$_{15}$ (■) and (P3TOPP/PDADMA)$_{15}$ (○) multilayers. Components in dotted line.

PDADMA layers increased the thickness of the polyelectrolyte multilayer enough to screen the substrate photoelectrons. The thickness of the (P3TOPP/Zr)$_{15}$ and (P3TOPP/PDADMA)$_{15}$ multilayers was measured with AFM to be 26.1 ± 2.5 and 46.0 ± 2.1 nm, respectively. Charged nitrogen of the PDADMA layers displays a considerable emission at 402.4 eV. The P 2p emission varies as a function of the oxygen environment. Only one P 2p doublet (unresolved, 2p$_{1/2}$ and 2p$_{3/2}$ components separated by 0.8−0.9 eV)[36,37] was found in P3TOPP/Zr films at 133.4 eV (for clarity, only the 2p$_{3/2}$ components are mentioned) whereas in P3TOPP/PDADMA multilayers two doublets could be observed with BEs 132.2 and 132.8 eV (Figure 7). Viornery et al. observed the P 2p signal at 133.4 eV when alkanephosphonic acid was complexed on Ti surface.[36] Similarly, values 133.2 and 133 eV have been reported for phosphonododecanoic acid on ITO and for zirconium-terminated phosphonic acids, respectively.[38,39]

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These values are in good accordance with the observed P 2p BE in the P3TOPP/Zr multilayers, which confirms the metal phosphonate character of these films.

The position of the Zr 3d signal agrees well with the values observed in polymeric metal phosphonate layers,[7] and no signal of uncomplexed ZrO_2 could be observed at 182.4 eV.[39] On the other hand, deprotonation of the oxygen atoms decreases the P 2p binding energy, and a shift from ca. 135 to 132.4 eV has been observed upon total deprotonation of the phosphoric acid group.[37] Therefore, the observed BEs in the P3TOPP/PDADMA multilayers (132.2 and 132.8 eV in an approximately 7:3 ratio) suggest that the phosphonic acid groups are in ionized form, a case expected for polyelectrolyte multilayers with ionic bonding. The observed values are surprisingly low and imply enhanced deprotonation of the phophonic acid groups although the deposition pH would suggest the prevalence of the monoionic species. The P3TOPP/Zr and P3TOPP/PDADMA multilayers display different O 1s binding energies, too, and only one main component at 532.1 eV and a minor component at 533.8 eV could be observed in the former. On the other hand, three peaks of similar intensity at 530.4, 531.6, and 532.7 eV and a smaller one at 533.4 eV were observed in P3TOPP/PDADMA multilayers. In phosphonates the O 1s binding energy is usually in the range 534−535 eV,[40] but Textor et al. have observed an unusually low binding energy for P=O (531.8 eV), attributed to interactions with water.[37] The small peak close to 534 eV in both multilayers is assigned to oxygen in the alkoxy side chain. In polyelectrolyte multilayers, the observed three BEs imply the coexistence of differently protonated phosphonate groups (and P=O). On the other hand, only one P−O species in the P3TOPP/Zr films indicates the equivalence of the phosphonate oxygens, a fact expected for coordination to metal via all oxygens. In addition, impurity oxygen (e.g., water) may have a small effect in the range 532−533 eV. The S 2p emission in both multilayers was observed at 164.0 eV, which is expected for sulfur in thiophenes.[41] In both cases a small peak at higher energy (168.7 eV) was also observed, perhaps due to contamination (also seen in ref 6). No sign of electrolyte ions was observed in the XPS spectra, which is characteristic for total intrinsic charge compensation in rinsed polyelectrolyte multilayers.[42] In summary, the XPS results prove the formation of two kinds of multilayer structures from P3TOPP, both a metal phosphonate and a polyelectrolyte multilayer.

XPS atomic concentrations and ratios, especially N:P, Zr:P, and Zr:S, can be used to study the stoichiometry of the multilayer structures. In P3TOPP/PDADMA layers the negative charge of the phosphonate groups is compensated with the positive charge of nitrogen in PDADMA. The polyelectrolyte multilayers exhibit extensive interpenetration, and the distribution of nitrogen and phosphorus can be considered nearly constant within the film. The observed N^+:P ratio is 1.51, and it is in accordance with the P 2p chemical shifts, which imply that ca. $^2/_3$ of the phosphonic acid groups are fully deprotonated and the rest exist as monoanions. On the other hand, the Zr:P and Zr:S ratios give information about the interlayer

chemistry in the metal phosphonate multilayers. The observed Zr:P ratio is 1.06 ± 0.1 (an average of four individual measurements), which is similar to the value of ca. 1.1 obtained by Hoekstra et al. for zirconium-capped alkylbis(phosphonic acid)s on glassy carbon substrates.[43] In layered structures the attenuation of the emission from the underlying layers affects the measured ratio. The attenuation of the XPS signals follows a simple Beer's law, and the ratio of the normalized peak areas can be expressed as a summation over the entire multilayer structure:[44,45]

$$\frac{A_{norm(Zr)}}{A_{norm(P)}} = \frac{m_{Zr} \sum\limits_{Zr\ atoms} e^{-d_{Zr}/\lambda_{Zn}}}{m_p \sum\limits_{P\ atoms} e^{-d_P/\lambda_P}} \qquad (1)$$

The multiplicity of atoms at a given depth (d) is based on a layer structure where two phosphonic acid groups are bound to one Zr^{4+} ion ($m_{Zr} = 1$, $m_P = 2$). The depth values are estimated from the total multilayer thickness determined by AFM (thickness per bilayer 17.4 ± 0.9 and 30.7 ± 1.6 Å respectively for $(P3TOPP/Zr)_{15}$ and $(P3TOPP/PDADMA)_{15}$ multilayers), and the mean free paths of photoelectrons ($\lambda = \lambda_0 \cos \alpha$, where α is the takeoff angle) depend on the element and the nature of the material in which the photoelectrons are generated. The experimental values for the electron free paths vary by more than an order of magnitude.[46] Mallouk et al. observed large photoelectron mean free paths in self-assembled multilayers of ordered alkyl α,ω-bis(phosphonic acid)s, which was explained by the channeling of photoelectrons along the alkyl chains.[45,47] In more disordered organic materials the free paths are smaller and an average value of $\lambda = 15$ Å is generally used for several elements.[48,49] However, the theoretical 1:2 stoichiometry requires an unreasonably low value of $\lambda \approx 5$ Å. On the other hand, the average value 15 Å (using interlayer spacing of 17.4 Å) leads to a stoichiometry of Zr:P $\approx 1:(1.45 \pm 0.15)$, which is close to that observed in multilayers of α-zirconium phosphate sheets (α-ZrP) and poly(allylamine hydrochloride) (PAH).[49] Similarly, assuming that the sulfur atoms occupy a position in the middle of the zirconium layers, a Zr:S ratio of 0.7 ± 0.1 is obtained, in reasonable accordance with the observed result 0.95 ± 0.07. Previous work has shown that a gradual loss of order takes place in metal phosphonate multilayers as the number of layers increases, and the deviation from the theoretical value may be explained by a decrease in the amount of P3TOPP deposited per layer. On the other hand, this seems to contradict our spectroscopic observations, which indicate a regular film growth (also observed, however, with α-ZrP/PAH multilayers). We may also suggest a tentative alternative explanation based on the fact that most of the XPS signal originates from the outermost layer(s) in our zirconium-terminated films. If an over-stoichiometric amount of zirconium is bound to the surface during the

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metal complexation step, the excess zirconium may be removed in the next step. In fact, the assumption that the outermost zirconium layer contains a 50% excess of zirconium can explain the observed Zr:P ratio using the theoretical 1:2 stoichiometry for the underlying layers. Similar partial removal of the previous layer has been observed in some polyelectrolyte multilayers.[50] However, only one BE component was observed in the XPS spectra. Therefore, the unambiguous reasons for the observed Zr:P stoichiometry remain open, and we cannot exclude the effects of, for example, structural disorder in the multilayers.

Conclusions

A water-soluble polythiophene derivative with pendant phosphonic acid side chains, poly(3-(3′-thienyloxy)propanephosphonate) (P3TOPP), has been synthesized and characterized. Although MALDI−TOF reveals that P3TOPP is an oligomer, consisting of ca. 10 monomer units, its electronic properties are comparable to those of polythiophenes. P3TOPP displays electroactivity and electrochromism in aqueous solution, but it can also be self-acid-doped. Addition of acid to alkaline solutions induced spectral changes similar to oxidation. These changes are attributed to partial protonation of the phosphonic acid groups, and a tentative mechanism, involving a tautomeric proton transfer from phosphonate to the thiophene backbone, has been suggested.

P3TOPP can be used to prepare two kinds of multilayers, based on either metal phosphonate linkages or electro-static interactions. The zirconium phosphonate multilayers were considerably thinner than the polyelectrolyte multilayers, but a regular layer-by-layer growth was observed in both cases. A clear evidence for the structure of the multilayers was obtained by XPS, which showed that the phosphonate group is ionized in polyelectrolyte multilayers. In Zr phosphonate films, the P 2p, Zr 3d, and O 1s binding energies were typical for metal phosphonates. The observed N:P ratio in polyelectrolyte multilayers was consistent with the ionization of the phosphonate side chains whereas in Zr−phosphonate films the Zr:P ratio indicated deviation from the theoretical stoichiometry. The observed stoichiometry was in accordance with values previously reported for similar systems and may be rationalized by partial removal of the Zr species during the polymer assembly process although the effects of possible film disorder cannot be excluded.

Supporting Information Available: The ^{1}H and ^{13}C NMR spectra of 3TOPPEt, the ^{31}P NMR spectra of P3TOPPEt and P3TOPP, the MALDI−TOF mass spectrum of P3TOPPEt, the XPS spectra, and the AFM topography images (contact mode) of dry Zr/P3TOPP and P3TOPP/PDADMA multilayers. This material is available free of charge via the Internet at http://pubs.ac.org.

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