Monomolecular Functionalization of Pulsed Plasma Deposited Poly(2-hydroxyethyl methacrylate) Surfaces

C. Tarducci, W. C. E. Schofield, and J. P. S. Badyal*

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, England, United Kingdom

S. A. Brewer and C. Willis

DSTL, Porton Down, Salisbury SP4 OJQ, England, United Kingdom

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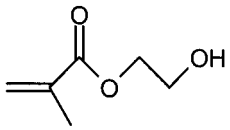
A combination of X-ray photoelectron, infrared, and nuclear magnetic resonance spectroscopies have shown that pulsed plasma polymerization of 2-hydroxyethyl methacrylate (HEMA) leads to the deposition of structurally well-defined poly(HEMA) films. The molecular weight and surface hydroxyl density of these plasma polymer layers can be controlled by varying the electrical discharge pulse duty cycle parameters. These films are found to display hydrogel behavior, and the surface hydroxyl groups readily undergo reaction with diethylchlorophosphite. The latter is shown to be a useful way of coordinating catalytic rhodium complexes to solid surfaces.

1. Introduction

Poly(2-hydroxyethyl methacrylate) (poly(HEMA)) surfaces have many technological applications; these include separation devices,[1,2] biosensors,[3] biocompatibility,[4] adhesion,[5] textile strengthening,[6] and metal ion absorption.[7] Thin films of this material are normally prepared by either graft copolymerization[6] or spin casting from polymer solution.[4,8] An alternative approach is to employ plasma polymerization. This offers a number of potential advantages, which include the fact that it is solventless, is energy efficient, and can be applied to a variety of complex geometry substrates. In the case of conventional continuous wave plasma polymerization of 2-hydroxyethyl methacrylate,[9−11] a variety of functional groups tend to be incorporated into the growing polymeric film because of severe fragmentation of the precursor within the electrical discharge.[12] However, more recently it has been shown for other monomers that pulsing the electric discharge on the ms−μs time scale can give rise to high levels of structural retention.[13−17] This can be ascribed to low levels of precursor fragmentation during the on-period in association with conventional polymerization reaction pathways predominating during the pulsed plasma duty cycle off-period. Examples of molecularly tailored substrates produced by this method include perfluoroalkyl-,[18] epoxide-,[19] anhydride-,[20] carboxylic acid-,[21] cyano-,[22] and amine-[23]functionalized surfaces.

In this article, the plasma polymerization of 2-hydroxyethyl methacrylate (HEMA) is investigated (Structure 1). A comparison is made between the surface chemistry of low-power continuous wave plasma, pulsed plasma, and conventional poly(HEMA) polymer films. Also, the reactivity of these functionalized surfaces has been explored in the context of water absorption, esterification, and precious metal complexation.



Structure 1: 2-hydroxyethyl methacrylate

* To whom correspondence should be addressed.

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2. Experimental Section

Plasma polymerization of 2-hydroxyethyl methacrylate (HEMA, Fluka, 99% purity, further purified using several freeze−pump−thaw cycles) was carried out in a cylindrical glass reactor pumped by a mechanical rotary pump via a liquid-nitrogen cold trap (base pressure = 1×10^{-3} mbar, leak rate = 1×10^{-8} mol s^{-1}). A copper coil wrapped around the reactor was coupled to a 13.56-MHz radio frequency power supply via an LC matching network. Prior to each experiment, the chamber was cleaned using a 50-W air plasma at 0.2 mbar for 30 min. Monomer vapor was then introduced into the system via a fine control needle valve at a pressure of 0.1 mbar and 4×10^{-8} mol s^{-1} flow rate. At this stage, the electrical discharge was ignited and film deposited for 15 min. In the case of pulsed plasma polymerization, a signal generator was used to trigger the RF supply. Typical conditions were 3-W power for continuous wave plasma and time on = 20 μs, time off = 20 ms, and peak power = 40 W for pulsed plasma.

A reference sample of conventional polymer was prepared by spin coating 4% w/v poly(HEMA) (Aldrich, average molecular weight ca. 300000) dissolved in methanol (Fisher, +99.8%) onto glass microscope slides.

The plasma polymer deposition rate was measured using an nkd-6000 spectrophotometer (Aquila Instruments Ltd). Transmittance−reflectance curves (over the 350−1000-nm wavelength ranges) were fitted to a Cauchy model for dielectric materials using a modified Levenburg−Marquardt method. Water absorption studies for the different types of film were carried out using a quartz crystal microbalance (Varian Model 985-7013).

X-ray photoelectron spectroscopy (XPS) analysis of the polymer surfaces was performed using a Kratos ES300 spectrometer equipped with a Mg Kα X-ray source and an hemispherical analyzer operating in fixed retard ratio mode (22:1). The photoelectrons were collected at a take-off angle of 30° from the substrate normal. Surface elemental composition was calculated using sensitivity (multiplication) factors derived from chemical standards: C(1s):O(1s):F(1s):P(2p):Cl(2p):Si(2p):Rh(3d) equals 1.00:0.57:0.67:0.73:0.42:1.02:0.12. All binding energies are referenced to the C(1s) hydrocarbon peak at 285.0 eV.

Infrared spectra were taken of plasma polymer films deposited onto NaCl plates using a Mattson Polaris FTIR instrument operating at a resolution of 4 cm^{-1} and averaged over 200 scans. In addition, conventional poly(HEMA) polymer was mixed with KBr powder and pressed into a pellet, while the monomer was analyzed by placing a drop of liquid between two NaCl plates.

Sessile drop contact angle measurements were carried out at 20 °C with a video capture apparatus (A.S.T. Products VCA2500XE) using high-purity water (B.S. 3978 Grade 1) as the probe liquid.

Plasma-deposited material was dissolved in deuterated dimethyl sulfoxide (Aldrich, 99.6 at. % D) and then characterized by ^{1}H and ^{13}C NMR spectroscopies using a Bruker AM 250 spectrometer operating at 250.13 and 62.90 MHz, respectively.

Polymer molecular weight determination was carried out by gel permeation chromatography (GPC) at 25 °C using a Viscotek TDA 300 instrument equipped with a refractive-index detector. A series of three PL gel columns with pore sizes of 10^3, 10^5, and 100 Å were used for separation. Poly(ethylene oxide) standards were used for calibration with dimethyl formamide (DMF) as the eluent (1 mL/min). A sample volume of 100 μL was used for each measurement. The molecular weight values obtained by this method for the plasma-deposited material were divided by the corresponding measurement taken for conventional poly(2-hydroxyethyl methacrylate).

Quantification of surface hydroxyl group density for each of the poly(HEMA) films required reaction with trifluoroacetic anhydride (Aldrich, 99%) vapor for 30 min. These samples were rinsed several times in methanol prior to subsequent surface analysis.

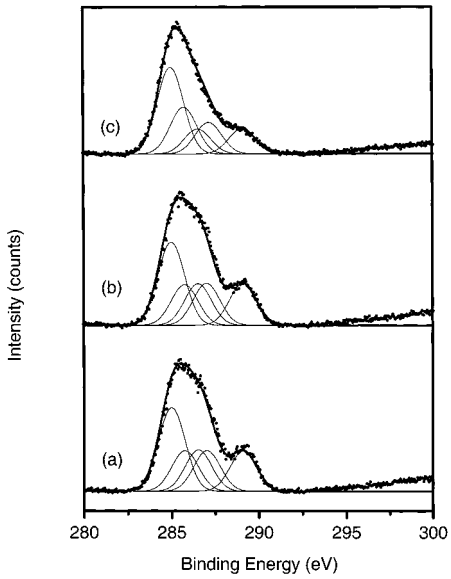

Figure 1. C(1s) XPS spectra of 2-hydroxyethyl methacrylate polymers deposited onto a flat glass substrate: (a) conventional polymer; (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W); and (c) 3-W continuous wave plasma polymer.

Table 1. XPS Elemental Analysis of 2-Hydroxyethyl Methacrylate Polymers

polymer	%C	%O	polymer	%C	%O
theoretical	66.6	33.3	pulsed	68 ± 0.8	32 ± 0.8
conventional	68 ± 1	32 ± 1	CW	76 ± 1	24 ± 0.6

Reaction of the poly(HEMA) surfaces with diethyl chlorophosphite (Aldrich 98%) vapor was carried out under continuous flow conditions in a glass reactor (0.4-mbar pressure for 30 min). Any absorbed material was pumped off in vacuum for an hour prior to sample analysis. Subsequent rhodium center complexation of these phosphite-functionalized surfaces was achieved by immersing each substrate into a 1% w/v solution of $RhCl_3 \cdot 3H_2O$ (Lancaster, Rh 40 wt %) dissolved in 1,4-dioxane (Aldrich, 99%) for 1 h. Prior to analysis, these slides were rinsed several times in pure 1,4-dioxane, followed by degassing under vacuum.

3. Results

(a) Characterization. Film thickness measurements indicated deposition rates of 13.4 ± 0.3 and 30.0 ± 0.1 nm min^{-1} for the pulsed and the continuous wave conditions, respectively. XPS elemental analysis of the continuous wave plasma polymer showed a depletion in oxygen compared to the theoretical monomer structure (Table 1), whereas the pulsed plasma polymer coating closely resembled the expected poly(HEMA) chemical composition.

The C(1s) envelope of the conventional polymer could be fitted to the following carbon environments:[24] 285.0 eV (−CH_2−), 285.8 eV (−CH−C=O), 286.5 eV (−CH_2−OH), 287.0 eV (−O−CH_2−), and 289.1 eV (C=O) (Figure 1). The C(1s) spectrum of the pulsed plasma polymer film strongly resembled the conventional polymer, whereas the continuous wave plasma polymer exhibited a more intense hydrocarbon component at 285.0 eV in

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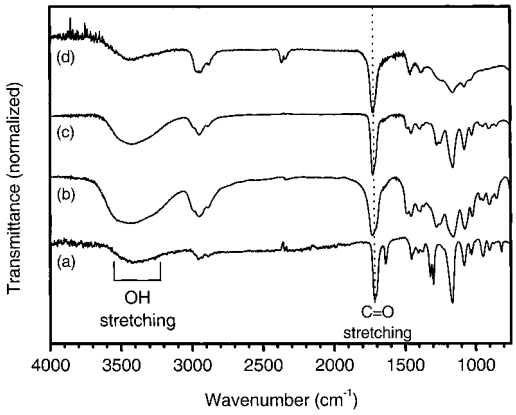

Figure 2. Infrared spectra of (a) 2-hydroxyethyl methacrylate monomer, (b) conventional poly(2-hydroxyethyl methacrylate) polymer, (c) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W), and (d) 3-W continuous wave plasma polymer. (The weak band in the 2360−2330-cm^{-1} region is due to residual CO_2 in the spectrometer.)

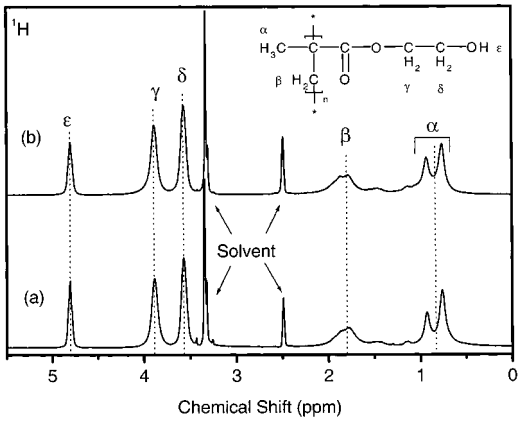

Figure 3. ^{1}H NMR spectra of (a) 2-hydroxyethyl methacrylate conventional polymer and (b) 2-hydroxyethyl methacrylate pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W).

conjunction with a lower concentration of oxidized carbon species.

A high retention of the monomer structure during pulsed plasma deposition (apart from the alkene bond) was confirmed by infrared analysis (Figure 2). In the case of the 2-hydroxyethyl methacrylate monomer, the following peak assignments were made:[25] O−H stretching (3500 cm^{-1}), acrylate C−H stretching (3112 cm^{-1}), saturated C−H stretching (2900−2800 cm^{-1}), C=O stretching (1722 cm^{-1}), C=C stretching (1636 cm^{-1}), =CH_2 wagging (942 cm^{-1}), and =CH_2 twisting (815 cm^{-1}). All of these absorbances were identified for both the conventional and pulsed plasma polymers (with the exception of the polymerizable C=C double-bond features). In contrast, poor structural definition was evident for the plasma polymer film deposited under continuous wave conditions.

Strong similarities were also noted between the ^{1}H NMR spectra for conventional and pulsed plasma polymers (Figure 3). The following assignments can be made: C$\underline{H}_3$ (0.74 and 0.91 ppm), C$\underline{H}_2$ (1.8 ppm), C$\underline{H}_2$−OH (3.55 ppm), C$\underline{H}_2$O (3.87 ppm), and O$\underline{H}$ (4.78 ppm).

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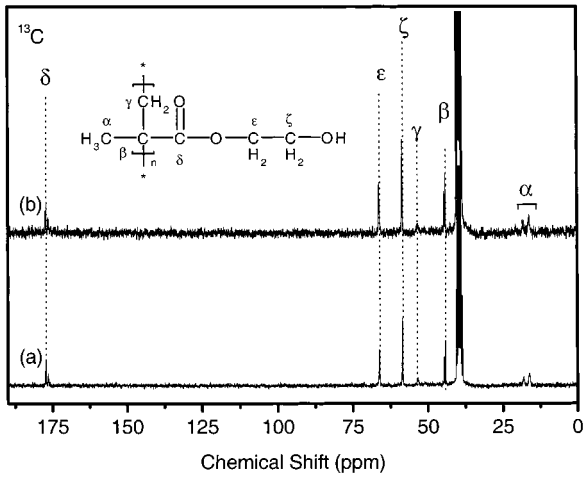


Figure 4. ^{13}C NMR spectra of (a) 2-hydroxyethyl methacrylate conventional polymer and (b) 2-hydroxyethyl methacrylate pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W). The off-scale signal is due to the methyl group present in the dimethyl sulfoxide solvent.

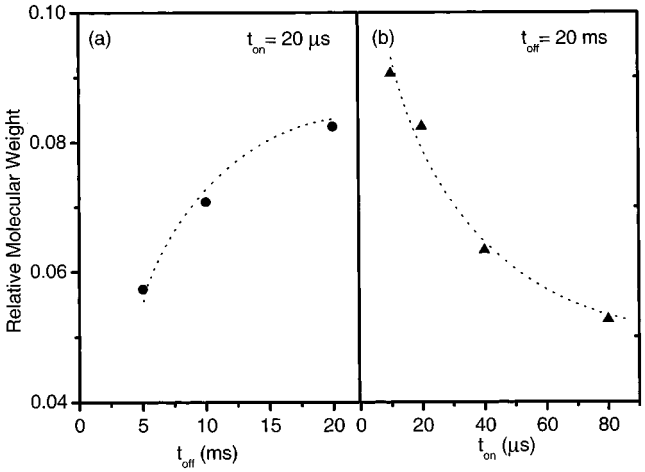


Figure 5. Variation of the ratio of the average molecular weight of the pulsed plasma polymers relative to the molecular weight of the reference conventional polymer as a function of duty cycle: (a) fixed t_{on} (peak power = 40 W) and (b) fixed t_{off} (peak power = 40 W).

A similar trend was noted for the ^{13}C NMR spectra (Figure 4). In this case, the following groups can be identified: C$\underline{H}_3$ (16.2 and 18.0 ppm), quaternary carbon (44.1 and 44.5 ppm), C$\underline{H}_2$ (55.0 ppm), C$\underline{H}_2$−OH (58.4 ppm), C$\underline{H}_2$−O−C (66.2 ppm), and C$\underline{=}$O (177.1 ppm).

Gel permeation chromatography (GPC) analysis of the pulsed plasma polymer films showed that they generally tended to have lower molecular weights compared to those of the reference conventional poly(HEMA) polymer employed in this investigation (Figure 5). There is also a clear trend in terms of how the molecular weight can be controlled by varying the pulsed plasma duty cycle (Figure 5). Shorter on-periods and longer off-periods lead to a higher molecular weight.

Water contact angle values of 17 ± 1° and 50 ± 2° were measured for the pulsed and continuous wave plasma polymer layers, respectively. This is consistent with greater structural retention (hydroxyl group incorporation) in the former case. Also, quartz crystal microbalance measurements showed a dramatic rise in weight following air exposure attributable to water

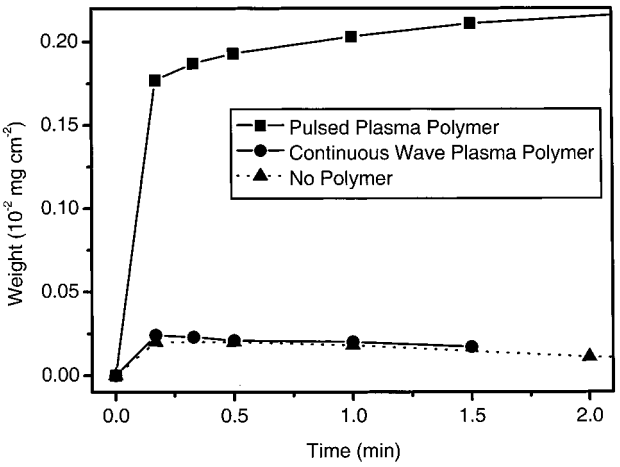
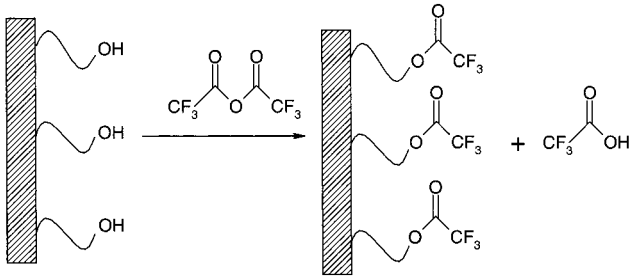


Figure 6. Variation of the weight of plasma polymer coatings following air exposure. (The weight of both types of deposited plasma polymer film prior to air exposure was 4.0×10^{-6} g cm^{-2}.)

Scheme 1. Reaction of Surface Hydroxyl Groups with Trifluoroacetic Anhydride



absorption from the laboratory atmosphere (Figure 6). The high concentration of hydroxyl groups in the pulsed plasma polymer film effectively means that this coating is behaving like a hydrogel.

(b) Surface Esterification. Surface hydroxyl concentration was determined via the esterification reaction with trifluoroacetic anhydride[26,27] (Scheme 1), followed by F(1s) XPS peak area analysis,

$$\%[F] = \frac{x[O]_0}{[C]_0 + [O]_0 + 2x[O]_0} \times 100 \qquad (1)$$

where x is the fraction of reacted hydroxyl groups, $[O]_0$ is the initial concentration of oxygen, $[C]_0$ is the initial concentration of carbon, and [F] is the percentage of fluorine detected by XPS at the surface. Similar reactivities were measured for the pulsed plasma polymer and spin-coated conventional poly(HEMA) films. The continuous wave plasma polymer exhibited comparatively low reactivity, which can be taken as being indicative of a smaller number of surface hydroxyl groups (Table 2). A corresponding trend was discernible in the C(1s) envelopes (Figure 7). The intensity of the CF_3 peak at 293.0 eV (indicative of reaction with trifluoroacetic anhydride) was found to be intense for the pulsed plasma and conventional polymer films,

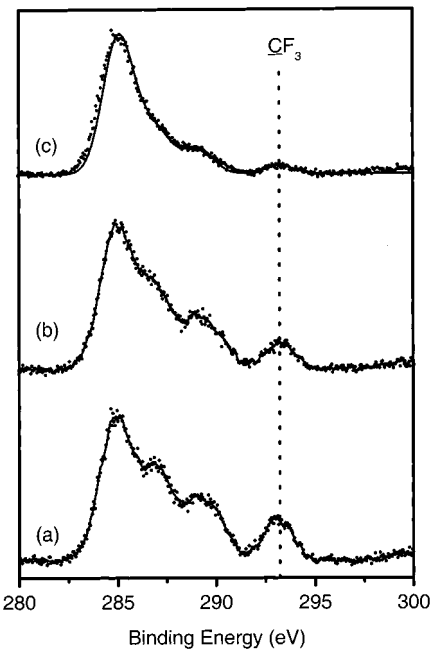


Figure 7. C(1s) XPS spectra of 2-hydroxyethyl methacrylate plasma polymers deposited onto a flat glass substrate and reacted with trifluoroacetic anhydride: (a) conventional polymer; (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W); and (c) 3-W continuous wave plasma polymer.

Table 2. XPS Elemental Analysis of 2-Hydroxyethyl Methacrylate Polymers Reacted with Trifluoroacetic Anhydride Vapor

polymer	%F	%C	%O	conversion x
theoretical	20	53.3	26.7	100
conventional	20 ± 2	54 ± 1	25.2 ± 0.1	100 ± 10
pulsed	17 ± 2	53.0 ± 0.2	23 ± 2	80 ± 12
CW	10 ± 2	67 ± 3	23 ± 2	52 ± 16

compared to the much lower level of chemical derivatization seen for the continuous wave deposited layer.

(c) Rhodium Complexation. Phosphine complexes of rhodium are widely employed for catalytic hydrogenation and hydroformylation reactions.[28,29] These complexes are often prepared using $RhCl_3$ as the precursor.[28] XPS analysis following reaction of diethyl chlorophosphite vapor with poly(HEMA) surfaces gave rise to the appearance of the P($2p_{3/2}$) peak at 132.7 eV (Scheme 2 and Table 3). A small amount of residual chlorine from either unreacted adsorbed reagent or HCl byproduct was also detected. The lower value for the conventional polymer is probably due to its higher molecular weight (lower chain mobility). The percentage of surface hydroxyl groups (x) that had reacted were calculated using the percentage of detected phosphorus following washing in 1,4-dioxane (%[P]):

$$\%[P] = \frac{\frac{1}{3}x[O]_0}{[C]_0 + [O]_0 + \frac{7}{3}x[O]_0} \times 100 \qquad (2)$$

This corresponded to 10 and 52% hydroxyl groups for

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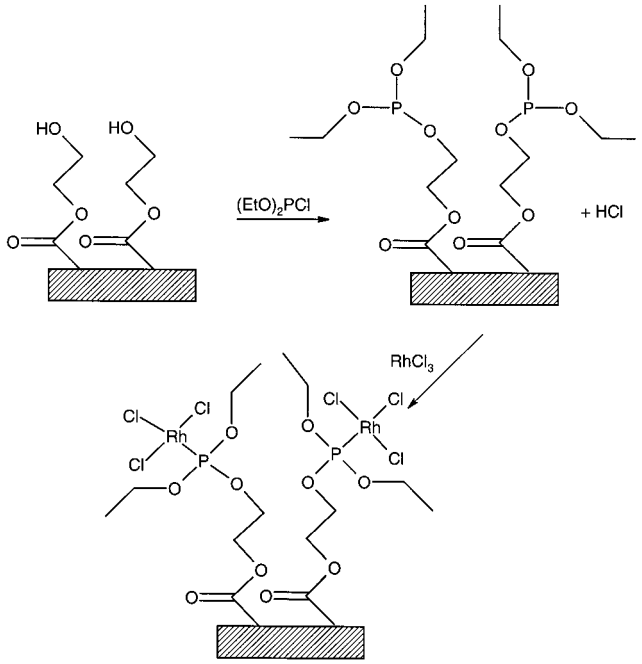
Table 3. XPS Elemental Analysis of 2-Hydroxyethyl Methacrylate Polymers Reacted with Diethyl Chlorophosphite

coating	%C	%Cl	%O	%P	%Rh	%Si
conventional + $(EtO)_2PCl$ unwashed	64 ± 2	0.90 ± 0.01	33 ± 2	2.50 ± 0.01	–	–
pulsed + $(EtO)_2PCl$ unwashed	60.8 ± 0.6	2.0 ± 0.4	31 ± 1	6 ± 1	–	–
CW + $(EtO)_2PCl$ unwashed	74 ± 4	0.35 ± 0.05	24 ± 4	1.0 ± 0.3	–	–
pulsed + $(EtO)_2PCl$ washed	64 ± 2	1.5 ± 0.7	30 ± 0.7	4 ± 1	–	–
CW + $(EtO)_2PCl$ washed	76 ± 3	–	23 ± 2	0.8 ± 1	–	–
pulsed + $(EtO)_2PCl$ + $RhCl_3$	54.2 ± 0.1	12.8 ± 0.3	24 ± 3	3.1 ± 0.3	4.0 ± 0.5	–
CW + $(EtO)_2PCl$ + $RhCl_3$	72.8 ± 0.6	1.8 ± 0.1	23.0 ± 0.1	–	0.7 ± 0.1	1.1 ± 0.5
pulsed + $RhCl_3$	69 ± 3	5 ± 2	25 ± 1	–	1.4 ± 0.7	–
CW + $RhCl_3$	75 ± 3	1.0 ± 0.2	24 ± 3	–	–	–

Scheme 2. Reaction of Surface Hydroxyl Groups with Diethyl Chlorophosphite Followed by Complexation of Rhodium Metal Centers



the continuous wave and the pulsed plasma polymer films, respectively. This type of phosphite ligand is known to readily coordinate catalytic rhodium centers.[30] To demonstrate the viability of carrying out such reactions at solid surfaces, the (diethyl phosphite)-functionalized poly(HEMA) plasma polymer films were reacted with $RhCl_3$. XPS analysis showed the appearance of a Rh(3d) doublet with the $3d_{5/2}$ peak at 310.6 eV corresponding to Rh(III) (Figure 8 and Table 3).[31] Also, it was found that there are 0.78 atoms of P for every atom of Rh (i.e., ≈1, as previously reported for bulky phosphite ligands[30]). A control experiment showed that the plasma polymer layer itself is capable of coordinating Rh species. However, this amount was much lower compared to when the diethyl phosphite group is also present at the surface (Table 3).

4. Discussion

Pulsed plasma polymerization is an effective method for incorporating specific reactive functionalities onto solid surfaces. The high level of structural retention observed for 2-hydroxyethyl methacrylate is consistent with polymerization proceeding via a conventional free radical mechanism during the pulsed plasma off-period, in conjunction with monomer activation during the on-period,[20] whereas extensive monomer fragmentation and rearrangement occurs during continuous wave conditions. The observed trend in pulsed plasma polymer molecular weight as a function of electrical discharge duty cycle can be explained on the basis of this reaction mechanism. Where the active species formed during the pulse time-on control the polymer chain growth during the off-period, greater chain scission (lower molecular weight) occurs when the time-on is increased. In addition, as the plasma on-time increases, the concentration of initiated monomers is greater, in which case termination by recombination will become more likely, thereby yielding lower molecular weight polymer.

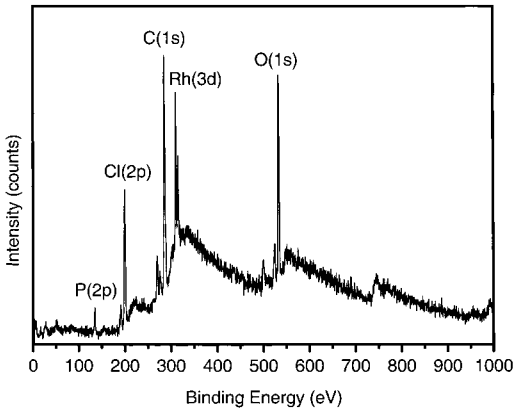


Figure 8. Wide scan XPS spectra of 2-hydroxyethyl methacrylate pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W) following reaction with diethyl chlorophosphite and then complexation to $RhCl_3$.

The hydroxyl groups present at the poly(HEMA) plasma polymer surface have been shown to readily undergo hydration, esterification, and also derivatization with diethyl chlorophosphite. The latter reaction has proven to be a useful method for immobilizing precious metal complexes onto solid surfaces for catalytic applications.

Conclusions

Pulsed plasma polymerization of 2-hydroxyethyl methacrylate provides a one-step solventless route for producing well-defined hydroxyl-functionalized solid surfaces. These surfaces can then be used as templates for carrying out conventional hydroxyl group derivatization reactions.

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