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Cyano-Functionalized Solid 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

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

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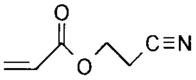
Pulsed plasma polymerization of 2-cyanoethyl acrylate leads to the deposition of structurally well-defined cyano-functionalized thin films. These layers are found to readily complex silver ions from solution and also exhibit pressure-sensitive adhesive behavior.

1. Introduction

Continuous wave plasma polymerization is known to lead to extensive monomer fragmentation and rearrangement during thin film deposition.[1] More recently, it has been shown that pulsing the electric discharge on the ms−μs time scale can give rise to high levels of structural retention.[2−6] This has been attributed to very little monomer fragmentation occurring during the on-period combined with conventional polymerization reaction pathways proceeding during the off-period of the pulsed plasma duty cycle. Examples of molecularly tailored substrates produced by this method include perfluoroalkyl-,[7] epoxide-,[8] anhydride-,[9] alcohol-,[10] and amine-functionalized[11] surfaces.

Here, we describe the pulsed plasma polymerization of 2-cyanoethyl acrylate to generate cyano-functionalized surfaces. This monomer contains two potentially reactive groups: the acrylate carbon−carbon double bond and the nitrile carbon−nitrogen triple bond. Preferential activation of the former is necessary in order to attain a simple one-step solventless route to cyano-functionalized thin films. Cyano groups are desirable for many technological applications because they possess a large dipole moment and readily complex metal ions. For instance, incorporation of silver ions at a substrate surface can lead to antibacterial properties.[12−17] Previous attempts aimed at preparing cyano-containing surfaces have included grafting,[18] gas-phase photochemical reactions involving cyanogen halides,[19] and also wet chemical functionalization of silica chromatography supports.[20] Toxicity and the requirement for solvents are considered to be drawbacks for these existing methods.



Structure 1: 2-cyanoethyl acrylate

2. Experimental Section

Plasma polymerization of 2-cyanoethyl acrylate (Aldrich, +85%, further purified using several freeze−pump−thaw cycles) was carried out in a cylindrical glass reactor (418-cm^3 volume) continuously pumped by a mechanical rotary pump via a liquid-nitrogen cold trap (base pressure 8×10^{-3} Torr and 1.61×10^{-8} mol s^{-1} leak rate). 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 Torr. Monomer was then introduced via a fine control needle valve at a pressure of 0.1 Torr and 5.2×10^{-9} mol s^{-1} flow rate. This was followed by ignition of the electrical discharge and film deposition for 5 min. In the case of pulsed plasma conditions, a signal generator was used to trigger the RF supply, and the corresponding pulse shape was monitored

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* To whom correspondence should be addressed.

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with an oscilloscope. The average continuous wave power output (P_P) of the R.F. supply spanned 5−90 W. Pulse on-times (t_{on}) and off-times (t_{off}) could be varied between 5 and 800 μs and 5−1200 μs, respectively. The average power $\langle P\rangle$ delivered to the system during pulsing was calculated using the following expression,

$$\langle P\rangle = P_P\{t_{on}/(t_{on} + t_{off})\}$$

where $t_{on}/(t_{on} + t_{off})$ is the defined as the duty cycle.[21]

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos ES300 spectrometer equipped with a Mg Kα X-ray source and a hemispherical analyzer operating in fixed retard ratio mode (22:1). Photoelectrons were collected at a takeoff angle of 30° from the substrate normal. Additional depth-profiling studies were undertaken by varying the takeoff angle. Elemental composition values were calculated using sensitivity factors derived from chemical standards, C(1s):O(1s):Ag($3d_{5/2}$):N(1s) equals 1.00:0.57:0.08:0.74. All binding energies are referenced to the C(1s) hydrocarbon peak at 285.0 eV.

Attenuated total reflectance infrared spectra of plasma polymer films deposited onto NaCl plates were acquired using a Graseby Specac Golden Gate ATR accessory fitted to a Mattson Polaris FTIR instrument. This was operated at 4-cm^{-1} resolution over the 400−4000-cm^{-1} wavenumber range. The deposited films were sufficiently thick for FTIR spectral analysis.

A spectrophotometer (Aquila Instruments, nkd-6000) was used to determine film thickness. Transmittance-reflection curves over the 350−1000-nm range were fitted to a Cauchy model using a modified Levenburg−Marquardt procedure.[22] Repeatability and sample homogeneity were assessed by recording multiple readings from several different samples.

^{13}C NMR spectra of the deposited films were taken using a Varian VXR-400S spectrometer operating at 100.57 MHz. In this case, deposited material was collected from the reactor and dissolved in deuterated acetonitrile (Aldrich, 99.6 atom % D).

Metal ion complexation studies comprised immersing plasma-polymer-coated glass slides into a 1 M aqueous solution of $AgNO_3$ (Johnson Matthey Chemicals, 99.99% purity) for 24 h (longer times did not give rise to further complexation). These surfaces were then rinsed several times in ultra-high-purity water prior to chemical analysis. The distribution of silver ions as a function of depth was determined by acquiring XPS spectra over a range of takeoff angles from the substrate normal.

The adhesive behavior of the deposited plasma polymer layers was evaluated by pressing together two coated strips of poly(tetrafluoroethylene) (PTFE, Goodfellow, 4 cm × 1 cm × 0.25 mm) between two glass plates for 10 min at a pressure of 3.04×10^3 Pa. The overlap was approximately 1 cm^2. Subsequently, single-lap adhesion tests were carried out using an Instron 5543 tensilometer operating at a crosshead speed of 1 mm min^{-1}.

3.Results

Elemental XPS analysis showed that pulsed plasma deposition yielded films with a chemical composition closely resembling the theoretical values expected from conventional free radical polymerization of 2-cyanoethyl acrylate via the carbon−carbon double bond (Table 1). In contrast, some degree of oxygen depletion was evident in the case of continuous wave conditions, even at the lowest powers (below 3 W, the electrical discharge became unstable). The pulsed plasma polymer films were found to be stable toward oxidation upon storage in air for a period of 3 months.

Table 1. XPS Elemental Analysis Composition of 2-Cyanoethyl Acrylate Plasma Polymers

conditions	%C	%O	%N	%Ag
theoretical	66.7	22.2	11.1	0
continuous wave[a]	68.8 ± 0.5	19.4 ± 0.1	11.8 ± 0.3	0
pulsed[b]	67.7 ± 0.5	21.2 ± 0.2	10.9 ± 0.3	0
silver ion complexation[c]	76.2 ± 0.3	16.1 ± 0.3	5.9 ± 0.2	1.6 ± 0.2

[a] $P_p = 3$ W. [b] $t_{on} = 20\ \mu$s, $t_{off} = 20$ ms, $P_p = 40$ W, $\langle P\rangle = 0.04$ W. [c] XPS takeoff angle equals 75°, while other values correspond to 30°.

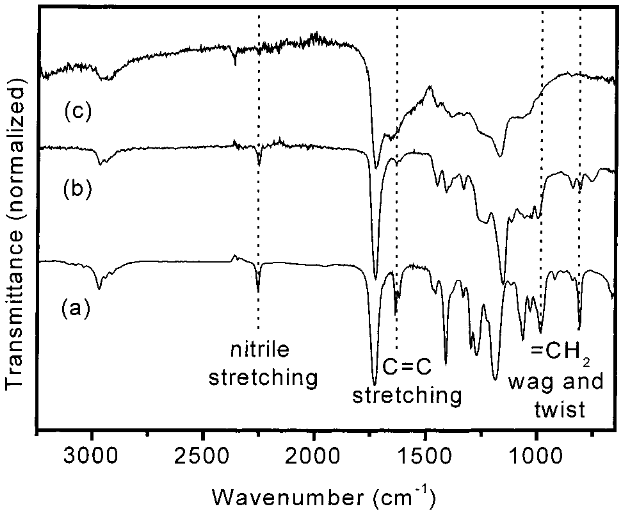

Figure 1. Infrared spectra of (a) 2-cyanoethyl acrylate monomer, (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W), and (c) 3-W continuous wave plasma polymer. (The weak band in the 2360−2330-cm^{-1} region is due to residual CO_2 in the spectrometer).

Fourier transform infrared spectroscopy identified the following characteristic structural features for the precursor monomer:[23] C═O stretching (1726 cm^{-1}), C═C stretching (1637 cm^{-1}), ═CH_2 wagging (985 cm^{-1}), ═CH_2 twisting (810 cm^{-1}), C−O stretching (two strong bands at 1273 and 1185 cm^{-1}), C−H stretching (3000−2900 cm^{-1}), and C≡N stretching (a weak band at 2254 cm^{-1}) (Figure 1). In the case of the pulsed plasma film, it was evident that polymerization had proceeded predominantly via the acrylate carbon−carbon double bond. The C═C stretching at 1637 cm^{-1} disappeared, while the following characteristic structural features remained intact: C═O stretching at 1726 cm^{-1}, C≡N stretching at 2254 cm^{-1}, and C−O stretching at 1180 cm^{-1}.[24] In the case of continuous wave plasma polymerization very little structural definition was evident. For instance, the cyano group stretching feature at 2254 cm^{-1} is hardly visible, reflecting the extensive rearrangement reactions taking place within the continuous wave plasma discharge.[25]

^{13}C NMR spectra obtained for the pulsed plasma polymer films (Figure 2) displayed the following shifts:

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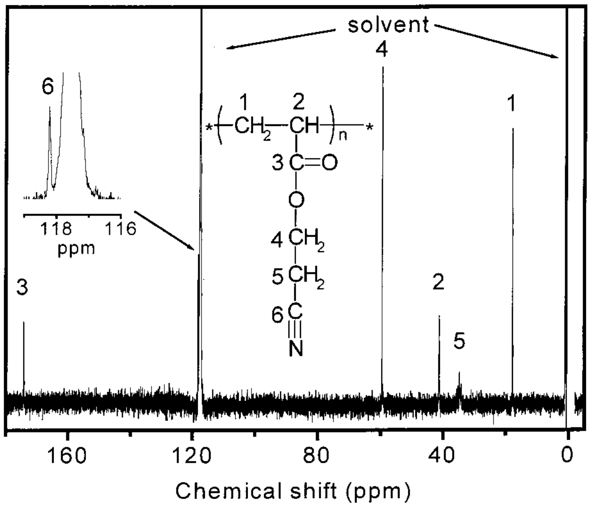

Figure 2. ^{13}C NMR spectrum of 2-cyanoethyl acrylate pulsed plasma polymer.

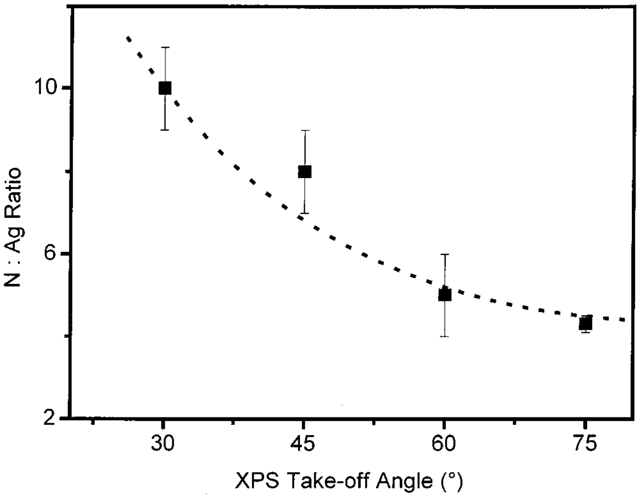

Figure 3. Variation in N:Ag ratio for silver ions complexed to 2-cyanoethyl acrylate pulsed plasma polymer layers as a function of the XPS takeoff angle (time on = 20 μs, time off = 20 ms, peak power = 40 W).

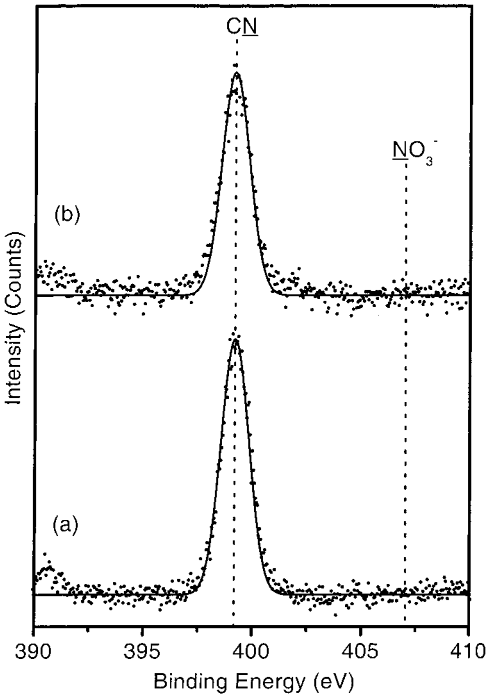

Figure 4. N(1s) spectra for 2-cyanoethyl acrylate pulsed plasma polymer layers (time on = 20 μs, time off = 20 ms, peak power = 40 W): (a) as deposited and (b) following complexation to silver ions and washing.

18.4 ppm $((\underline{C}H_2{-}CH)_n)$, 34.5 ppm $({-}\underline{C}H_2{-}CN)$, 41.9 ppm $((CH_2{-}\underline{C}H)_n)$, 60.2 ppm $(O{-}\underline{C}H_2)$, 118.8 ppm $({-}\underline{C}N)$, and 174.8 ppm $((\underline{C}{=}O)O)$. These assignments are based on NMR spectra reported for conventional linear poly(2-cyanoethyl acrylate) prepared by solution-phase free radical polymerization.[26] The continuous wave plasma polymer product was found to be insoluble in acetonitrile due to its highly cross-linked nature.

Although the pulsed plasma polymerization conditions were much milder in nature compared to those in continuous wave, the corresponding deposition rate was found to be substantially greater, 194.7 and 8.0 nm min^{-1}, respectively.

Soaking substrates coated with the 2-cyanoethyl acrylate pulsed plasma polymer in aqueous $AgNO_3$ solution followed by rinsing in water gave rise to 1.0 ± 0.2 atom % silver ion complexation to the surface (as measured by XPS—ignoring hydrogen). This corresponds to approximately 1 silver ion for every 10 nitrogen atoms. However, angle-resolved XPS depth-profiling studies showed that the silver-to-nitrogen ratio increased to 1:4 at shallower sampling depths (Figure 3). The absence of trapped nitrate species was checked for by examining the N(1s) envelope (expected at 407 eV); in fact, only the $C{\equiv}\underline{N}$ environment was observed at 399.2 eV (Figure 4).[27] In contrast, the continuous wave plasma polymer deposited layers were found to delaminate away from the substrate upon immersion in aqueous $AgNO_3$ solution.

The adhesive performance of plasma-polymer-coated PTFE substrates was evaluated using a lap-shear test (Figure 5). A maximum load of 24 ± 2 N was measured for the pulsed plasma polymer layer, whereas no adhesion was observed in the case of continuous wave deposition (even for comparable thickness films). Coating of only one piece of PTFE with pulsed plasma polymer was also found to be insufficient. Interestingly, the adhesive joint could be subsequently reformed following failure by simply repressing the two pieces together. This suggests that the interface fails cohesively. In this case, only a slight deterioration in adhesive performance was observed compared to that of the original joint (19 ± 2 N). The lower strain measured during adhesion testing of the reassembled joint can be attributed to loss of elasticity (stretching) of the PTFE substrate during the first lap-shear experiment.

Apart from the lowest power continuous wave and optimum pulsed plasma polymerization conditions described above, intermediate duty cycle parameters (i.e., longer t_{on}) were found to give rise to a corresponding deterioration in the chemical and functional properties

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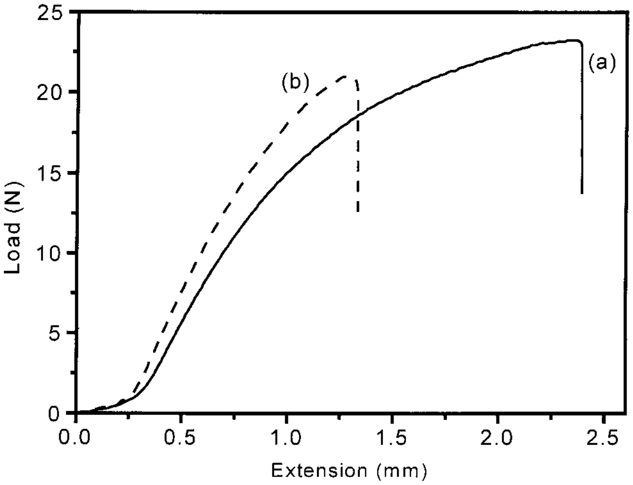


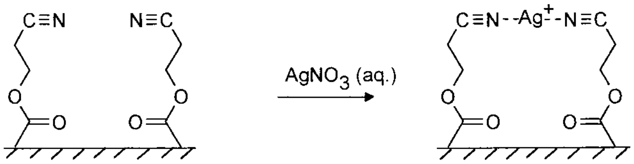
Figure 5. Tensilometer stress/strain curves of (a) 2-cyanoethyl acrylate pulsed plasma-polymer-coated PTFE single-lap joint (time on = 20 μs, time off = 20 ms, peak power = 40 W) and (b) repetition of the test after reassembling (the lower strain is due to loss of elasticity of the substrate during the subsequent run).

of the deposited films. Similar trends have been previously observed for other monomer systems.[9]

4. Discussion

Continuous wave plasma polymerization of molecules containing cyano groups[18] (e.g., acrylonitrile,[25,28,29] fumaronitrile,[28,29] tetracyanoethylene,[29,30] tetracyanobenzene,[30] tetracyanoquinodimethane,[30] acetonitrile,[25,30] diaminomeleonitrile,[30] and phthalonitrile[30]) has previously been shown to lead to extensive molecular rearrangement reactions and the formation of amide, amino, and ketene−imine groups. In the present study, pulsed plasma polymerization of 2-cyanoethyl acrylate gave rise to excellent structural retention of the cyano functionality. This can be attributed to the acrylate bond undergoing selective conventional polymerization during the off-period of the plasma duty cycle.[9] Whereas in the case of continuous wave conditions, the electrical discharge became unstable below 3 W.

Scheme 1. Complexation of Ag^+ Ions onto the Surface of 2-Cyanoethyl Acrylate Pulsed Plasma Polymer Films



Complexation of Ag^+ ions (Scheme 1) onto these pulsed plasma polymer surfaces can be attributed to metal coordination by the C≡N groups via donation of nonbonding electrons from the nitrogen atom.[31] For instance, silver ions are reported to form 1:2 stoichiometric complexes with acetonitrile in solution.[31] In the present case, XPS analysis indicated that coordination was limited to the outermost 1.5-nm (XPS sampling depth at a 75° takeoff angle from the substrate normal[32]) of the plasma polymer film, where a 1:4 silver: cyano group ratio was measured. This could be due to either incomplete coordination because of geometrical constraints or complexation occurring at just the very outer surface.

The adhesive behavior measured between two pulsed plasma-polymer-coated surfaces is most likely to originate from polymer chain interdiffusion across the solid−solid interface.[33] The large dipole moment of the cyano groups will promote strong interactions between interpenetrating polymer chains.[31] The slightly lower maximum load measured for the reformed joint can be associated with the loss of tackiness at the surface (i.e., changes in the polymer chains ability to diffuse). Whereas, the absence of adhesion noted for the continuous wave plasma polymer coatings arises from the rigidness (cross-linking) introduced by high-energy plasma species bombarding the surface of the growing film throughout deposition as well as the absence of highly polar cyano groups.

5. Conclusions

Solventless functionalization of solid surfaces with cyano groups can be achieved by pulsed plasma polymerization of 2-cyanoethyl acrylate. Variation of the pulsing conditions allows the extent of structural group retention to be controlled. In this way, complexation of silver ions to solid surfaces and also their adhesive behavior can be tailored.

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