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The preparation and characterisation of polymeric macrostructures (command surfaces) using electropolymerisation

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Polymeric films of acrylonitrile, acetic acid and 2-cyanoprop-1-en-3-ol have been electrodeposited to a thickness of ~300 nm onto silver electrodes, using a 2-step polymerisation method, under both cathodic and anodic conditions. Raman microscopy was used to confirm (i) that polymerisation had occurred and (ii) that anodic and cathodic conditions produced different polymeric structures. AFM analysis showed the films to be microscopically smooth (RMS roughness 1–6 nm) but characterised by deep crevices when produced anodically. The polymers have the potential to be used as a command surface for the attachment of surface moieties.

1. Introduction

In 1981, Lecayon and co-workers showed that polymers can be grafted electrochemically onto a metal surface,[1] for example, the electropolymerisation of acrylonitrile led to the formation of a thin film of poly(acrylonitrile) on nickel and platinum surfaces.[2,3] Of particular interest is the difference in the nature of the metal/polymer interface depending on whether cathodic or anodic polymerisation is used. When the substrate metal (nickel or platinum) acts as a cathode it behaves as a basic initiator for anionic polymerisation through a 1,4 Michael-type addition from the metallic surface to the vinylic carbons to form a polymeric structure as shown in Fig. 1(a). However, when the metal substrate is made an anode, it acts as a Lewis acid towards the acrylonitrile molecules, resulting in either (i) a 1,2 nucleophilic addition on the nitrile groups which affords a 'conjugated' structure [Fig. 1(b)] or (ii) the formation of a cumulene type structure *via* the 1,4-addition of the nitrile group to the vinyl carbon [Fig. 1(c)]. Thus by changing the nature of the metallic surface either end of the acrylonitrile (and also the methacrylonitrile[4]) molecule may be chemically bonded to the metal surface.

Recent work by Jerome and co-workers[5] has shown that it is possible also to 'debond' the grafted poly(acrylonitrile) by increasing the cathodic potential beyond that required for bonding. This is an exciting development since it suggests a means of producing thin, free-standing polymeric membranes.

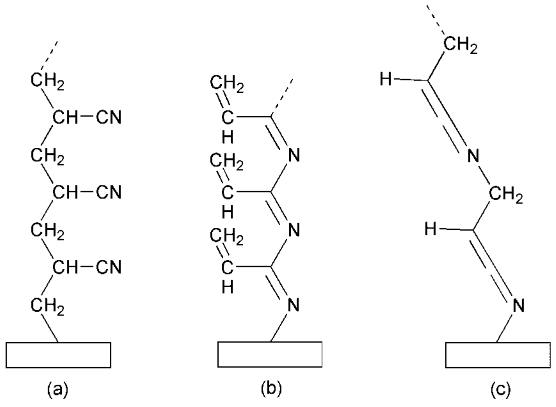


Fig. 1 Polymer structure when synthesised by (a) Michael-type addition, (b) 1,2 nucleophilic addition on the nitrile group and (c) 1,4 addition through the nitrile group and the vinyl carbon.

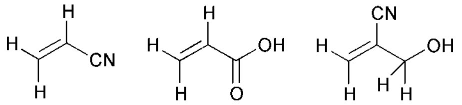
Furthermore, the work to date indicates that acrylonitrile-based polymer films may well be suited to the preparation of functionalised macrostructures or command surfaces which could be useful in sensor or optical applications. Although much is already known about the electropolymerisation process, there is still some doubt as to the actual mechanism of polymerisation and little is known about either (a) the tacticity of the polymer or (b) the effects of functional groups on the polymerisation process.

In this paper we present the preliminary results of an investigation into the cathodic and anodic polymerisation of the three monomers shown in Fig. 2. Electropolymerisation of monomers **2** and **3** will result in a command surface, *i.e.* a surface functionalised polymeric macrostructure. In a subsequent step (not investigated here) such a surface should allow the attachment of different types of active moieties, for example a sensor unit, NLO chromophore or a liquid crystal unit, as shown in Fig. 3.

2. Experimental procedures

Acrylonitrile (**1**) and acrylic acid (**2**) were purchased from Aldrich and used without further purification.

2-Cyanoprop-1-en-3-ol (**3**) was synthesised using a procedure first described by Villeras and Rambaud.[6] Diethyl cyanomethyl phosphate (50 g, 0.282 mol) was added to formaldehyde solution with rapid stirring at room temperature. Saturated potassium carbonate solution (68 g) was added slowly over 45 minutes while maintaining the temperature below 30 °C. The solution was stirred for a further 2.5 hours at room temperature. Saturated ammonium chloride solution (125 mL) was added with effervescence. The product was extracted into diethyl ether (3 × 125 mL) and the combined



1 **2** **3**

Fig. 2 Monomers used for polymerisation, acrylonitrile **1**, acrylic acid **2** and 2-cyanoprop-1-en-3-ol **3**.

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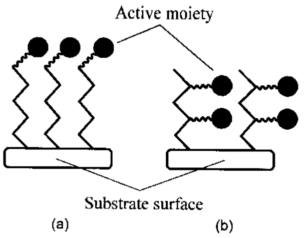

Fig. 3 Possible addition of active moieties: (a) surface macrostructure and (b) in-plane macrostructure.

ethereal extracts were then dried ($MgSO_4$). The diethyl ether was removed by distillation under reduced pressure (water pump) to leave a slightly viscous, yellow liquid. The product was purified by distillation under reduced pressure (water pump) to afford (**3**) as a pale yellow liquid. The product, collected in the range 110–120 °C with a 56% yield (13.2 g), gave a single spot on thin layer chromatography (silica gel, 1 : 1 mixture of diethyl ether and dichloromethane).

The structure of (**3**) was confirmed by ^{1}H NMR (JEOL JNM-GX 270 MHz spectrometer), infrared spectroscopy (Perkin Elmer Model 783 Grating Spectrophotometer) and mass spectrometry (Finnegan-MAT 1020G/MS spectrometer). ^{1}H NMR ($CDCl_3$): δ 6.05 (s, 1H), 4.25 (s, 2H), 2.80–3.05 (s, broad, 1H); IR (KBr): 3100–3600, 2970, 2890, 2220, 1625, 1450, 1040, 950 cm^{-1}; *m*/*z*: 83 (M^+), 66 (M−OH).

Solutions of acrylonitrile, acrylic acid and 2-cyanoprop-1-en-3-ol (approximately 0.4 M) with supporting salt (tetraethylammonium perchlorate, 5×10^{-2} M) were prepared in acetonitrile. Electropolymerisation was achieved by placing 40 mL of solution in a standard three electrode cell connected to a potentiostat/galvanostat (EG+G Model 273A). The working electrode was formed by evaporating a silver film (100 nm thick) onto a glass microscope slide precoated with a keying layer of chromium (20 nm thick). During film growth, approximately 30 mm^2 of the electrode was immersed into the monomer solution. The counter electrode was formed from a thin platinum foil 7 mm^2 in area with a clean silver wire used as a pseudo-reference electrode. Prior to polymerisation, the monomer solution was de-aerated by purging with nitrogen for 20 minutes.

Polymerisation followed the two-step technique suggested initially by Garnier and co-workers[7] and adapted by Taylor and Gomes[8] for poly(3-methylthiophene), in which a high potential was applied for a short time to nucleate the growth followed by a lower potential for a longer time during which most of the film was grown. The growth conditions for both anodic and cathodic electropolymerisation are given in Table 1. At the end of the growth stage, polymer-coated substrates were retrieved from the cell, washed with acetone to remove residual monomer solution, dried under a gentle stream of bottled nitrogen and stored under vacuum prior to characterisation.

Raman spectra, covering the range 500–3500 cm^{-1}, were obtained for all the monomers and for polymer films grown both cathodically and anodically, using a Renishaw Ramascope 1000 Raman spectrometer fitted with a 633 nm helium–neon laser. To measure the electrical properties of the deposited films circular aluminium electrodes approximately 2.5 mm^2 in area were evaporated onto the free surface of the films in a turbomolecular pumped evaporator. The electrical conductivity of the sandwich structures was measured under ambient conditions using a Tektronix Model 571 Current/Voltage plotter revealing essentially linear characteristics over a 2 V range. The morphology of the deposited films was studied by Atomic Force Microscopy (Digital Instruments, Nanoscope IIIA) operating in tapping mode. The AFM was also used to measure film thickness by scoring and peeling away part of the polymer using a sharp blade.

3. Results

All three monomers were electropolymerised successfully onto the silver substrates giving stable, robust films between 0.2 and 0.4 μm thick (Table 2) under both anodic and cathodic conditions. Film growth was much more rapid under cathodic conditions. Even though the time allowed for growth was some 50% greater for anodic polymerisation, the resulting films were 20–30% thinner than those produced cathodically. Films of poly(acrylic acid) showed the most rapid growth rates for both anodic and cathodic polymerisation. Taking acrylonitrile as the reference, these preliminary results indicate that replacing the *gem*-hydrogen has little effect on the rate of electropolymerisation. However, replacing the cyano group with another electron-withdrawing group produces a significant effect.

None of the deposited films could be washed off the silver surfaces by rinsing in dimethylformamide (DMF), tetrahydrofuran (THF) or dichloromethane (DCM) at room temperature. Furthermore, the vacuum-dried films resisted attempts at removal with adhesive tape suggesting that they are strongly bonded to the silver surface.

AFM images of polyacrylonitrile produced under both anodic and cathodic conditions and given in Fig. 4 are typical of all three materials investigated. Anodic films were exceptionally smooth and although punctuated by deep crevices [Fig. 4(b)] did not show the nodules projecting from the surface that are characteristic of the cathodic film [Fig. 4(a)]. At higher magnification [Fig. 4(c) and 4(d)] the underlying surface morphologies differ only slightly with the RMS roughness of all films in the range 1–6 nm (Table 2).

Interestingly, films from the two cyano-containing compounds are smoother than those from acrylic acid, which may well reflect the slower growth rate of the cyano-containing films (Table 2). The presence of crevices are suggestive of a more rigid film expected when conjugated structures such as Fig. 1(b) or 1(c) are growing. AFM probing showed that the crevices found in the anodic polymer films did not penetrate the full depth of the layer.

The conductivities of the polymers ranged from 1.4×10^{-3} to 2.8×10^{-3} S m^{-1} (Table 2). Despite their supposed conjugated structure, the anodically grown films were generally of lower conductivity than those produced cathodically. This provides some confirmation of the AFM observation that the crevices in the film did not penetrate the whole film and indeed had little effect on the electrical properties.

The Raman spectra for the three monomers and their respective polymers are shown in Figs. 5–7. All monomers [curves labeled (c)] show the ν(CH=CH) peak at approximately 1620 cm^{-1} and the ν(C–H) peak of the CH=CH moiety just above 3000 cm^{-1}. The sharp band characteristic of ν(C≡N) is clearly visible at approximately 2225 cm^{-1} in both acrylonitrile and 2-cyanoprop-1-en-3-ol, while in the latter material bands

Table 1 Conditions used for polymer growth

	Nucleation step		Growth step	
Type of polymerisation	Applied potential/V	Time applied/s	Applied potential/V	Time applied/s
Anodic	2.8	10	1.8	1200
Cathodic	−2.8	10	−1.8	600

Table 2 Typical properties of the electropolymerised films grown from the monomers listed

	Thickness/nm		RMS roughness 500 nm^2 area/nm		Conductivity/S m^{-1}	
Monomer	anodic	cathodic	anodic	cathodic	anodic	cathodic
Acrylonitrile	220	320	2.3	3.0	$1.45\times10^{-3}\pm2.5\times10^{-5}$	$2.28\times10^{-3}\pm2.3\times10^{-6}$
Acrylic acid	300	360	6.6	1.2	$1.54\times10^{-3}\pm1.3\times10^{-5}$	$2.13\times10^{-3}\pm8.8\times10^{-6}$
2-Cyanoprop-1-en-3-ol	230	310	1.5	2.2	$2.81\times10^{-3}\pm8.5\times10^{-6}$	$2.56\times10^{-3}\pm1.1\times10^{-4}$

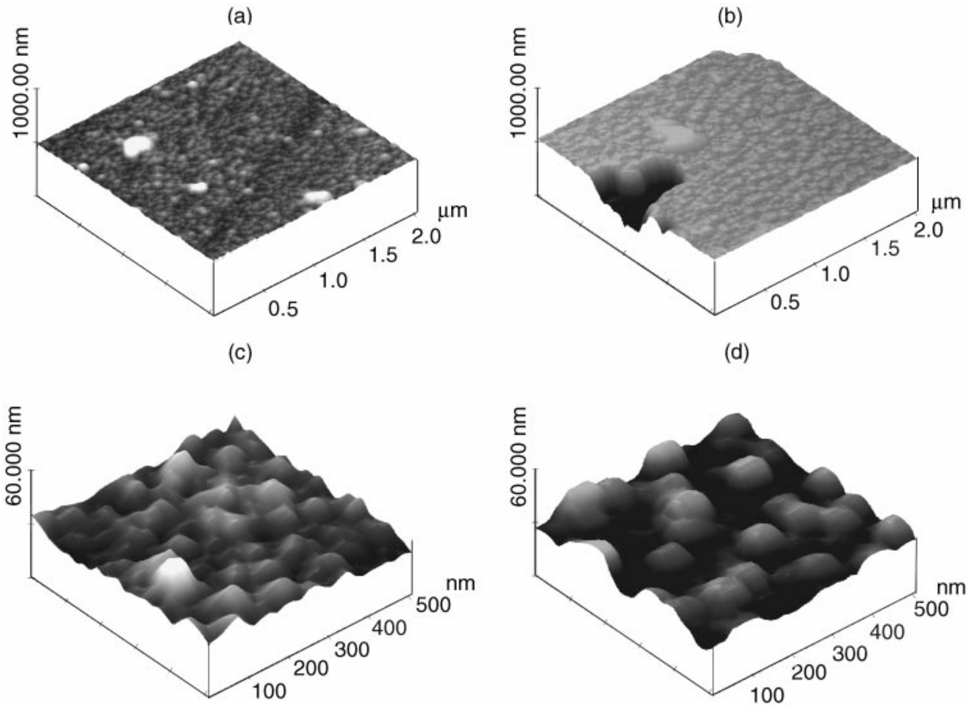

Fig. 4 AFM micrographs of cathodically, (a) and (c), and anodically, (b) and (d), polymerised acrylonitrile. [In (a) and (b), area = 2 × 2 µm, z-range = 500 nm div^{-1}; in (c) and (d), area = 500 × 500 nm, z-range = 30 nm div^{-1}.]

due to ν(C–H) in the CH_2 moiety are seen just below 3000 cm^{-1}.

The spectra obtained for the electrodeposited films show clear evidence for polymerisation: (a) the C–H stretch vibration of the CH=CH moiety above 3000 cm^{-1} has disappeared to be replaced by the C–H stretching vibration of the saturated CH–CH moiety just below 3000 cm^{-1}; (b) the appearance of a broad absorption band in the range 1200–1700 cm^{-1}. Interestingly, the detailed structure of the band in this region is different in the cathodic and anodic polymers, consistent with the different polymerisation schemes in Fig. 1.

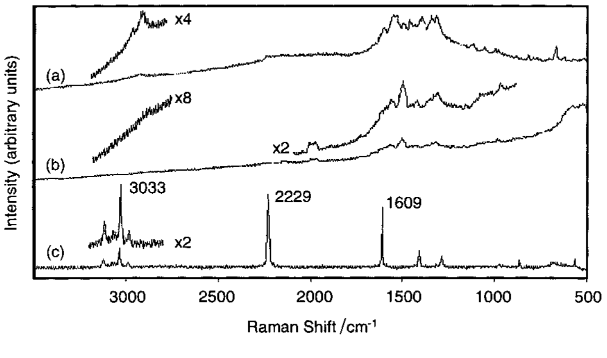

Fig. 5 Raman spectra of acrylonitrile (a) anodically polymerised, (b) cathodically polymerised and (c) monomer. (Expanded regions above main spectra show detail for that area.)

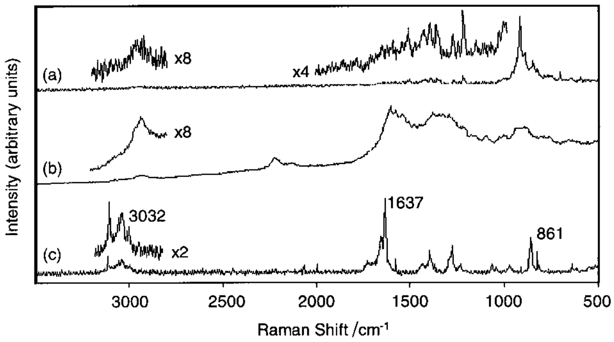

Fig. 6 Raman spectra of acrylic acid (a) anodically polymerised (b) cathodically polymerised and (c) monomer. (Expanded regions above main spectra show detail for that area.)

4. Conclusions

For the first time, a series of ethylene homopolymers has been prepared by both anodic and cathodic electropolymerisation. The rate of electropolymerisation (as judged by film thickness) was dependent on both the nature of the electropolymerisation and the structure of the monomer. Polymers grown under both anodic and cathodic conditions were found to be very smooth with an RMS roughness between 1 and 7 nm, however, the anodically grown films were found to contain crevices suggesting a rigid, conjugated polymer structure.

Polymerisation was confirmed using Raman spectroscopy to compare the spectra of the polymers with those of their respective monomers. The polymers all displayed peak broad-

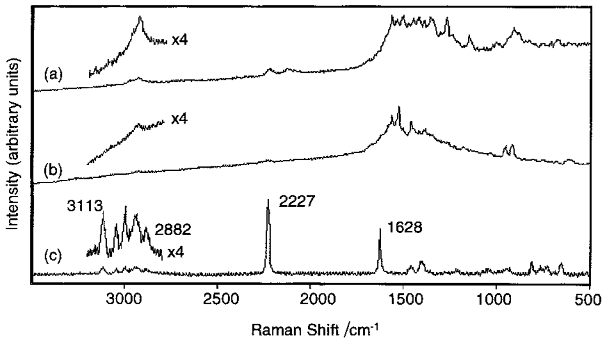

Fig. 7 Raman spectra of 2-cyanoprop-1-en-3-ol (a) anodically polymerised, (b) cathodically polymerised and (c) monomer. (Expanded regions above main spectra show detail for that area.)

ening between 1200 and 1700 cm^{-1} indicative of polymerised C–C. Also the ν(C–H) band just above 3000 cm^{-1} (characteristic of CH=CH) was replaced by a new band just below 3000 cm^{-1} characteristic of the CH–CH moiety. In all cases the spectra of the cathodic and anodic polymers were different in detail consistent with different polymerisation schemes in the two cases.

The polymers were found to have conductivities of approximately 2×10^{-3} S m^{-1} which seemed to be independent of the presence of the crevice-like defects in the anodic films.

References

1 G. Lecayon, C. LeGressus and A. LeMoel, *Eur. Pat.*, No. 0038244, 1981; G. Lecayon, Y. Bouizem, C. LeGressus, C. Reynaud, C. Bioziau and C. Jurer, *Chem. Phys. Lett.*, 1982, **91**, 506; G. Lecayon, P. Viel, C. LeGressus, C. Boiziou, S. Leroy, J. Perreau and C. Reynaud, *Scanning Microscopy*, 1987, **1**, 85.

2 R. Jerome, M. Mertens and L. Martinot, *Adv. Mater.*, 1995, **7**, 807.

3 N. Baute, P. Teyssie, L. Martinot, M. Mertens, P. Dubois and R. Jerome, *Eur. J. Inorg. Chem.*, 1998, 1711.

4 C. Bureau, G. Deniau, F. Valin, M.-J. Buittet, G. Lecayon and J. Delhalle, *Surf. Sci.*, 1996, **355**, 177.

5 M. Mertens, C. Calberg, L. Martinot and R. Jerome, *Macromolecules*, 1996, **29**, 4910.

6 J. Villeras and M. Rambaud, *Synthesis*, 1982, 924.

7 F. Garnier, G. Horowitz and D. Fichou, *Synth. Met.*, 1989, **28**, C275; J. Roncali, A. Yasser and F. Garnier, *J. Chem. Phys.*, 1989, **86**, 85.

8 D. M. Taylor, H. L. Gomes, A. E. Underhill, S. Edge and P. I. Clemenson, *J. Phys. D: Appl. Phys.*, 1991, **24**, 2032; D. M. Taylor and H. L. Gomes, *J. Phys. D: Appl. Phys.*, 1995, **28**, 2554.