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Hyperthermal Intact Molecular Ions Play Key Role in Retention of ATRP Surface Initiation Capability of Plasma Polymer Films from Ethyl α-Bromoisobutyrate

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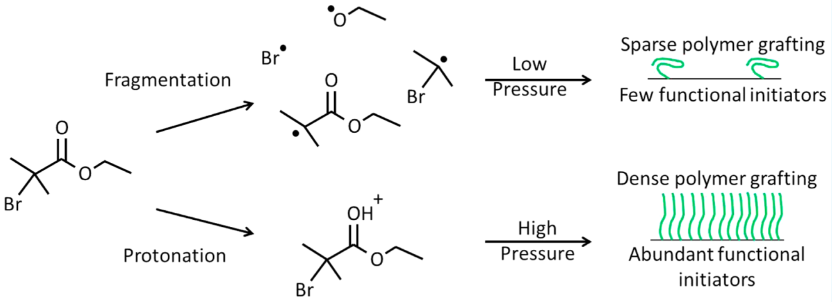

ABSTRACT: We report a systematic study of the plasma polymerization of ethyl α-bromoisobutyrate (EBIB) to produce thin film coatings capable of serving as ATRP initiation surfaces, for which they must contain α-bromoisobutyryl functional groups. In the deposition of polymeric coatings by plasma polymerization there generally occurs considerable fragmentation of precursor ("monomer") molecules in the plasma; and the retention of larger structural elements is challenging, particularly when they are inherently chemically labile. Empirical principles such as low plasma power and low pressure are usually utilized. However, we show that the α-bromoisobutyryl structural moiety is labile in a plasma gas phase and in low pressure plasma conditions, below the collisional threshold, there is little retention. At higher pressure, in contrast, fragmentation of this structural motif appears to be reduced substantially, and coatings useful for ATRP initiation were obtained. Mass spectrometry analysis of the composition of the plasma phase revealed that the desired structural moiety can be retained through the plasma, if the plasma conditions are steered toward ions of the precursor molecule. Whereas at low pressure the plasma polymer assembles mainly from various neutral (radical) fragments, at higher pressure the deposition occurs from hyperthermal ions, among which the protonated intact molecular ion is the most abundant. At higher pressure, a substantial population of ions has low kinetic energy, leading to "soft landing" and thus less fragmentation. This study demonstrates that relatively complex structural motifs in precursor molecules can be retained in plasma polymerization if the chemical and physical processes occurring in the plasma phase are elucidated and controlled such that desirable larger structural elements play a key role in the film deposition.

KEYWORDS: *hyperthermal polyatomic ions, molecular ion, plasma polymerization, ATRP, surface grafting, ethyl α-bromoisobutyrate, plasma analysis*

1. INTRODUCTION

The ability to control the chemical composition of the surface of materials and devices presents enormous opportunities for a wide range of applications, but there still are scientific challenges in developing exquisite control of surface chemistries, ultrathin coatings, and grafted layers of polymers and molecules.[1,2] An area of considerable interest is the grafting of polymeric layers onto and also from the surfaces of solid materials and nanostructures, for a variety of applications including sensors, biomedical devices, lab-on-a-chip platforms, microelectronics, and others.[3−5] Surface initiated atomic transfer radical polymerization (SI-ATRP) is one method for covalently grafting polymeric layers from material surfaces, enabling high graft-density polymer brushes to be obtained that can be used in a wide range of variations to achieve well-controlled/"living" polymer graft layers that enable structural complexity from the nano to the micro scale.[6,7]

For a solid material surface to be able to allow SI-ATRP grafting, a specific chemical motif is necessary for initiation: a terminal halogen bond that can be homolytically cleaved to result in an electronically stabilized radical.[8] Because materials do not natively possess this specific chemical arrangement, substrates must be prepared for ATRP initiation through derivatization reactions that attach this reactive halogen motif. Usually, materials have been functionalized with ATRP initiators via specific, complementary solution chemical

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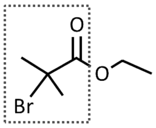
coupling techniques. Approaches have also been reported for producing substrate-independent, one-step, ATRP-ready surfaces, but they rely on multistep techniques to synthesize and purify first α-bromo-isobutyryl derivatives of silanes, thiols, xylylenes, and catechols, and their surface immobilization is tied to specific surface chemical groups such as silicates or noble metals, and/or is reliant on wet chemical immobilization or pyrolysis. For example, catechol-based adhesive compounds have been used to attach ATRP-active moieties onto substrate materials in wet-chemical dipping procedures,[9] and xylylene-based compounds can be conjugated with *tert*-butyl bromine moieties for use in chemical vapor deposition that polymerizes pyrolyzed compounds onto surfaces.[10] In each case, a conjugation reaction between the brominated compound and the facilitating molecule (xylylene or dopamine) is required first.

It would thus be highly desirable to develop methods for facile, one-step derivatization of a wide range of materials with ATRP initiation motifs; this would facilitate scale-up and eventual large-scale industrial use. The most interesting motif is the widely used α-bromo-isobutyryl entity, which is also the key structural element of the highly popular solution ATRP initiator ethyl α-bromoisobutyrate (EBIB; Scheme 1). This compound is sufficiently volatile for it to be usable in chemical vapor deposition. Using the method of plasma polymerization[11,12] to deposit thin coatings bearing α-bromo-isobutyryl surface groups would seem to be a promising route toward facile production of SI-ATRP-ready surfaces on a wide range of substrate materials, given the well-known fact that plasma polymer coatings coat uniformly and adhere well on a wide range of solid materials comprising polymers, metals, and ceramics.

Scheme 1. Molecular Structure of EBIB[a]



[a] The dashed box denotes the structural motif that must remain intact to enable initiation of surface-initiated ATRP.

To prepare ATRP surfaces, a previous study used plasma polymerization of 2-bromo-ethyl acrylate,[13] which, however, has a rather poor halogen leaving group and consequently the SI-ATRP grafting reaction is slow. EBIB has been utilized recently[14] to create SI-ATRP gradient surfaces. However, these studies were empirical, and fundamental understanding of how to retain such complex chemical structures in plasma deposition is lacking, nor is it established how to optimize the surface density of such initiator functional groups. The present work was thus undertaken so as to acquire fundamental understanding of key aspects of the plasma gas phase under various plasma conditions and how they affect to what extent the resultant coating bears the desired initiator motifs. Such understanding would, we expected, lead to rational design and optimization not only of EBIB plasma polymers but also other plasma coatings that need to retain fragile motifs through the plasma process, and assist in the transfer of ATRP initiation coatings to different plasma apparatus and eventual scale-up.

Although the process of plasma polymerization is attractive for its ability to deliver high-quality coatings on a wide range of substrates[15−17] and has been scaled up for a number of substantial industrial products,[18] plasma deposition is, however, often regarded as lacking specificity and resulting in cross-linked films that bear moderate resemblance to the starting monomer and to polymers prepared by conventional polymerization techniques.[11,12,19] Plasma polymerization usually entails extensive fragmentation of the volatile precursor molecule ("monomer") and reassembly of the various fragments from the plasma gas phase into a solid polymeric coating. Considerable scrambling of molecular structural elements is evident for *n*-heptylamine for example in the resultant plasma polymer showing a N content of the order of 7 to 9%, which means that a substantial fraction (30−50%) of amine groups are lost during deposition[20] and the retained N is a mix of primary, secondary, and tertiary amines. To reduce fragmentation and thus enhance retention of desirable chemical motifs, researchers have often used low power or pulsed plasma operation, as for example for carboxylic acid groups,[21] but these approaches also much reduce the deposition rate. Moreover, despite good carboxyl retention it is known that these materials lose much of the original hydrogen.[22] It is against this background that the challenge of getting a larger and inherently more labile chemical structure such as α-bromo-isobutyryl through a plasma gas phase and optimizing its surface density must be assessed, given the labile nature of the C−Br bromo-ester bond.

Often, researchers have used low pressure (collision-less regime) to achieve retention of desirable chemical groups in plasma polymers,[21,23] but others have obtained good retention of aldehyde and epoxy functional groups at higher pressure (collisional regime).[24,25] Thus, there is no consensus and hence no way to predict what might work best for plasma polymerizing EBIB with the aim of optimal retention of α-bromo-isobutyryl structures. Clearly, there is insufficient understanding of the complexity of plasma processes and consequently an inability to "tune" as required. Here we report how the plasma polymerization of EBIB varies markedly with pressure as the main variable; only the collisional regime produces EBIB plasma coatings that enable efficient surface-initiated ATRP. Analyses of the plasma gas phase revealed the causative plasma-chemical processes; to retain the fragile α-bromo-isobutyryl motif it is necessary to steer the plasma phase chemistry toward the intact molecular ion, deposition from ions rather than neutrals, and "soft landing" of ions. Such insights enable the tailoring of plasma deposition conditions toward optimal retention of desired functional structural elements in the feed vapor.

2. EXPERIMENTAL SECTION

Materials. Water was purified (>18 MΩ cm) by either a Millipore Gradient or EASYpure RoDi Ultrapure Water Purification System. Ethyl 2-bromoisobutyrate (EBiB, 98%), 2-hydroxyethyl methacrylate (HEMA, 98%), copper(I)bromide (99.99%), and copper(II) bromide (≥99%), were purchased from Sigma-Aldrich. Ethanol (100% undenatured and methanol (99.9%) were purchased from Chem-Supply and Merck.

Plasma Polymerization. Plasma polymer (pp) coatings from ethyl α-bromoisobutyrate (EBIB, 98%, Sigma-Aldrich) process vapor were deposited using a stainless steel vacuum chamber. The plasma reactor used has been described and characterized elsewhere.[28] The chamber was pumped down by a two-stage rotary pump to reach a base pressure below 0.002 mbar. EBIB "monomer" vapor was introduced into the chamber via a ball valve after degassing using liquid nitrogen. Then plasma was ignited using an RF power generator (13.56 MHz, RFG050 Coaxial Power Systems, UK) with a matching

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network (AMN150, Coaxial Power Systems, UK). Thin films discussed below were deposited at RF input power settings ranging from 5 to 50 W and under two different pressures of 0.02 and 0.08 mbar. Silicon wafers were used as substrates after solvent-cleaning with ethanol and acetone followed by drying under a stream of dry nitrogen.

ATRP Procedure. All experiments were carried out at room temperature. A glovebox with an antechamber was evacuated with a vacuum pump for approximately 10 min prior to being filled with nitrogen. EBIB plasma coated substrates were rinsed with water and dried using nitrogen and then transferred into the antechamber under a nitrogen atmosphere. A solution of HEMA (2.14 g) in water (13.86 g) was degassed using nitrogen bubbling for 5 min. In a separate container, CuBr (159.3 mg), 2,2-bipyridine (bpy) (488 mg), and $CuBr_2$ (72 mg) were combined.

All materials were transferred into the glovebox antechamber after 15 min of nitrogen purging. In the glovebox, CuBr, 2,2-bipyridine (bpy), and $CuBr_2$ were added to the degassed HEMA/water solution, and the solution turned dark brown. 4 mL aliquots of the solution were then placed into screw-capped vials containing the EBIB plasma coated substrates. These vials were then sealed and transferred to ambient atmosphere and placed on an orbital shaker (150 rpm). After the ATRP reaction was allowed to proceed for 18 h, the grafted samples were rinsed with methanol, ethanol, and water and dried under nitrogen.

Ellipsometery. The thickness of the deposited plasma polymer was determined using a J.A. Woollam (Model MC-200) V-Vase spectroscopic ellipsometer. Ellipsometry measurements of the EBIB/HEMA ATRP surfaces were conducted over a wavelength range of 400−1100 nm in 10 nm steps at alignment angles of 65°, 70°, and 75°. The experimental data were then fitted using the supplied modeling software WVASE32 (Ver. 3.770) using a Cauchy overlayer model on a silicon background. By refining the optical parameters, the mean squared error of the fit was minimized from which the EBIB thin film and EBIB/HEMA ATRP surfaces thickness were obtained.

Plasma Mass Spectrometry (MS). A quadrupole mass spectrometer (Hiden EQP1000 energy resolving mass spectrometer) was mounted along the reactor midline axis. A grounded 100 μm orifice was used during sampling. The system was differentially pumped during operation using a turbomolecular pump. The internal pressure remained below 3×10^{-7} mbar. The mass spectrometer was operated in residual gas analysis (RGA) and positive ion mode to acquire spectra of both plasma-phase neutral species, and ions, respectively. In addition, the ion energy distribution of the molecular ion at different RF powers was measured. The ion optics were tuned to give a maximum signal at the monomer molecular weight of 195 m/z. For RGA, neutral species entered the mass spectrometer and were ionised using an electron impact source at 100 μA and an energy of 70 eV. In positive ion mode, the ion optics were first tuned to the peak ion energy at each power for the protonated precursor by acquiring the ion energy distribution. The positive ion mass spectra were then collected at this peak ion energy in the range 0−400 m/z.

X-ray Photoelectron Spectroscopy (XPS). XPS was used to determine the chemical composition of the surface layers of the plasma polymer films. EBIB coated samples were analyzed using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) equipped with a monochromatic Al Kα source. Samples were analyzed at a photoelectron emission angle normal to the sample surface. Survey spectra were acquired at 120 eV pass energy and high-resolution C 1s spectra were recorded at 20 eV pass energy. Spectra with high resolution were recorded for C, Br, and O peaks. Quantifications of atomic percentages and curve fitting analysis were performed by Casa XPS software (ver. 2.3.16 Pre rel. 1.4, Casa Software Ltd.). Spectra were corrected by offsetting the binding energy relative to the C−C component of the C 1s spectrum, which was set to 285.0 eV.

OctIV Probe. The ion flux to the rf electrode was measured using an Impedans OctIV ion flux probe (Impedans, Dublin) placed in series between the matching network and the rf electrode. For a collisionless sheath, the ion flux is given by

$$\Gamma_i = 0.61 n_i \sqrt{\frac{kT_e}{M_i}}$$

where n_i is the ion density, k is Boltzmann's constant, T_e is the electron temperature, and M_i is the ion mass; so the ion flux is proportional to the ion density and electron temperature. For a homogeneous plasma then, although the ion energy may change due to bias voltages, the ion flux to all surfaces in contact with the plasma is constant.[27,26] Therefore, the ion flux to the substrate was taken to accord with the measured ion flux to the rf electrode.[28]

3. RESULTS AND DISCUSSION

As discussed above, existing literature did not allow prediction of which plasma conditions might be best for the production of EBIB plasma polymer coatings that would bear α-bromoisobutyryl functional groups on their surface and thus allow such films to be used as ATRP-initiating surfaces on a wide range of substrate materials. Varying the pressure of the plasma phase and varying the RF input power are commonly used to produce, from a given precursor ("monomer") molecule, a range of plasma-deposited films with differing properties. As shown previously,[29] the physics and chemistry of the plasma changes with pressure, with a marked shift at approximately 0.06 mbar. Below this pressure, ionization and fragmentation due to electron impacts with neutral species occur in the plasma bulk and the frequency of collisions in the sheath region close to surfaces is very low; ions are accelerated across the sheath voltage unimpeded and low energy electrons are repelled from the surface. This is termed the collision-less regime,[27] though strictly speaking the frequency of collisions is much reduced rather than zero. Above ~0.06 mbar (the collisional regime), several physical and chemical processes change. First, electrons in the bulk gain less energy between collisions due to the lower mean free path, which decreases the degree of ionization and fragmentation, and the bulk plasma density decreases. Importantly, in the sheath, collisions between ions, neutrals and electrons increase in frequency, opening the possibility for a variety of chemical reactions to occur in the sheath, including precursor molecule ionization and oligomer formation. Loss of energy due to ion/neutral collisions also decreases the energy of ions impacting the surface, which affects their probability of depositing on the surface[30] and ability to form reactive surface radical sites. Thus, the chemistry of the plasma and the dominant mechanism of deposition may both change with pressure. Accordingly, we initially performed plasma polymerization of EBIB at various pressure settings either side of the threshold pressure, but for the sake of conciseness, we here detail and compare EBIB pps and the characterization of their plasma gas phases at two pressures: 0.02 mbar ("low pressure", in the low collisions regime) and 0.08 mbar ("high pressure", in the collisional regime).

Indeed, we found that the plasma processing conditions markedly affected the resultant chemical nature and the utility of EBIB plasma polymers (pps). As shown in Table 1 for

Table 1. XPS Data Recorded with EBIB Plasma Polymers

sample	C (%)	O (%)	Br (%)
reference: EBIB molecule	66.7	22.2	11.1
EBIB pp 5 W/0.02 mbar	64.23	3.56	32.21
50 W/0.02 mbar	73.63	4.24	22.13
5 W/0.08 mbar	76.64	6.1	17.26
50 W/0.08 mbar	77.65	7.51	14.84

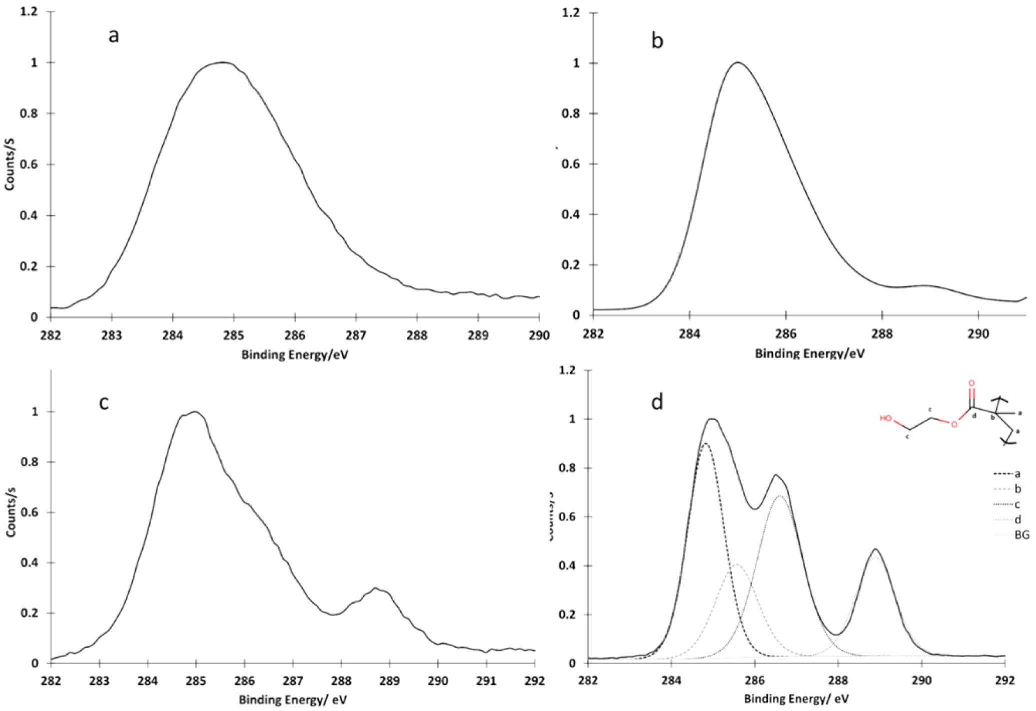


Figure 1. XPS C 1s spectra of (a) EBIB plasma polymer deposited at 0.02 mbar and 5 W, (b) EBIB pp deposited at 0.08 mbar and 50 W, (c) EBIB pp in panel a after HEMA ATRP, and (d) EBIB pp in panel b after HEMA ATRP.

representative EBIB pps deposited under low and high pressure conditions and at the two extremes of the RF power settings used, the compositions of EBIB pps vary markedly with plasma conditions. In all cases, however, the O content was much less than for the precursor molecule, indicating that there was substantial fragmentation of EBIB molecules in the plasma gas phase and considerable loss of the ester moiety; this is probably due to the ease of formation of CO_2 which then escapes reintegration into the growing pp films. In contrast, all EBIB pps showed a higher Br content than the original molecule; this Br content must arise from Br abstraction by cleavage of the C−Br bond in some of the molecules and subsequent incorporation of Br into the pp film. Thus, the XPS data indicate substantial fragmentation and scrambling of molecular structures in EBIB plasmas and preferential reduction of the content of some moieties, particularly the ester group, but they also suggest that this may be less pronounced under higher pressure conditions. For low pressure deposition, XPS data show the resultant pps to contain remarkably high percentages of Br (up to 33% atomic %) but oxygen incorporation was low (<5%), which indicates that <8% of the Br can still be within the original α-bromo-isobutyryl moiety. Films deposited at higher pressure, on the other hand, possessed more oxygen and less Br, yet the O/Br ratio was again substantially >1, indicating that the majority of the Br again was not part of the desired α-bromo-isobutyryl moieties but instead had been detached and then reattached elsewhere.

The low pressure EBIB pps were characterized by XPS C 1s spectra that did not contain substantial amounts of ester and carbonyl groups (Figure 1a) and led to sparse SI-ATRP of hydroxy-ethyl methacrylate (HEMA), with very thin graft layers (Figure 1), presumably due to a low surface density of α-bromo-isobutyryl initiation groups. This accords with the inference from XPS at. % data in Table 1 that the large majority of the Br found in these EBIB pps no longer is part of an α-bromo-isobutyryl moiety. In contrast, deposited from higher pressure plasmas, EBIB pps showed evidence of ester and carbonyl groups in XPS C 1s spectra (Figure 1b) and were able to initiate much denser grafting of HEMA (Figure 1d), using identical grafting conditions. Table 2 lists the thickness and atomic compositions of poly-HEMA graft layers.

Table 2. Elemental Compositions Measured by XPS and Thickness Measured by Ellipsometry of Poly-HEMA Graft Coatings on EBIB Plasma Polymers[a]

EBIB pp used for grafting onto	C (%)	O (%)	Br (%)	poly-HEMA graft thickness (nm)
5 W/0.02 mbar	78.14	17.78	4.08	9.3 ± 0.6
50 W/0.02 mbar	77.38	19.99	2.63	14 ± 1
5 W/0.08 mbar	74.6	25.4		24.3 ± 1.1
50 W/0.08 mbar	67.75	32.25		62.7 ± 0.6

[a] Thickness values are expressed as the average of three determinations with uncertainty of one standard deviation.

Thus, all EBIB pps were able to initiate some grafting of HEMA, but the differences in the amounts of grafted pHEMA suggest considerable differences in the surface densities of α-bromo-isobutyryl initiation groups on these pps. Interestingly, coatings found to be useful for SI-ATRP had a substantially lower Br content as observed by XPS. It is therefore clear that the amount of Br in the EBIB pps is not a measure of the retention of the desired α-bromo-isobutyryl groups through the plasma deposition process. Evidently, when plasma polymerization was performed in the lower pressure range, there occurred a high extent of cleavage of the C−Br bond in monomer molecules in the plasma; the Br atom was then retained in the plasma gas phase and eventually reacted with a radical (created by other fragmentation plasma reactions) to form a new C−Br bond, but this occurred nonspecifically at

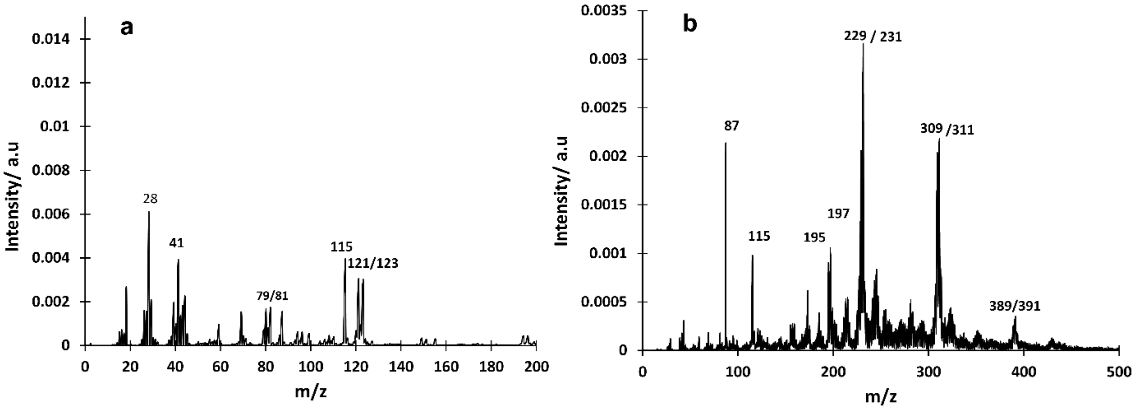


Figure 2. Plasma phase mass spectrometry of low pressure (0.02 mbar), 5 W EBIB plasma; neutral species (left) and positively charged ions (right).

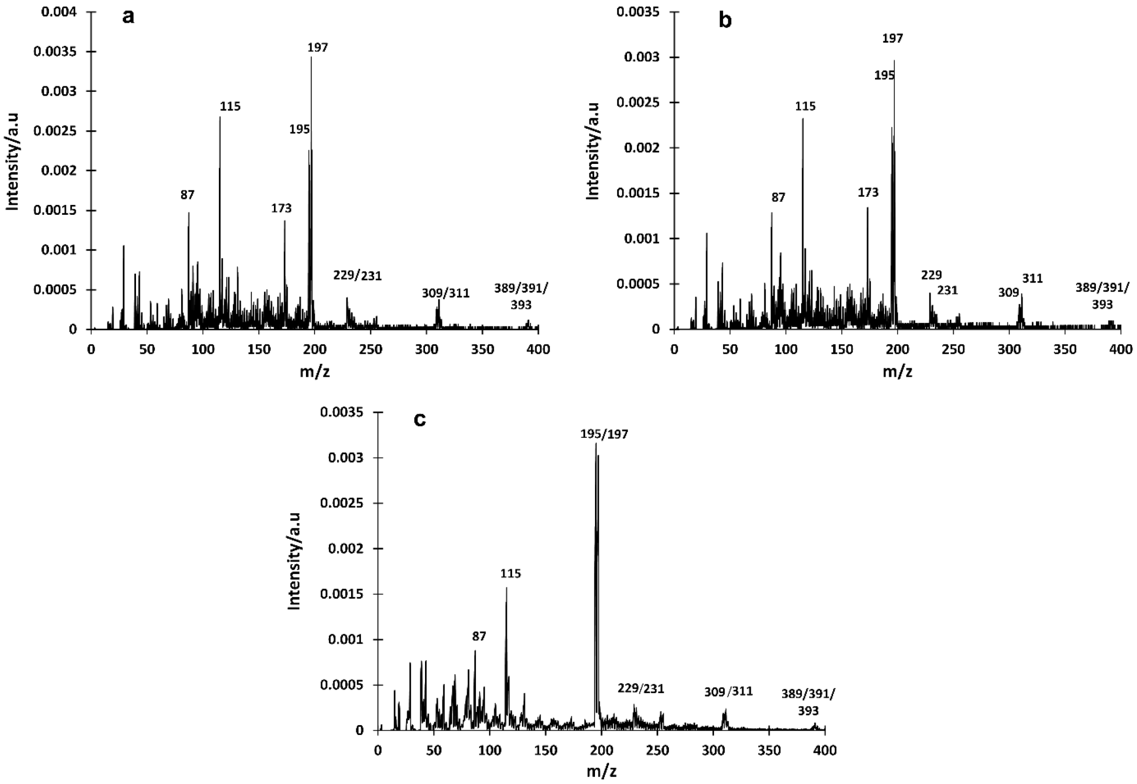


Figure 3. Mass spectra of positive ions in EBIB plasmas at 0.08 mbar and RF powers of (a) 5 W, (b) 10 W, and (c) 50 W.

various C atoms. Apparently, a substantial proportion of the terminal bromine atoms, the essential leaving group for ATRP, become eliminated from, or "scrambled" within, the α-bromo-isobutyryl structure, resulting in chemically ill-defined surface coatings that have limited ability to surface initiate ATRP for dense pHEMA layers. Such extensive fragmentation of the precursor molecules commonly occurs in the plasma polymerization of many monomers.

In contrast, when EBIB plasma polymers were deposited at pressures above the plasma collisional threshold, SI-ATRP-useful EBIB pps were obtained. Remarkably, thicker (denser) pHEMA graft layers were obtained on EBIB pps deposited at higher pressure and higher RF power settings, suggesting a higher density of surface initiation sites. Although fragmentation of monomer molecules might be offset at higher pressure (i.e., more molecules), the electrical sheath around surfaces becomes collisional and, consequently, higher pressure and higher power is not a regime ordinarily investigated when seeking retention of functional groups in plasma polymerization.

We tested whether the EBIB plasma polymers indeed allow SI-ATRP specifically through surface-located α-bromo-isobutyryl groups, or whether perhaps surface-located metastable radicals might play a nonspecific initiation role. To this end, ethyl isobutyrate (the analogue to EBIB but without a Br atom) was plasma polymerized under identical conditions. It was found that the EIB pp surface was incapable of SI-ATRP (data not shown).

Why would incorporation of the desired structural motif into the plasma polymer surface be much more efficient at higher pressure and, particularly contrasting with conventional wisdom, at higher power? Clearly, without understanding the interplay between plasma chemistry and physics behind monomer fragmentation and film deposition within an

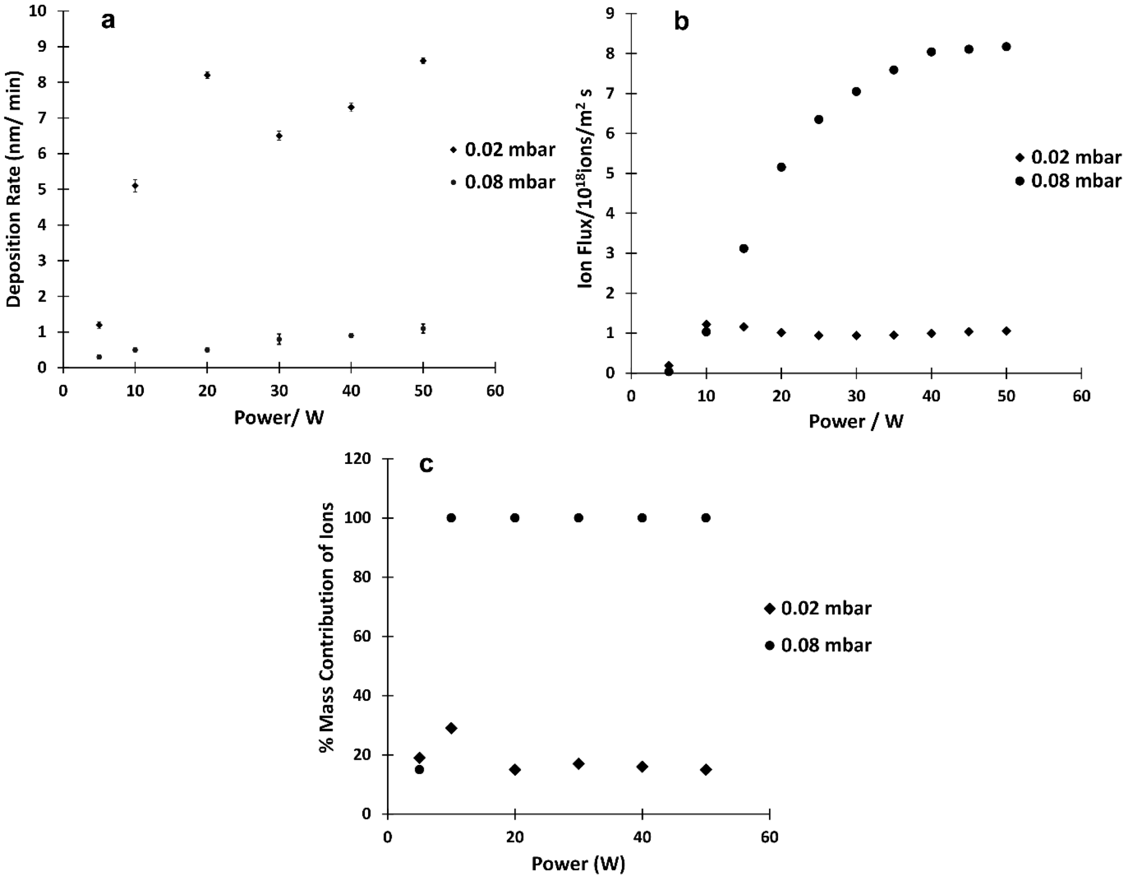


Figure 4. (a) Deposition rate measured by ellipsometry, assuming density of 1.2 g/cm^3. (b) Ion flux measured by an OctIV probe. (c) % Contribution of ions to the deposition; (◆) at 0.02 mbar, (●) at 0.08 mbar.

energetic plasma environment, we are not able to advance detailed interpretation, nor can we establish fundamental guidelines for rational optimization of the process. Accordingly, we performed detailed analyses of EBIB plasmas with the aim of elucidating principles for guided optimization of the deposition process and retention of the labile structural element, principles that might apply not only to EBIB but also to other delicate monomers.

Plasma phase mass spectrometry of the neutral species revealed marked differences between spectra recorded in the two pressure regimes (Figures 2 and 3). Under conditions of low pressure, the abundance of uncharged EBIB molecules is quite low, as shown by low intensity of the peaks at 194 and 196 m/z, attesting to significant fragmentation of the precursor molecule in the plasma, even under quite mild plasma conditions (Figure 2a). Peaks at m/z 79 and 81 (atomic Br) reveal a considerable extent of cleavage of the C−Br bond in the EBIB plasma. Accordingly, there are major peaks at 28, 41, 44, and 115 m/z, which do not contain Br and result from fragmentation of the precursor molecule. Among the fragments with significant intensity, only a fragment species assignable to α-bromoisobutyl (121/123 m/z) still contains Br, but having become detached from the ester group, this fragment, when included in the EBIB pp, does not confer ATRP initiation capability because it cannot stabilize a radical after Br abstraction for ATRP initiation. The only species seen in the neutral mass spectrum that still contains an ATRP-useful structural element is 149/151 m/z, which is produced by cleaving the C−O bond of the ester group in EBIB. This doublet signal is, however, of quite low intensity, consistent with the low density of surface groups capable of SI-ATRP in low pressure EBIB pps. Thus, this mass spectrum reveals considerable fragmentation of the EBIB molecule, in ways that break up the α-bromo-isobutyryl group. Hence the ensuing pp film deposition produces a chemically diverse composition with extensive scrambling of the original precursor (EBIB) chemical structure. The substantial amount of atomic Br produced in the plasma is highly reactive for reincorporation reactions and accords with the very high bromine content of the low pressure, low power plasma polymer surface.

The mass spectrum of the positive ions (Figure 2b), on the other hand, contains significant peaks assignable to protonated EBIB (at 195 and 197 m/z), which reveal that a measurable percentage of the EBIB precursor molecules can be retained intact in the plasma phase in a protonated form. The spectrum also shows that dimer ions are formed, as shown by a triplet signal at 389/391/393 m/z, though the intensity is rather low. Additionally, a major doublet at 309/311 m/z is also observed; it can be assigned to the dimer $(2M + H)^+$ that has lost a single Br atom. These ionic species contain the α-bromo-isobutyryl moiety, and if they are incorporated into the depositing plasma polymer film, they should endow the surface with functional sites for ATRP initiation. We note, however, that the most intense peak, at m/z 231, is assignable to a protonated dimer of EBIB minus both Br atoms, and other major peaks at m/z 87 and 115 also attest to the presence of protonated ions without an intact α-bromo-isobutyryl moiety. Thus, although evidently there is some fragmentation of the ionic species also, this is far less pronounced than for the neutrals; among the positive ions, several possess the ethyl isobutyrate structure, both as monomers and dimers and with and without one or both Br, respectively. In summary, although signals from ions without that functional group are more intense, there are positively charged ions that contain the α-bromo-isobutyryl structural motif, and their incorporation into the growing film could account for the (limited) initiation.

When EBIB pps are deposited at high pressure, mass spectrometry of the plasma phase shows that for the neutral species the spectrum (not shown) was similar to that recorded at low pressure and thus the same interpretation can be drawn, with various fragmentation pathways including production of Br. The mass spectra of the positive ions recorded with 0.08 mbar EBIB plasmas at various RF powers, on the other hand, differed substantially from their low pressure counterparts. As shown in Figure 3 for various applied RF powers the protonated precursor molecular ion signals are again observed at m/z = 195 and 197, and are in fact the most intense (base) peaks at all power settings. Thus, the intact protonated EBIB molecule is clearly the most abundant constituent among the protonated ions in the high pressure EBIB plasma phase, much more so than for the low pressure case. Protonated dimer ions with and without one or both Br are also evident but relatively much less abundant than at low pressure. Also observed are lower mass fragments that do not contain an intact α-bromo-isobutyryl group.

Remarkably, when the power is increased, the normalized intensity of the doublet peak assignable to the protonated EBIB molecule increases compared to the smaller fragments, in accord with the inference of less fragmentation based on the XPS data. This is inconsistent with the conventional empirical wisdom in plasma polymerization that low levels of applied RF power should be used to reduce the extent of fragmentation of precursor molecules in the plasma gas phase. At this point, we can conclude that the relative abundance of the ion signal assignable to the protonated intact molecular ion could explain the better capability for surface initiation and particularly its higher efficiency when higher RF power input was used during plasma polymerization.

Although the mass spectra do show significant differences between low and high pressure EBIB plasmas, in both cases the plasmas contain positive ions that contain the intact α-bromo-isobutyryl structural element, though the relative intensities differ substantially. The question arises whether the mass spectra can, by themselves, suffice to provide an interpretation for the marked differences in ATRP initiation capability of the EBIB pps deposited under the two pressure conditions. Hence we investigated another possible contributing factor. It is known that plasma polymers can be formed from plasma phase components that are neutral (uncharged) molecules or radicals, and also from charged molecules and radicals. The relative importance of neutrals versus ions in building plasma polymers appears to vary widely for different precursor molecules and with plasma conditions; it is not understood which factors in molecular structures lead to differences in the relative importance of neutrals versus ions. For allylamine, ions have been shown to increase in importance with an increase in plasma power, through an increase in the ion mass flux to mass flux ratio.[31]

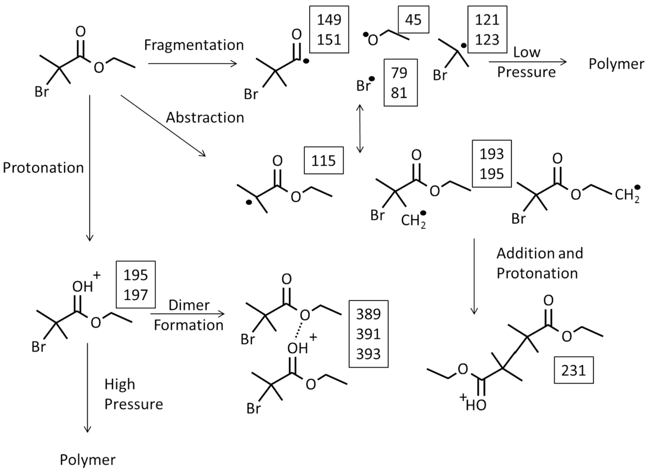
For EBIB plasma polymerization, the relative contributions of neutrals and ions were not predictable; accordingly, we measured the deposition rates and the ion fluxes to the surface. The data in Figure 4 compare the deposition rates of films of EBIB from high pressure plasma (0.08 mbar) with that of low pressure plasma (0.02 mbar) over the power range of 5 W (low) to 50 W (high). The ion flux data are also presented for both pressures. From these data, it can be appreciated that at low pressure the deposition rate is significantly greater than at high pressure. Conversely, above 10 W the ion flux at high pressure is much greater than that at low pressure. Comparing the results at 10 W for example, the ion fluxes are almost identical, but the deposition rate is approximately 10 times higher at low pressure. This indicates that substantially different mechanisms of deposition apply on the two sides of the collisional threshold pressure, with a marked difference in the relative contributions by neutrals and ions.

Using the ion flux data and average ion mass determined by plasma mass spectrometry, the ion mass flux can be determined.[32] Assuming a reasonable value for the sticking probability of ions with an energy in the range of 5−15 eV of 10%,[30] we can estimate the deposition rate due to ions. This can then be compared to the measured deposition rate to calculate the contribution of ions to the film deposition. The results of such calculations (Figure 4c) show that at low pressure, ions account for ∼15−30% of the deposited mass across all powers. In this case, 70−85% of the particles depositing on the surface are neutrals, which, as shown in Figure 2a, consist of various fragments that no longer contain intact α-bromo-isobutyryl groups.

In contrast, the deposition of EBIB pps at higher pressure is dominated by ionic species, among which the protonated intact molecular ion is most abundant. Thus, the growing pp film appears to be assembled to a large extent from intact protonated EBIB molecules, a conclusion which accords with the observed efficient surface initiation.

Scheme 2 summarizes the key processes occurring in EBIB plasmas and the ensuing film deposition. Fragmentation by impact-induced homolytic scission of C−C or C−O bonds produces a diversity of smaller radical fragments, as shown by the neutrals mass spectra. Abstraction of a H from a C−H bond or of Br produces radicals that can then fragment or combine. Larger uncharged entities produced by radical addition reactions appear to have limited stability in the plasma, as shown by their low abundance in neutrals mass spectra, but

Scheme 2. Key Processes Occurring in EBIB Plasmas and the Ensuing Film Deposition



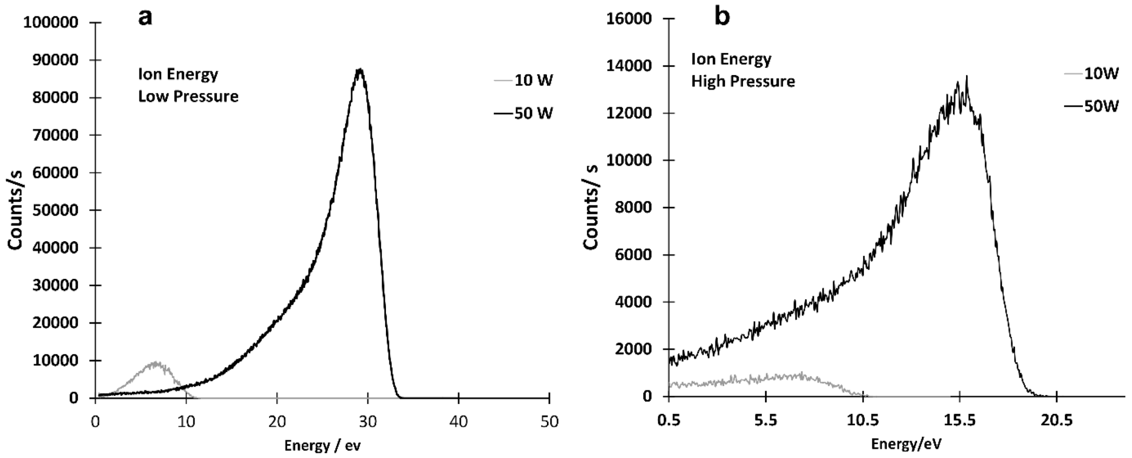


Figure 5. Distribution of ion energies arriving at a grounded surface from an EBIB plasma for pressures of (a) 0.02 and (b) 0.08 mbar and plasma power inputs of 10 and 50 W.

they are clearly visible after protonation. Only the protonated dimer produced by the combination of two molecules that both have lost their Br is shown in Scheme 2, as the signal at m/z 231 is prominent, but of course many other combinations are possible. However, some signals have masses that are not consistent with dimers produced by formation of a new C–C bond but, instead, are consistent with assignment to noncovalent dimers, as shown for the example of m/z 389, 391, and 393 (the triplet arising from the combinations of the two isotopes of Br). Protonation appears to be essential for holding together these noncovalent dimers, presumably via hydrogen bonding as shown. Such protonated cluster ions have been observed previously in low power, low pressure RF plasmas of acrylic and propionic acid using a selected ion flow tube.[33]

Scheme 2 also indicates the main species that are involved in the formation of the plasma polymers in the two pressure regimes. Again this schematic depiction is simplified, since Figure 4 indicates that there is a non-negligible contribution of ions to the deposition of EBIB pps at low pressure, but the intention is to emphasize the difference in the dominant process

Yet, the XPS data of Table 1 show that the high pressure EBIB pps have a composition that differs significantly from that of EBIB, and hence it would be erroneous to conclude, from the dominance of ionic deposition and the relative abundance of the protonated EBIB molecule, that the films form largely by condensation of protonated intact EBIB molecules (and charge neutralization reactions). The reason for this discrepancy may lie in processes that occur when the protonated EBIB molecules (and less abundant other ionic species) arrive at the surface.

In Figure 5 are shown the distribution of ion energies arriving at a grounded surface for plasma pressures of 0.026 and 0.08 mbar. For a power input of 50 W at the lower pressure, we see an ion energy distribution that is representative of a scenario wherein most of the ions originate from outside the sheath region and pass through the sheath without collision, giving a peak ion energy of 29 eV at 50W, with a low energy tail. At higher pressure, the sheath is largely collisional and the peak ion energy is ∼15.5 eV, with a more pronounced low energy tail. A large proportion of the ions at high pressure have ion energies below 10 eV, whereas the proportion of ions in this band at low pressure is very small. For a power input of 10 W, the ion energy is <10.5 eV at both pressures, but again the distribution differs, with the higher pressure leading to an extended tail of low energy ions.

The low energy of a significant population of the ions leads to their "soft landing"[34] and thus lessened probability of breakup of those desirable species when they impinge on the surface of the substrate and then that of the growing film. Comparing the two pressure regimes, the greater percentage of low energy ions arriving from the higher pressure plasma leads us to expect that the probability of retention of the intact α-bromo-isobutyryl structural motif upon impact onto the surface is significantly higher from a higher pressure plasma compared with a low pressure plasma. This effect also works toward a higher density of surface groups capable of surface initiation when depositing EBIB plasma polymers from a plasma in the collisional regime.

Hence, in summary, we can interpret the differences in EBIB plasma polymers deposited below and above the collisional plasma threshold, and their markedly different ability to initiate ATRP, as follows. The low pressure EBIB pps are assembled mainly from neutral species in the plasma gas phase, but those neutrals are, almost completely, low molecular weight fragments that do not possess intact α-bromo-isobutyryl groups. Among the positive ions, some do contain the intact α-bromo-isobutyryl structural motif, but the majority of the positive ions do not, and, moreover, the incorporation of ions into the growing pp is relatively inefficient. Thus, the resultant low pressure EBIB pps possess relatively low densities of α-bromo-isobutyryl groups on their surfaces and accordingly provide sparse initiation of ATRP.

In contrast, when the EBIB plasma polymerization is performed at 0.08 mbar, ions dominate the deposition process for power settings above 10 W. Among these positively charged ions, the most abundant is, as shown in Figure 4, the protonated intact EBIB ion. Moreover, lower average ion energy at higher pressure leads to softer landing and thus a reduced probability of fragmentation upon impact. Thus, there are three reasons why higher pressure EBIB pps possess a substantially higher surface density of intact α-bromo-isobutyryl groups.

This insight provides a rational means of optimizing the plasma polymerization of EBIB such as to maximize the retention of its desirable functional structural motif. Clearly, the protonated intact precursor ion confers SI-ATRP capability to the deposited film; accordingly, adjusting the external plasma conditions (pressure, power, as well as others not explored in this study, such as RF frequency) so as to maximize the intensity of this doublet signal in the positive ion mass spectrum of the plasma gas phase should result in the efficient optimization of plasma conditions when transferring the EBIB plasma polymerization process to different plasma systems and for industrial scale-up.

The combination of plasma phase mass spectrometry and analysis of the mechanisms of deposition indicates that using high pressure in the plasma promotes ionic deposition, and that we can use the protonated intact precursor ion signals at 195/197 m/z to optimize functional retention of the α-bromo-isobutyryl group. Thus, avoidance of a considerable extent of fragmentation of the monomer molecule, via collisions, and a significant and sustainable flux of these relatively large ions to the substrate surface are the key considerations for incorporating the α-bromo-isobutyryl structure into EBIB pp coatings for SI-ATRP utility. This major contribution by ions of the original "monomer" molecule in the plasma polymerization process is interesting and unprecedented; it should also be noted that these ions are "hyperthermal", as they are accelerated across a plasma sheath toward surfaces. The ion energy at high pressure is, however, below 20 eV for all RF powers tested here. When this energy is distributed among all bonds, this reduces the effect of molecular rearrangements on the surface due to ion sputtering,[35] creating "soft landings", as described by Hanley.[34]

The key role that the protonated molecular precursor ion plays in the film building process and "softer landing" due to collision-induced lower average ion energy provide a mechanistic explanation for why there is considerable incorporation of intact α-bromo-isobutyryl groups into high pressure EBIB films. Could, analogously, other plasma polymerization processes be optimized for functional group retention by using higher pressure conditions with dominant ionic deposition and retention of intact protonated precursor molecules through the plasma gas phase? Although often low power, low pressure conditions have been used in empirical studies of functional group retention, we note that other studies, again empirical, have used plasma conditions above the collisional threshold to generate coatings with intact functional groups such as epoxides[24] and aldehydes.[25] Perhaps molecular ions also played a key role in the successful retention of those groups. For the time being, we note the utility of mass spectrometry of the plasma gas phase for rational analysis and optimization, and speculate that the present finding of efficient functional group retention via protonated intact precursor ions in higher pressure plasmas might also be applicable to other monomers and thus provide a novel approach for the rational design of plasma conditions for plasma polymer coatings with high surface densities of various functional groups.

4. CONCLUSIONS

Plasma polymerization is a facile, industrially viable means of depositing coatings onto a wide range of substrate materials and hence is promising for the generation of thin coatings bearing functional groups capable of initiating surface grafting, to make materials ready for grafting polymer brushes. The retention of functional structures such as the α-bromo-isobutyryl group through a plasma deposition process is, however, challenging because organic molecules tend to fragment extensively in plasma gas phases. Plasma polymer films deposited from the "monomer" ethyl α-bromoisobutyrate exhibit substantial differences in their ability to initiate grafting, suggesting substantial differences in the surface density of intact α-bromo-isobutyryl groups on their surfaces.

Mass spectrometry analysis of EBIB plasmas shows substantial differences in the composition of EBIB plasma gas phases depending on the process pressure. Below the collisional threshold pressure, neutral species are mostly fragments that no longer bear an intact α-bromo-isobutyryl group, but among the positively charged ions there is a minority of ions that do possess that structure. In contrast, above the collisional threshold pressure the protonated intact precursor molecule is the most abundant ion, whereas the neutral species again are mostly small fragments. Analysis of the mechanism of deposition shows an even clearer difference: at higher pressure the film deposition occurs predominantly from ions, whereas at low pressure, neutrals account for ~85% of the film's mass. A third factor is the average ion energy: at higher pressure it is lower, leading to softer landing on the surface and hence less fragmentation.

Thus, plasma polymerization of EBIB at higher pressure leads to coatings with a much higher density of α-bromo-isobutyryl groups because the protonated EBIB ion is much more abundant in the plasma gas phase, the deposition becomes predominantly reliant on ionic species, and the lower average ion energy leads to reduced fragmentation upon surface impact. Interestingly, and contrary to empirically derived conventional wisdom in plasma polymerization, low power was not best; the molecular ion became more abundant at higher RF powers. This study thus demonstrates a novel, unique, and rational approach for the preparation of plasma polymers with functional surface groups, supported by detailed analyses of physical and chemical processes in the plasma gas phase. This approach might open up a novel avenue for the plasma polymerization of other fragile starting compounds, by optimizing at high pressure/moderate power the arriving flux and softer landing of desired ions.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Matyjaszewski, K.; Tsarevsky, N. V. Nanostructured Functional Materials Prepared by Atom Transfer Radical Polymerization. *Nat. Chem.* **2009**, *1*, 276−288.

(2) Wang, J. S.; Matyjaszewski, K. Controlled/" Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.

(3) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. Polymer Brushes Via Surface-Initiated Polymerizations. *Chem. Soc. Rev.* **2004**, *33*, 14−22.

(4) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühe, J. *Polymer Brushes*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004.

(5) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H. A. Polymer Brushes Via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, And Applications. *Chem. Rev.* **2009**, *109*, 5437−5527.

(6) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. Polymer Brushes by Atom Transfer Radical Polymerization. In *Polymer Brushes*; Advincula, R. C., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004.

(7) Matyjaszewski, K.; Tsarevsky, N. V. Macromolecular engineering by atom transfer radical polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 6513−6533.

(8) Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; Matyjaszewski, K. Understanding Atom Transfer Radical Polymerization: Effect of Ligand and Initiator Structures on the Equilibrium Constants. *J. Am. Chem. Soc.* **2008**, *130*, 10702−10713.

(9) Zhu, B.; Edmondson, S. Polydopamine-Melanin Initiators for Surface-Initiated ATRP. *Polymer* **2011**, *52*, 2141−2149.

(10) Jiang, X. W.; Chen, H. Y.; Galvan, G.; Yoshida, M.; Lahann, J. Vapor-Based Initiator Coatings for Atom Transfer Radical Polymerization. *Adv. Funct. Mater.* **2008**, *18*, 27−35.

(11) Kitching, K. J.; Pan, V.; Ratner, B. D.; Biederman, H. *Plasma Polymer Films*; Imperial College Press: London, 2004.

(12) Flamm, D. L.; Auciello, O. *Plasma Deposition, Treatment, and Etching of Polymers: The Treatment and Etching of Polymers*; D 'Agostino, R., Ed.; Academic Press: Cambridge, 2012.

(13) Teare, D. O. H.; Barwick, D. C.; Schofield, W. C. E.; Garrod, R. P.; Ward, L. J.; Badyal, J. P. S. Substrate-Independent Approach for Polymer Brush Growth by Surface Atom Transfer Radical Polymerization. *Langmuir* **2005**, *21*, 11425−11430.

(14) Coad, B. R.; Styan, K. E.; Meagher, L. One Step ATRP Initiator Immobilization on Surfaces Leading to Gradient-Grafted Polymer Brushes. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7782−7789.

(15) Decoste, J. B.; Peterson, G. W.; Smith, M. W.; Stone, C. A.; Willis, C. R. Enhanced Stability of Cu-BTC MOF Via Perfluorohexane Plasma-Enhanced Chemical Vapor Deposition. *J. Am. Chem. Soc.* **2012**, *134*, 1486−1489.

(16) Min, Y. S.; Bae, E. J.; Oh, B. S.; Kang, D.; Park, W. Low-Temperature Growth of Single-Walled Carbon Nanotubes By Water Plasma Chemical Vapor Deposition. *J. Am. Chem. Soc.* **2005**, *127*, 12498−12499.

(17) Im, S. G.; Bong, K. W.; Kim, B. S.; Baxamusa, S. H.; Hammond, P. T.; Doyle, P. S.; Gleason, K. K. Patterning Nanodomains with Orthogonal Functionalities: Solventless Synthesis of Self-Sorting Surfaces. *J. Am. Chem. Soc.* **2008**, *130*, 14424−14425.

(18) Roy, S.; Chen, X.; Li, M.H.; Peng, Y.; Anariba, F.; Gao, Z. Mass-produced nanogap sensor arrays for ultrasensitive detection of DNA. *J. Am. Chem. Soc.* **2009**, *131*, 12211−12217.

(19) Michelmore, A.; Steele, D. A.; Whittle, J. D.; Bradley, J. W.; Short, R. D. Nanoscale Deposition of Chemically Functionalised Films Via Plasma Polymerisation. *RSC Adv.* **2013**, *3*, 13540−13557.

(20) Gengenbach, T. R.; Chatelier, R. C.; Griesser, H. J. Characterization of the Ageing of Plasma-deposited Polymer Films: Global Analysis of X-ray Photoelectron Spectroscopy Data. *Surf. Interface Anal.* **1996**, *24*, 271−281.

(21) O'Toole, L.; Beck, A. J.; Short, R. D. Characterization of Plasma Polymers of Acrylic Acid And Propanoic Acid. *Macromolecules* **1996**, *29*, 5172−5177.

(22) Peter, S.; Graupner, K.; Grambole, D.; Richter, F. Comparative Experimental Analysis of The aC: H Deposition Processes Using CH {Sub 4} And C {Sub 2} H {Sub 2} As Precursors. *J. Appl. Phys.* **2007**, *102*, 053304.

(23) Beyer, D.; Knoll, W.; Ringsdorf, M.; Wang, J. H.; Timmons, R. B.; Sluka, P. Reduced Protein Adsorption on Plastics via Direct Plasma Deposition of Triethylene Glycol Monoallyl Ether. *J. Biomed. Mater. Res.* **1997**, *36*, 181−189.

(24) Thierry, B.; Jasieniak, M.; de Smet, L. C. P. M.; Vasilev, K.; Griesser, H. J. Reactive Epoxy-Functionalized Thin Films by a Pulsed Plasma Polymerization Process. *Langmuir* **2008**, *24*, 10187−10195.

(25) Coad, B. R.; Scholz, T.; Vasilev, K.; Hayball, J. D.; Short, R. D.; Griesser, H. J. Functionality of proteins bound to plasma polymer surfaces. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2455−2463.

(26) Michelmore, A.; Whittle, J. D.; Short, R. D.; Boswell, R. W.; Charles, C. An Experimental and Analytical Study of an Asymmetric Capacitively Coupled Plasma Used for Plasma Polymerization. *Plasma Processes Polym.* **2014**, *11*, 833−841.

(27) Liebermann, M. A; Lichtenberg, A. J. *Principles of Plasma Discharges and Materials Processing*, 2nd ed.; John Wiley & Sons. Inc: New York, 2005.

(28) Barton, D.; Shard, A. G.; Short, R. D.; Bradley, J. W. The Effect of Positive Ion Energy on Plasma Polymerization: A Comparison between Acrylic and Propionic Acids. *J. Phys. Chem. B* **2005**, *109*, 3207−3211.

(29) Saboohi, S.; Jasieniak, M.; Coad, B. R.; Griesser, H. J.; Short, R. D.; Michelmore, A. Comparison of Plasma Polymerization under Collisional and Collision-less Pressure Regimes. *J. Phys. Chem. B* **2015**, *119*, 15359−15369.

(30) Brookes, P. N.; Fraser, S.; Short, R. D.; Hanley, L.; Fuoco, E.; Roberts, A.; Hutton, S. J. The Effect of Ion Energy on The Chemistry of Air-Aged Polymer Films Grown from The Hyperthermal Polyatomic Ion Si 2 Ome 5+. J. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *121*, 281−297.

(31) Beck, A. J.; Candan, S.; Short, R. D.; Goodyear, A.; Braithwaite, N. S. J. The Role of Ions In The Plasma Polymerization of Allylamine. *J. Phys. Chem. B* **2001**, *105*, 5730−5736.

(32) Beck, A. J.; France, R. M.; Leeson, A. M.; Short, R. D.; Goodyear, A.; Braithwaite, N. S.J. Ion Flux and Deposition Rate Measurements in the Rf Continuous Wave Plasma Polymerisation of Acrylic Acid. *Chem. Commun.* **1998**, 1221−1222.

(33) Mayhew, C. A.; Short, R. D. Selected Ion Flow Tube Studies to Investigate the Formation of Acrylic And Propionic Acid Protonated Clusters in Low Power, Low Pressure RF Plasmas. *Chem. Commun.* **2009**, 659−661.

(34) Hanley, L.; Fuoco, E.; Wijesundara, M. B. J.; Beck, A. J.; Brookes, P. N.; Short, R. D. Chemistry and Aging of Organosiloxane and Fluorocarbon Films Grown From Hyperthermal Polyatomic Ions. *J. Vac. Sci. Technol., A* **2001**, *19*, 1531−1536.

(35) Jacobs, D. C. Reactive Collisions of Hyperthermal Energy Molecular Ions with Solid Surfaces. *Annu. Rev. Phys. Chem.* **2002**, *53*, 379−407.

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