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Initiated chemical vapor deposition of polyvinylpyrrolidone-based thin films

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Abstract

Initiated chemical vapor deposition (iCVD) is used for the first time to deposit a non-acrylic carbon-based polymer, polyvinylpyrrolidone (PVP). PVP is known for its hydrophilicity and biocompatibility, and its thin films have found many applications in the biomedical community, one of which is as antibiofouling surfaces. From vapors of 1-vinyl-2-pyrrolidone (VP) and *tert*-butyl peroxide (TBPO), iCVD produces PVP thin films that are spectroscopically identical to bulk PVP without using any solvents. iCVD works by selectively fragmenting gaseous TBPO with heat to create radicals for initiation of polymerization. This selectivity ensures that the monomer VP does not disintegrate to form species that do not conform to the structure of PVP. Fourier-transform infrared (FTIR), nuclear magnetic resonance, and X-ray photoelectron spectroscopy (XPS) show full retention of the hydrophilic pyrrolidone functional group. Number-average molecular weights range between 6570 and 10,200 g/mol. The addition of ethylene glycol diacrylate (EGDA) vapor to the reaction mixture creates a cross-linked copolymer between VP and EGDA. Films with different degrees of cross-linking can be made depending on the partial pressures of the species. Methods for quantifying the relative incorporation of VP and EGDA using FTIR and XPS are introduced. The film with the lowest degree of cross-linking has a wetting angle of 11°, affirming its high hydrophilicity and iCVD's ability to retain functionality.

Keywords: Chemical vapor deposition; Polyvinylpyrrolidone; Polymer thin films

1. Introduction

Initiated chemical vapor deposition (iCVD) is a novel technique for depositing polymer thin films. In contrast to plasma-enhanced chemical vapor deposition (PECVD), which is a common dry technique for polymer thin-film synthesis, iCVD does not use an electric discharge but instead thermal energy for the initiation of polymerization. The absence of electric discharge prevents undesired bond dissociation in the gas phase and allows films with high structural integrity to be made. For instance, iCVD has been used to deposit thin films of poly(2-hydroxyethyl methacrylate) (PHEMA) [1], poly(methyl methacrylate) [2], poly(cyclohexyl methacrylate) [3], and poly(glycidyl methacrylate) [4] that are spectroscopically indistinguishable from their bulk counterparts. The ability to retain chemical functionality to a high extent allows iCVD, a dry technique, to compete with spin-on deposition (SOD), a wet process, for thin-film applications that require the structures of the polymers to be well defined. While SOD is easy to use, iCVD offers many advantages. Chemical vapor deposition (CVD) allows films of nanoscale thicknesses with macroscale uniformity to be produced and can be applied to not only flat surfaces but also complex geometries [5]. In addition, there are no surface tension or non-uniform wetting effects, so films can be made on surfaces with nanoscale features. Most distinctively, CVD is able to coat materials that would otherwise dissolve in SOD. This advantage has motivated research in using CVD polymer coatings for encapsulation to control drug release rates [6].

The work in this paper extends iCVD's capability to deposit carbon-based polymers beyond polymethacrylates. Polyvinylpyrrolidone (PVP) is an important biopolymer and has found extensive use in the pharmaceutical industry because of its biocompatible properties [7]. For example, it is used as an

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implant coating to diminish non-specific interactions and prevent irreversible adsorption of proteins and cells to the surface, which can cause implant rejection, infection, and inflammation [8–10].

While PECVD has been researched as a technique for depositing PVP [8,11–13], iCVD can be regarded as complementary when the requirement for structural integrity is stringent and/or custom copolymers with well-defined compositions are needed. The ability of iCVD to control the degree of cross-linking via adjustment of flow conditions has been documented in the deposition of cross-linked PHEMA [1]. In order for PVP to be used as a coating in an aqueous environment, it has to be cross-linked or copolymerized with a comonomer. In this paper, a one-step iCVD process to make cross-linked PVP thin films is presented. In contrast, SOD is unable to produce as-deposited, cross-linked films, and post-treatment is necessary to achieve cross-linking.

This paper first reports the deposition of PVP homopolymer, which makes use of 1-vinyl-2-pyrrolidone (VP) as the monomer and *tert*-butyl peroxide (TBPO) as the initiator (Fig. 1). Thermal energy inside a vacuum chamber breaks down TBPO to form radicals to initiate polymerization of VP. Details of the mechanistic aspects of iCVD can be found elsewhere [1,4]. The second part of the paper is concerned with the addition of ethylene glycol diacrylate (EGDA, Fig. 1) as a cross-linker. The spectral properties of both linear and cross-linked films as well as the technique for quantifying the incorporation of EGDA are discussed.

2. Experimental methods

Films were deposited on 100-mm-diameter silicon (Si) substrates in a custom-built vacuum reactor (Sharon Vacuum). The reactor was cylindrical with a height of 3.3 cm and a radius of 12 cm. The inlet of precursor gases and the exhaust were at opposite ends of the reactor. The top of the reactor was covered by a removable quartz plate (∼15 cm radius and 2.5 cm thick), allowing visual inspection, laser interferometry, and placement of substrate. The reactor was equipped with a filament array, which provided thermal energy for selective decomposition of molecules, and a backside-cooled stage (35 °C) on which the substrate was placed. The clearance between the filaments and the stage was 29 mm. The Nichrome filaments (80% Ni/20% Cr, AWG 26, Omega Engineering) were resistively heated to 280 °C, as measured by a thermocouple (Type K, AWG 36, Omega Engineering) directly attached to one of them. The reactor pressure was maintained at a set value with a throttling butterfly valve (Intellisys, Nor-Cal).

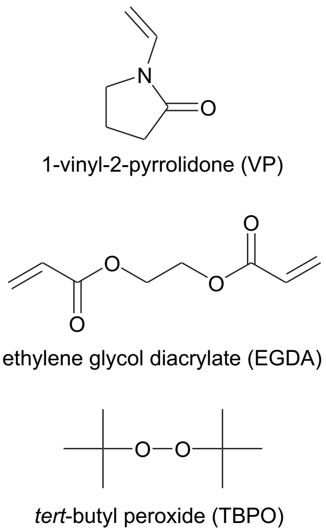

Fig. 1. Monomer, cross-linker, and initiator used in this study.

The monomer VP (99.0%+, Aldrich) and the cross-linking agent EGDA (90%, Aldrich) and the initiator TBPO (98%, Aldrich) were used without further purification. VP and EGDA liquids were vaporized in glass jars that were maintained at 80 ± 1 and 65 ± 1 °C, respectively. VP and EGDA vapors were metered into the reactor through mass-flow controllers (Model 1152C, MKS). TBPO was maintained at room temperature in a glass jar, and its vapor was also metered into the reactor through a mass-flow controller (Model 1479A, MKS). All vapors were mixed together before entering the reactor through a side port. Depositions were monitored using an interferometry system equipped with a 633-nm HeNe laser source (JDS Uniphase). The cycle thickness was calculated by dividing the actual thickness, as measured using variable-angle spectroscopic ellipsometry (VASE), by the number of interferometric cycles. VASE was performed on a J. A. Woollam M-2000 spectroscopic ellipsometer with a xenon light source. Data were acquired at three angles (65°, 70°, and 75°) and 225 wavelengths, and the Cauchy–Urbach model was used to fit the data.

Two series of films were prepared. For the homopolymer experiments (linear PVP, denoted L1–L5 in Table 1), no EGDA was introduced into the reactor. The flow rate of VP was varied between 5 and 7 sccm in increments of 0.5 sccm, whereas that of TBPO was kept constant at 1 sccm. A patch flow of nitrogen was also introduced into the reactor to keep the total flow rate at 10 sccm. This arrangement ensured the same residence time of 5 s for all experimental runs. The pressure was maintained at 500 mTorr for this set of films. For the cross-linking experiments (cross-linked PVP, denoted X1–X5 in Table 1), both the flow rates of VP and EGDA were varied

Table 1
Details of experimental runs

Sample	Flow rate (sccm)				Partial pressure (mTorr)	
	VP	EGDA	TBPO	N_2	VP	EGDA
Linear series (500 mTorr)						
L1	7.0	–	1.0	2.0	350.0	–
L2	6.5	–	1.0	2.5	325.0	–
L3	6.0	–	1.0	3.0	300.0	–
L4	5.5	–	1.0	3.5	275.0	–
L5	5.0	–	1.0	4.0	250.0	–
Cross-linked series (420 mTorr)						
X1	10.0	0.0	1.0	1.0	350.0	0.0
X2	9.5	0.5	1.0	1.0	332.5	17.5
X3	9.0	1.0	1.0	1.0	315.0	35.0
X4	8.5	1.5	1.0	1.0	297.5	52.5
X5	8.0	2.0	1.0	1.0	280.0	70.0

while those of TBPO and nitrogen were kept constant. The total flow rate was maintained at 12 sccm. The reactor pressure was 420 mTorr for cross-linked films. All runs were carried out to produce films with thicknesses of ~1.4 μm.

Fourier-transform infrared (FTIR) measurements were performed on a Nicolet Nexus 870 ESP spectrometer in normal transmission mode using a DTGS KBr detector over the range of 400–4000 cm^{-1} at a 4-cm^{-1} resolution averaged over 64 scans. All spectra were baseline corrected and normalized to a thickness of 1 μm (intensity divided by thickness). No other processing was performed on the spectra. X-ray photoelectron spectroscopy (XPS) was done on a Kratos Axis Ultra spectrometer equipped with a monochromatized Al Kα source. Solution-phase proton nuclear magnetic resonance (NMR) spectroscopy was carried out in a Varian Unity 300 spectrometer at 300 MHz. The polymer was scraped off from the Si substrate and subsequently dissolved in deuterium oxide (D_2O) for NMR spectroscopy. Wetting-angle measurements were performed on a goniometer equipped with an automatic dispenser (Model 500, Ramé-Hart). Samples L1 and L5 were submitted to Polymer Standards Service-USA, Inc. (Warwick, RI), for gel permeation chromatography (GPC). Dimethylformamide (DMF) with 5 g/L lithium bromide (LiBr) was used as the eluent in PSS-Gram 30, 3000 Å 10 μm column (ID 8 mm × 300 mm). The analysis was performed at 70 °C with TSP P100 HPLC pump at a flow of 1.0 mL/min and an injection volume of 100 μL. Shodex Refraktometer RI-71 was used as the detector. Polystyrene standards dissolved in DMF with 5 g/L LiBr were used for calibration.

As a reference, a PVP standard was obtained from Aldrich (PVP360) and was dissolved in water and cast onto a Si substrate for FTIR and XPS analyses. The same standard was dissolved in D_2O for NMR spectroscopy.

3. Results and discussion

3.1. Deposition of polyvinylpyrrolidone homopolymer

3.1.1. Spectral properties

Fig. 2 compares the FTIR spectra of sample L3 and the PVP standard obtained from Aldrich. All samples in the linear series have identical FTIR spectra. As seen in the figure, the iCVD-synthesized polymer is spectroscopically indistinguishable from conventionally polymerized PVP. The retention of the pyrrolidone functionality in the iCVD film is evident for the strong intensity of carbonyl (C=O) stretching centered at approximately 1682 cm^{-1}, close to the previously reported 1678 cm^{-1} for PVP [14]. The absence of a distinct peak at 1631 cm^{-1}, the position of the strong absorption of the vinyl bond of the monomer [14], signifies that polymerization has indeed occurred.

The polymer was also characterized using XPS. Fig. 3 shows the high-resolution scans of the C 1s core level of both sample L3 and the PVP standard obtained from Aldrich. Both scans show four carbons of different oxidation states, consistent with the structure of the polymer. As can be seen, the two spectra match very well with each other in terms of binding energies and peak positions. Quantitative comparison of the two spectra and data regarding the O 1s and the N 1s scans are provided in Table 2.

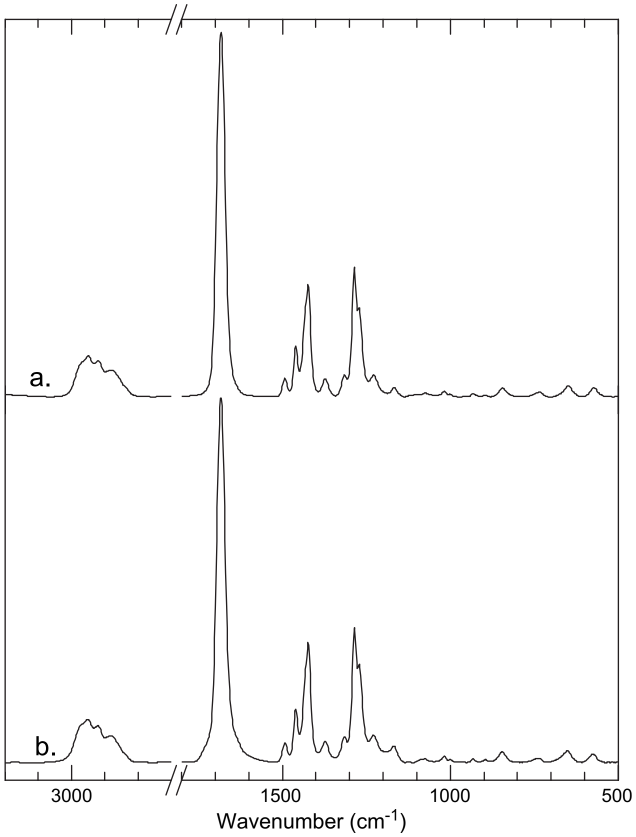

Fig. 2. Absorbance infrared spectra of (a) iCVD PVP film (sample L3) and (b) PVP standard obtained from Aldrich.

Fig. 4 shows the solution proton NMR spectra of both sample L3 and the PVP standard obtained from Aldrich. The ability of iCVD to produce linear polymers allowed sample L3 to be dissolved in D_2O for NMR analysis. The spectra are virtually identical except for the presence of some additional sharp peaks in the iCVD spectrum. These sharp peaks at 4.5, 3.5, and 2.4 ppm align well with the peaks in the monomer spectrum (not shown, Sigma–Aldrich P/N V3409) and are therefore due to the presence of monomer absorbed in the film during the iCVD process. A repeat analysis yielded the same spectrum with the same additional peaks.

In addition to FTIR, XPS, and NMR analyses, GPC also shows that the resulting materials are indeed polymers. Sample L5 has a number-average molecular weight (M_n) of 6570 g/mol and a polydispersity index (PDI) of 2.00. Sample L1 has an M_n of 10,200 g/mol and a PDI of 4.54. This trend of increasing M_n with increasing VP partial pressure is due to the increased monomer surface concentration [15]. The solubility of films in DMF and D_2O affirms the linearity of the iCVD polymer.

The results in this section show the ability of iCVD to produce linear PVP that spectroscopically resembles conventionally prepared PVP. The retention of the pyrrolidone functionality is crucial to the hydrophilicity of the polymer and its ability to swell in water when cross-linked.

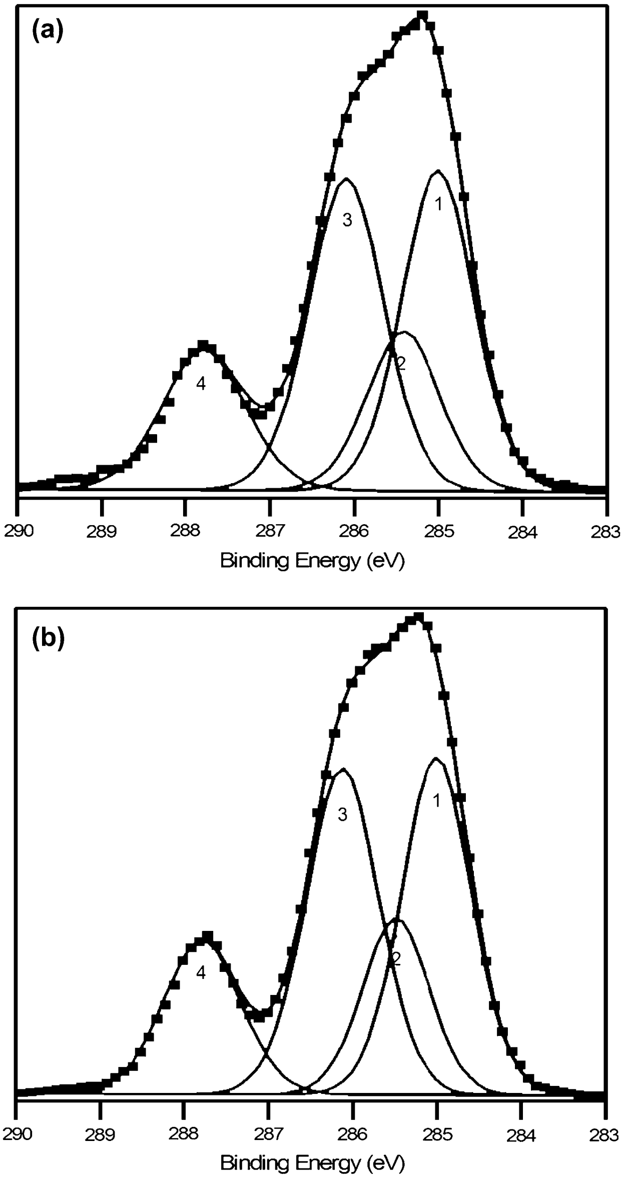

Fig. 3. X-ray photoelectron spectroscopy high-resolution scans of C 1s core level of (a) iCVD PVP film (sample L3) and (b) PVP standard obtained from Aldrich.

3.1.2. Deposition rate

Fig. 5 plots the deposition rate as a function of VP partial pressure in the vacuum chamber. These data points are the results of the linear series listed in Table 1. As seen in the table, both the total flow rate and the total pressure were kept constant using a patch flow of nitrogen while the monomer partial pressure was varied. This configuration was to ensure that the monomer partial pressure was the only changing parameter. A previous iCVD study [15] has indicated that the deposition rate depends strongly on the monomer surface concentration and that chain propagation occurs predominantly on the surface. Therefore film growth can be regarded as surface polymerization with adsorbed monomers, which is initiated by the incoming radicals generated from the decomposition of TBPO. The monomer surface concentration increases with increasing monomer partial pressure and contributes to the increase in deposition rate. The non-linearity at high partial pressures is possibly due to the onset of multilayer adsorption of monomer on the surface. A similar trend has also been observed in the iCVD of PHEMA films [1].

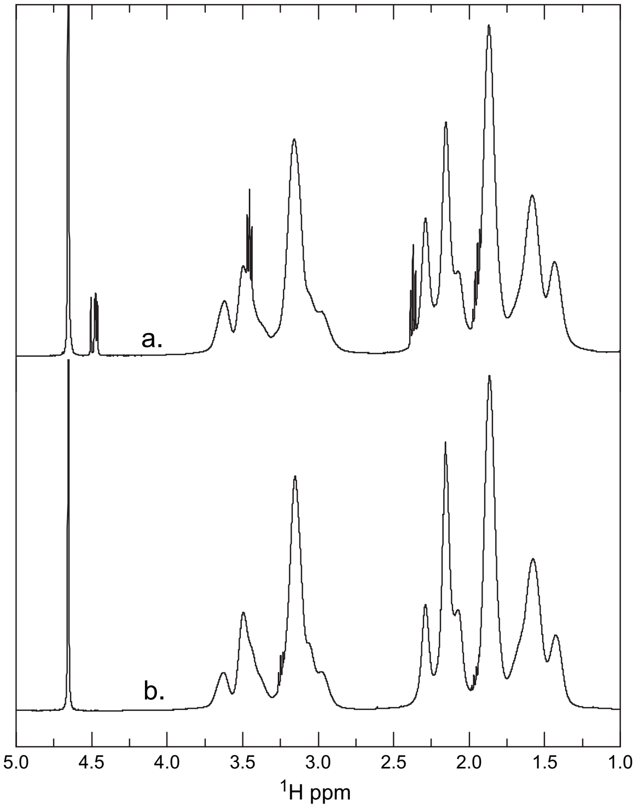

Fig. 4. Solution proton nuclear magnetic resonance spectra of (a) iCVD PVP film (sample L3) and (b) PVP standard obtained from Aldrich. Deuterium oxide was used as the solvent, and the peak at 4.7 ppm is the proton peak from water.

Table 2
Quantitative comparison between the X-ray photoelectron high-resolution scans of iCVD PVP film (sample L3) and PVP standard obtained from Aldrich

Core level	Peak	Origin	iCVD film		PVP reference	
			Binding energy (eV)	Area (%)	Binding energy (eV)	Area (%)
C 1s	1	$-CH_x-C^*H_2-CH_x-$	285.00	33	285.00	34
	2	$-C^*H_2-(C{=}O)-$	285.41	17	285.36	17
	3	$-N-C^*H_x-$	286.09	33	286.16	33
	4	$-C^*{=}O$	287.78	17	287.79	15
O 1s			531.34		531.30	
N 1s			399.89		399.88	

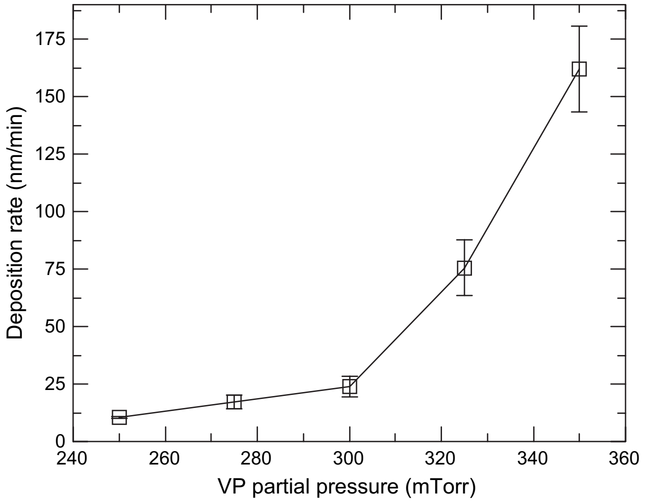

Fig. 5. Deposition rate as a function of VP partial pressure in the vacuum chamber. The discontinuity in the plot likely stems from onset of multilayer adsorption at 300 mTorr.

The highest deposition rate recorded in this work is 162 ± 19 nm/min. While pulsed PECVD (PPECVD) can also produce films with high degree of functionality retention [13], it requires pulsation on the millisecond on-second off timescale that results in a low deposition rate (on the order of 1 nm/min).

3.2. Deposition of cross-linked polyvinylpyrrolidone

EGDA was introduced into the vacuum chamber in a separate series of experiments (samples X1–X5 in Table 1) to produce cross-linked PVP thin films. The ratio between the partial pressures of VP and EGDA was varied to effect films with different degrees of cross-linking. The total pressure and the total flow rate were kept constant, so that only the partial pressures changed.

3.2.1. FTIR analysis

FTIR was used to characterize the films and the results are shown in Fig. 6. The bottommost spectrum is the iCVD film deposited from EGDA and TBPO only. Comparison between this spectrum and that of sample X1, which contains no EGDA, indicates that the carbonyl stretching frequency of the pyrrolidone functionality is different from that of the acrylate functionality. The C=O stretching of PVP is at 1682 cm^{-1}, while that of the EGDA-only film is at 1735 cm^{-1}. The FTIR spectra of samples X2–X5 clearly show both of these C=O stretching peaks, indicating the incorporation of both VP and EGDA, but at different relative intensities. The intensity of the acrylate C=O stretching peak relative to that of the pyrrolidone C=O stretching peak increases with increasing EGDA-to-VP feed ratio. This result shows that the incorporation of the cross-linking agent in the film can be tuned by controlling the feed ratio between EGDA and VP. While FTIR does not prove that samples X2–X5 are cross-linked, these films are insoluble in water, a known solvent for PVP. This insolubility infers that EGDA and VP do cross-react to form a networked polymer. The intensity ratio between the carbonyl peaks is therefore an indication of the degree of cross-linking of the resulting polymer, but it is not directly equivalent to the incorporation ratio because the C=O bonds have different oscillator strengths.

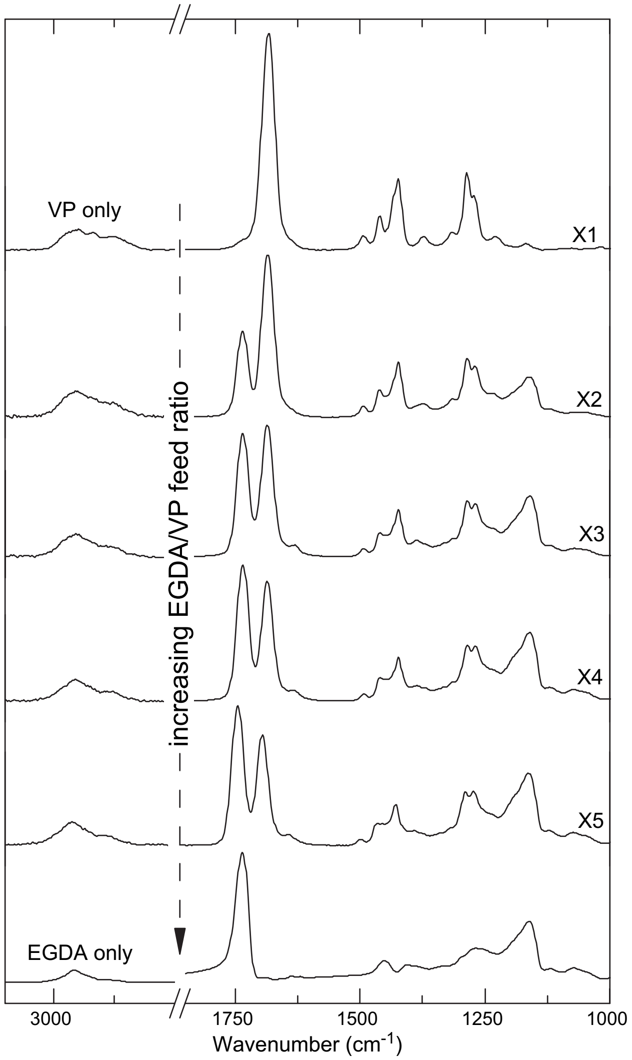

Fig. 6. FTIR spectra of films with varying degrees of EGDA incorporation.

3.2.2. XPS analysis

XPS is useful for determining the compositions of the cross-linked films because VP has a nitrogen atom but EGDA does not. The ratio between the number of carbon atoms and that of nitrogen atoms can be calculated using the areas under the high-resolution scans of the C 1s and the N 1s core levels. In theory, the O 1s core level can also be used, but the hygroscopic nature of PVP discourages the use of this core level. The calculation of the compositions starts with the establishment of the relative sensitivity factors (RSF) of the core levels. Reference RSFs are available for use, but they are non-specific averages. The spectral analyses of the iCVD homopolymer film prove that it is structurally identical to the PVP standard. One can therefore be confident that the ratio of carbon to nitrogen atoms, *r*, in the iCVD homopolymer film is 6 (Fig. 1) and use the following equation to determine the RSFs using the area under the C 1s peak, A_{C1s}, and that under the N 1s peak, A_{N1s}.

$$\frac{A_{\mathrm{C1s}}/\mathrm{RSF}_{\mathrm{C1s}}}{A_{\mathrm{N1s}}/\mathrm{RSF}_{\mathrm{N1s}}} = r = 6 \tag{1}$$

with $\mathrm{RSF}_{\mathrm{C1s}}$ arbitrarily fixed at 1.00, $\mathrm{RSF}_{\mathrm{N1s}}$ was calculated to be 1.73. Computation based on the high-resolution scans of the PVP standard gives the same value, further confirming the structural equivalence between the iCVD homopolymer and conventional PVP. Since EGDA has zero nitrogen atoms (Fig. 1), the incorporation of EGDA in the film will result in $r > 6$. Based on the fact that EGDA has eight carbon atoms, the following equation can be used to determine the ratio of EGDA to VP in the film.

$$\frac{[\mathrm{EGDA}]}{[\mathrm{VP}]} = \left(\frac{r-6}{8}\right) \tag{2}$$

The EGDA/VP ratio in the film is plotted against the EGDA/VP feed ratio in Fig. 7, which shows that the incorporation of EGDA increases with increasing feed ratio. It also infers that the degree of cross-linking can be controlled by adjusting the flow rates of the two components. It should be noted that a feed ratio of 0.05 pivots to an incorporation ratio of ~0.5. The same incorporation ratio requires a feed ratio of 0.5 in the case of the HEMA–EGDA system [1]. This pivoting is likely a result of the difference in propagation kinetics—the addition of an EGDA unit to a VP chain end is more probable than that of a VP unit, or the addition of an EGDA unit to an EGDA chain end is more probable than that of a VP unit, or both. As EGDA is difunctional, the maximum incorporation ratio with no interconnection between any two EGDA units in the film, statistically, is 0.5. A ratio exceeding 0.5 would correspond to an overdose of the cross-linking agent EGDA. Fig. 7 shows that good control of degree of cross-linking would require fine adjustment of feed ratio between 0.00 and 0.05. Such an adjustment would in turn necessitate fine control of flow rates.

PVP-based films deposited using iCVD show high hydrophilicity. The film with the lowest degree of cross-linking (EGDA/VP = 0.5) has a wetting angle of 11°. This result agrees with spectral analyses that the hydrophilic pyrrolidone functionality is retained in the iCVD process. The wetting angle can be lowered further by reducing the EGDA/VP ratio. It should be noted that the same analysis cannot be performed on PVP homopolymer film because PVP dissolves completely in water.

3.2.3. Comparison between FTIR and XPS results

FTIR is easier to use than XPS because it is a non-vacuum technique. The time required to analyze a sample using FTIR is considerably less than using XPS. As mentioned before, the FTIR spectra in Fig. 6 cannot be used directly to determine compositions because of the difference in oscillator strengths. This difference, however, can now be quantified using the XPS data. This quantification can be performed by comparing the XPS results in Fig. 7 to the area ratios of the two carbonyl peaks in Fig. 6. Fig. 8 plots the EGDA/VP ratio in the film based on XPS data against the area ratio between the EGDA and the VP carbonyl peaks. Firstly, the good linear fit between the two sets of data affirms their validity. Secondly, the slope of ~1 means that the C=O oscillator strength of VP is approximately twice of that of EGDA because EGDA has two C=O bonds while VP has one. Using this result, the composition of a VP–EGDA system can be computed using FTIR measurements without employing XPS.

4. Conclusions

The results in this paper show that iCVD is successful in depositing PVP-based thin films and allows control of film composition via adjustment of flow rates. The specific thermal breakdown of initiator molecules inside the iCVD chamber

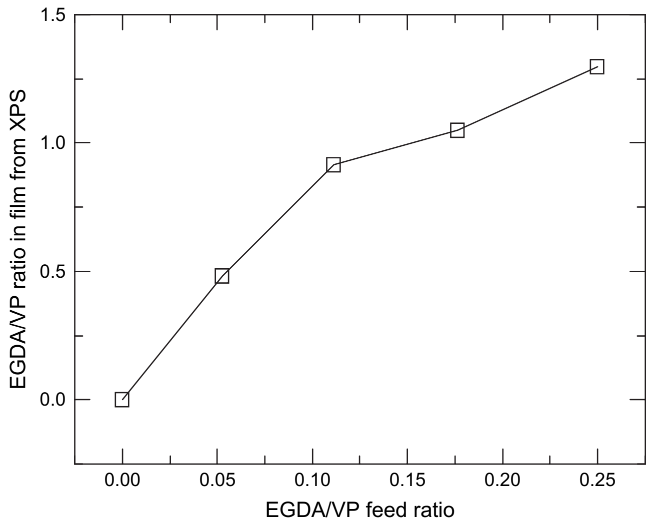

Fig. 7. EGDA/VP ratio in film against EGDA/VP feed ratio.

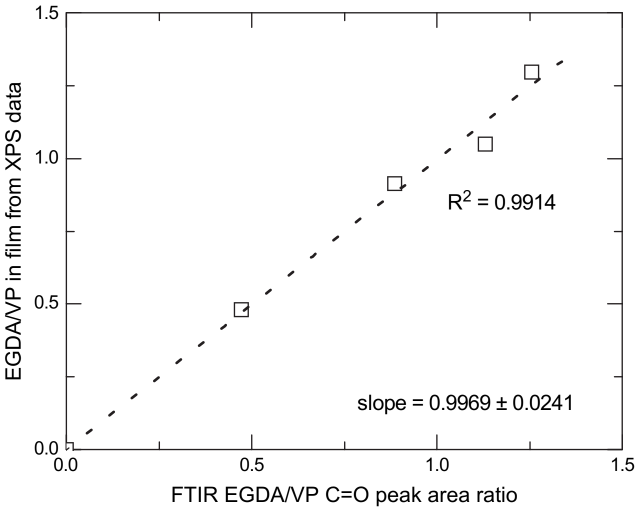

Fig. 8. EGDA/VP ratio in film from XPS against EGDA/VP C=O peak area ratio from FTIR.

prevents loss of functionality. Spectral analyses confirm structural integrity of the iCVD-deposited polymer and coherently prove full retention of pyrrolidone rings, and GPC results show that long-chained molecules were formed. This retention is exemplified by the low wetting angle, 11°, measured for the least cross-linked film. The advantages of using iCVD as method to deposit PVP thin films are multifold: (1) iCVD bears all the characteristics of conventional CVD, allowing conformal films to be grown in a dry manner on complex geometries such as a stent; (2) it offers a higher deposition rate; (3) it retains the pyrrolidone functional group to the highest extent, which is crucial for the film to function as a hydrophilic coating (e.g., an antibiofouling surface); and (4) custom copolymers may be deposited with control of flow conditions. iCVD can substitute SOD and PECVD as the deposition method of choice not only because it can make PVP thin films efficiently but also of its potential for engineering new copolymers on surfaces of substrates simply via control of flow of vapors.

Acknowledgements

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