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Spectroscopic and topographic characterization of the effect of monomer feed ratio in electrocopolymerization of N-vinylcarbazole-co-3-methylthiophene on carbon fiber

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In the case of conductive polymer films, with thickness in the nanometer range, electrografted onto carbon fiber, the characterization is difficult and requires the development of new analysis procedures and methods. Recently we have successfully applied the reflectance FTIR method for the characterization of electrocoated thin conductive polymeric films (poly[carbazole-co-acrylamide], and poly[carbazole-co-methylthiophene]) [1–3] onto carbon fiber. Atomic force microscopy (AFM) analysis was performed on highly oriented pyrolytic graphite (HOPG) as a model system [4], and the adhesion properties of Poly[carbazole-co-acrylamide] on carbon fiber has been determined [5]. These methods allow a non-destructive characterization of the surface coating and can give information on the structure of electrocoated polymers and copolymers. In this paper we have investigated the electrografting of the copolymer poly[N-vinylcarbazole-co-3-methylthiophene] (hereafter NVCzMeTh) onto carbon fiber by reflectance FTIR, X-ray photoelectron spectroscopy (XPS) and AFM. Reflectance FTIR analysis was carried out on a single fiber. AFM was used to gain information about the morphology of the copolymer electrografted onto carbon fiber. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were also performed to study the morphology and composition of such coatings.

Polyacrylonitrile (PAN) based, Hexcel AS4C 12 K carbon fibers (12 000 single filaments in a roving) were used for the electrocopolymerization (diameter of ~5–6 μm). The electrocopolymerization procedure was carried out as described previously [3]. Electrodeposition of polymers on the carbon fiber microelectrodes was performed galvanostatically at 40 °C at a constant current density of ~10 A/cm^2, using the carbon fibers as anode. For sample NVCzMeTh1 the initial concentration of monomer used was $[\mathrm{NVCz}]_0 = 0.05$ M (Fluka), $[\mathrm{MeTh}]_0 = 0.067$ M (Fluka, >98%); for sample NVCzMeTh4 the initial concentrations were $[\mathrm{NVCz}]_0 = 0.017$ M and $[\mathrm{MeTh}]_0 = 0.240$ M. The solvent was DMF (Fluka, puriss. grade) containing 0.1 M TMAP (Fluka) as supporting electrolyte. After the electrolysis, the carbon fibers were washed thoroughly with water and distilled acetone and with THF (Merck, analytical grade), and afterwards the fibers were dried overnight in air.

Both polymers and copolymers electrografted onto carbon fiber surface were analyzed by FTIR reflectance spectrometry (Perkin Elmer, Spectrum One, Überlingen, Germany with an ATR attachment Universal ATR—with a diamond and ZnSe crystal). AFM measurements were performed with an Explorer$^{\mathrm{TM}}$ ThermoMicroscope in non-contact mode. The fibers were fixed on a silicon piece by resin. XPS analysis was performed on the as-introduced samples by using a Kratos Axis 165 spectrometer. A monochromatic Al K_α (energy = 1486.6 eV) radiation source with an energy resolution of 0.5 eV at pass energy of 20 eV was used with 10 mA current and 15 kV voltage. SEM was performed by using a Hitachi S-2700 scanning electron microscope, which was connected to an EDX-microanalyzer. The excitation energy was 10 keV at a beam current of 0.5 nA.

Table I summarizes the reflectance FTIR absorption peaks for the copolymers, which were prepared at different initial concentrations of each monomer and the individual homopolymers. The appearance of characteristic peaks in the copolymer of sample NVCzMeTh4, where the initial content of MeTh was high, confirms the inclusion of MeTh into the copolymeric coating structure. Also FTIR results clearly show the presence of characteristic peaks of NVCz (Figs 1 and 2 show that the difference between homopolymer and copolymer was obvious from FTIR-ATR). Also from XPS results (Table II), the incorporation of either of the monomers into the structure of the copolymer coating can be observed although the initial composition in the monomer feed ratio was not maintained in the surface of the resulting copolymer coatings. For example the ratio of S content of NVCzMeTh4 to that of NVCzMeTh1 was found to be ~2.0. Similarly the N ratio was ~0.6, resulting in a ratio of S/N = 3.3, where the ratio of initial concentrations of the same sequence was 10.5.

The EDX measurements of electrografted MeTh, NVCzMeTh1 and NVCzMeTh4 polymer and copolymers onto carbon fiber are shown in Fig. 3. The presence of Cl and O atoms indicates the inclusion of perchlorate anions from the supporting electrolytes.

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TABLE I Assignments for the reflectance FTIR absorption frequencies observed for electrografted copolymers on carbon fiber with respect to functional groups of copolymer (assignments of stretching, and in-plane deformation of $(C—S)_{ring}$, $(C{=}C)_{ring}$, $(C—C)_{ring}$ of NVCz, and ClO_4^- are in agreement with literature values [6, 7])

Wavenumbers (cm^{-1}) NVCz	Wavenumbers (cm^{-1}) MeTh	Wavenumbers (cm^{-1}) NVCzMeTh1	Wavenumbers (cm^{-1}) NVCzMeTh4	Assignments	
2928		3308 (w)		$\gamma(C—H)$	Asym. stretch. arom. struct.
2094, 2649	2332, 2105		2094, 2306, 2649	$\gamma(C—C)_{ring}$	Ring of 3-MeTh and NVCz
1649	1600	1651	1654	$\gamma(C{=}C)_{ring}$	3-MeTh and NVCz
1451		1451	1449 (w)-	$\gamma(C{=}C)_{ring}$ $\gamma(C—C)_{ring}$	Ring vibration of NVCz
1222		1224	1250 (w)	$\gamma(C—N)$	NVCz
1016		1090, 1056	1087	ClO_4^-	Supporting electrolyte (TMAP)
	920		924 (w)	$\gamma(C—S)_{ring}$	3-MeTh
745		747	724 (w)		Subst. aromatic ring of NVCz
		621 (w)	615 (w)	$\delta(ClO_4^-)$	Supporting electrolyte (TBAP)

Note: γ represents stretching, δ in-plane deformation, w, weak.

These inclusions are due to the doping of the copolymer by anions of the supporting electrolyte as a result of further oxidation during the electro-oxidative coating process [2, 3].

Table II shows the relative amounts of C, Cl, N, O and S for the two copolymer treated coatings. It also includes similar analyses for the MeTh-coated fiber. The Cl/Cl+S, O/C+S and N/N+S ratios are calculated

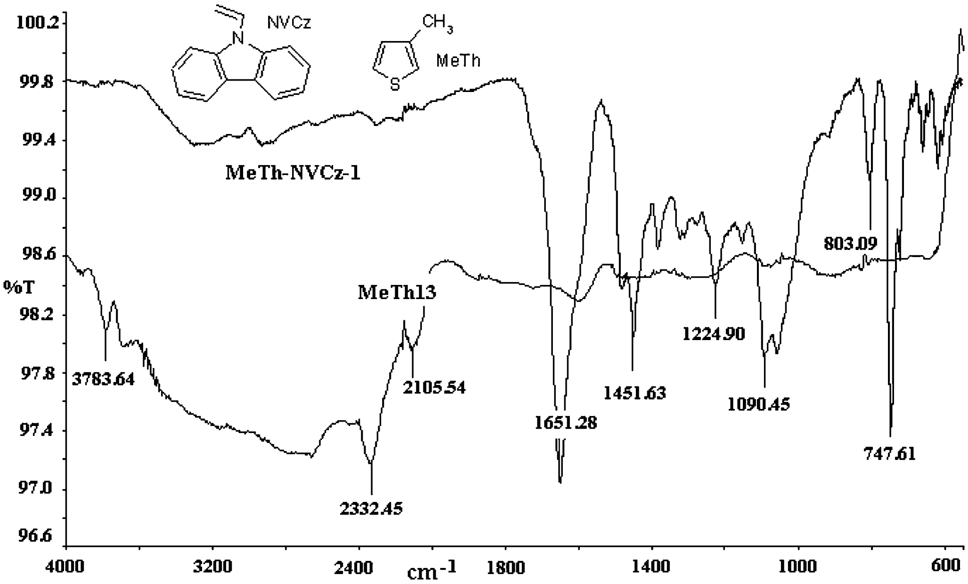


Figure 1 FTIRATR of NVCzMeTh1 and MeTh 13.

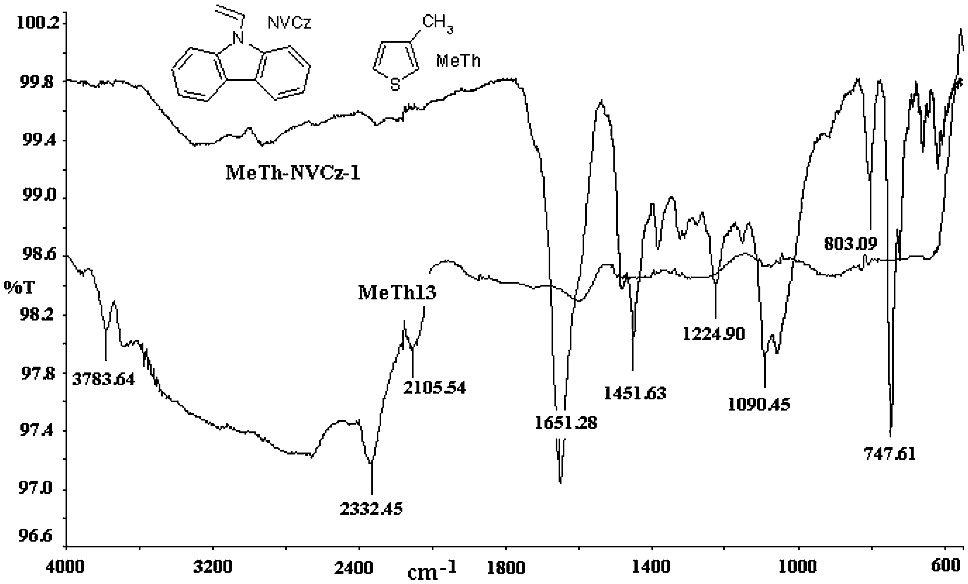


Figure 2 FTIRATR of electrografted nanosize coating of NVCzMeTh4.

TABLE II Effect of monomer feed ratio on surface and bulk composition as obtained from XPS and EDX studies. The values in parentheses are obtained from EDX (as a qualitative indication)

Fraction and feed ratio	NVCzMeTh1 [a]$z = 0.57$ $[\text{NVCz}]_0$:$[\text{MeTh}]_0 = 0.75$	NVCzMeTh4 [a]$z = 0.93$ $[\text{NVCz}]_0$:$[\text{MeTh}]_0 = 0.07$	MeTh [a]$z = 1$ –
From XPS			
C (at%)	78.32	77.47	71.56
Cl (at%)	0.51	1.35	1.20
N (at%)	3.56	2.19	2.47
O (at%)	14.31	13.94	17.58
S (at%)	1.17	2.36	2.31
Cl/C+S	0.006 (EDX: 0.122)″	0.017 (EDX: 0.012)	0.016 (EDX: 0.008)
O/C+S	0.180 (EDX: 0.113)[c]	0.175 (EDX: 0.020)[c]	0.238 (EDX: 0.012)[c]
N/N+S	0.753	0.481	
Calculated[b] N/N+S ratio from model $(\text{NVCZ})_x/(\text{MeTh})_y$	0.754	0.505	–
Structure fit to experimental value (XPS): $(\text{NVCZ})_x/(\text{MeTh})_y$	7/1	7/3	–

[a] Fraction of initial MeTh in total $z = [\text{MeTh}]_0/\{[\text{NVCz}]_0+[\text{MeTh}]_0\}$.

[b] Calculated on the basis of theoretical formula of $[C_{14}NH_9]_x$ $[C_5SH_4]_y$.

[c] Calculated from EDX results, difference in values can be attributed to the difference in sensitivity and measurement depths of both techniques.

from these amounts. Similar ratios are calculated from the EDX measurements and are given in the parentheses. It can be seen that in the coating where the MeTh feed ratio, x is lower (0.57, corresponding to a higher proportion of NVCz), the Cl content both at the surface and at the bulk is high. This is also true for the bulk level of O as revealed from the EDX, while the relative amount of O at the surface, as revealed from

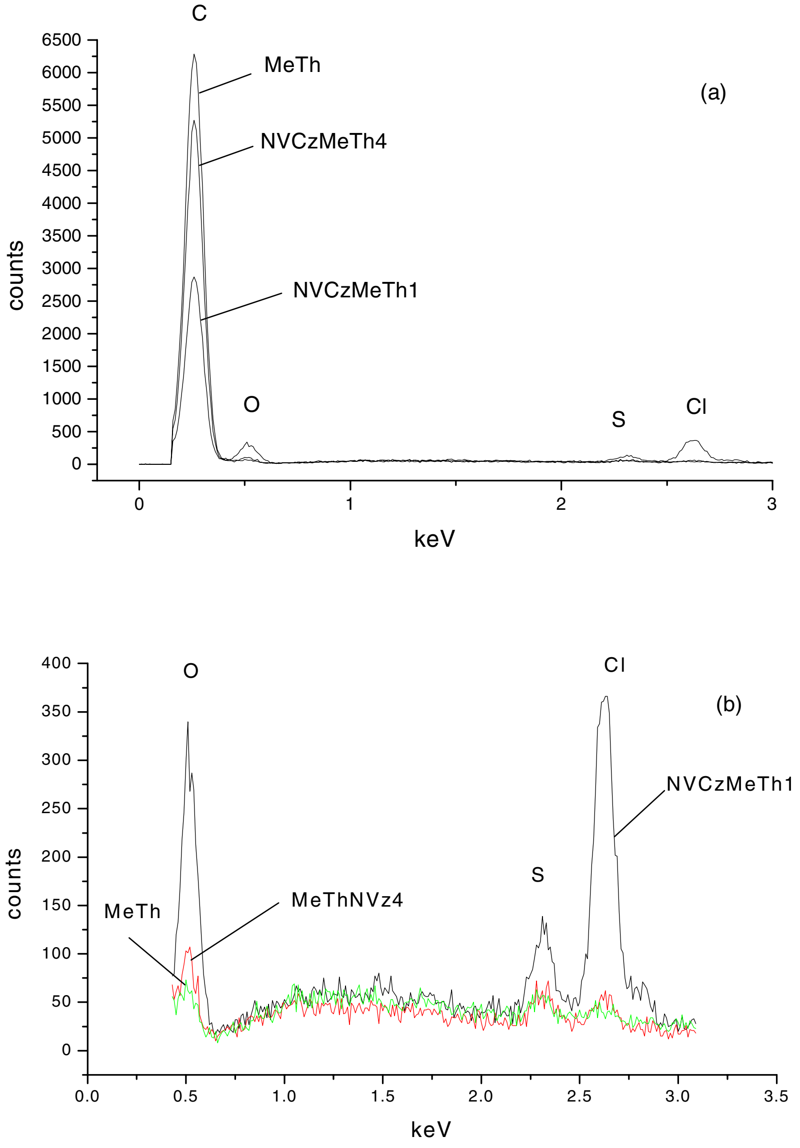


Figure 3 (a) EDX of electrografted MeTh, NVCzMeTh1 and NVCzMeTh4 onto carbon fiber (b) enlarged y-scale section of (a): between 0.4–3.0 keV.

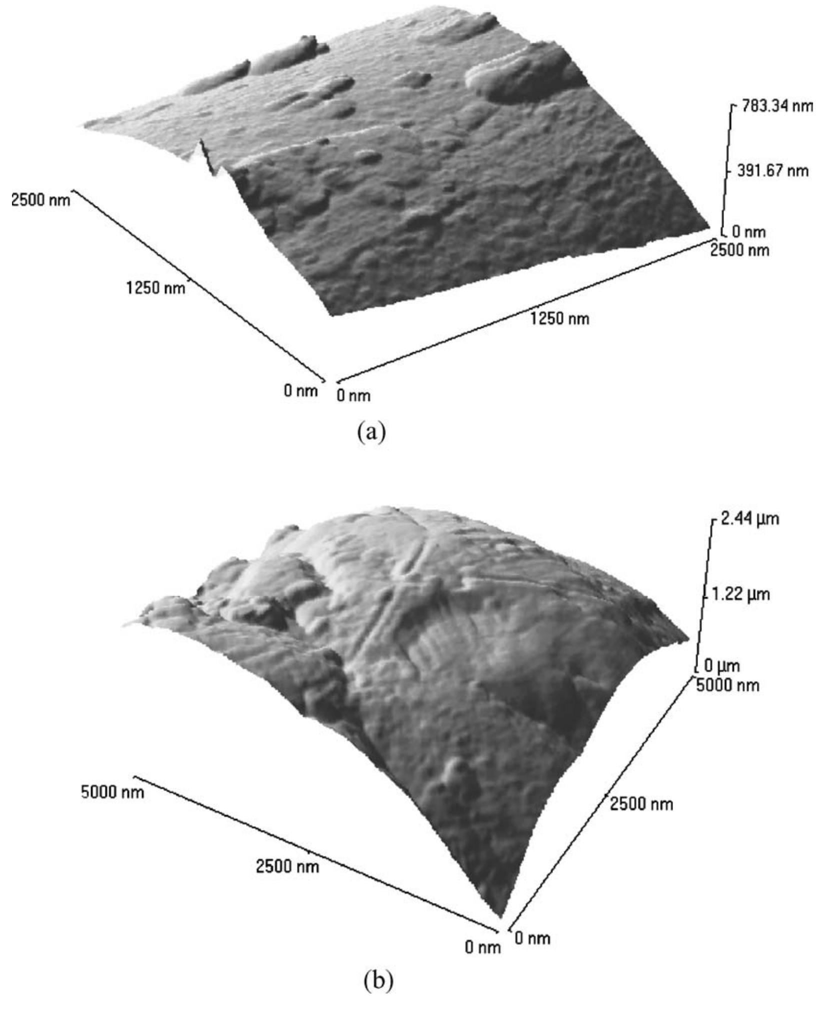
XPS, remains practically insignificant to the change in feed ratio. In other words, this indicates that an increase in the amount of NVCz in the copolymer produces a higher doping by the anion of the supporting electrolyte. The presence of oxygen at the copolymer surface can be due to two reasons: further oxidation of copolymer during oxidative coating process and/or oxygen contained in the dopant anion (ClO_4^-). The relative amounts of Cl can be taken as an indicator of the doping level of the electrografted coating. The doping level ranges from 0.51% for NVCzMeTh1 to 1.35% for NVCzMeTh4.

The N/{S+N} ratio was calculated from XPS results, and experimental values were compared and fitted to the model copolymer structure $(NVCz)_x$-$(MeTh)_y$ for NVCz and MeTh electrocopolymerization onto carbon fiber. Under two different ratios of comonomers the N/[N+S] values were found to be 0.75 (experimental), and 0.754 (theoretical) for NVCzMeTh1, while for NVCzMeTh4 the values were 0.48 (experimental) and 0.51 (theoretical). The x/y ratios were 7/1 and 7/3 for NVCzMeTh1 and NVCzMeTh4 respectively. The presence of N was also found in poly-MeTh electrocoated carbon fiber. This could be due to the composition of the original fiber itself (PAN based carbon fiber) that remains in part exposed even after electrocoating with poly-MeTh (see AFM image in Fig. 7), or to the contamination by the TMAP supporting electrolyte.

For the $[NVCz]_0/[MeTh]_0$ feed ratio of 0.75 (NVCzMeTh1), the x/y ratio was calculated from the XPS analyses to be 7/1 (Table II). For the case of NVCzMeTh4, where the initial feed ratio of NVCz was lower (0.07), the calculated x/y ratio was found to be 7/3. Therefore, even when there was a very low amount of NVCz present on the initial feed ratio, due to its higher reactivity, its inclusion in the copolymer structure was higher in comparison to MeTh.

AFM and SEM analysis are shown in Figs 4–7. Fig. 4 shows images of the surface of NVCz-MeTh1. In this case the surface shows inhomogeneity with areas of different coating thicknesses. The AFM image of the NVCzMeTh4 electrocoated carbon surface is shown in Fig. 5. The electrocoating leads to grains with an average radius of 140 nm. The agglomerations of grains have a radius of 1 micron (an SEM image of the same sample is given in Fig. 6). The difference between these two samples lies in their initial feed ratios. In sample NVCzMeTh4 the amount of initial $[MeTh]_0$ is 14 times larger than in sample NVCzMeTh1, leading to a large difference on the coating morphology. The presence of MeTh in larger quantity induces a rougher surface.

Fig. 7 shows the carbon surface electrocoating obtained with MeTh. Due to the low reactivity of MeTh in the conditions used in this work the electrocoating led to a general thin film formation on the carbon fiber surface with sporadic growth of polymer grains that



(a)

(b)

Figure 4 AFM 3D images of sample NVCzMeTh1.

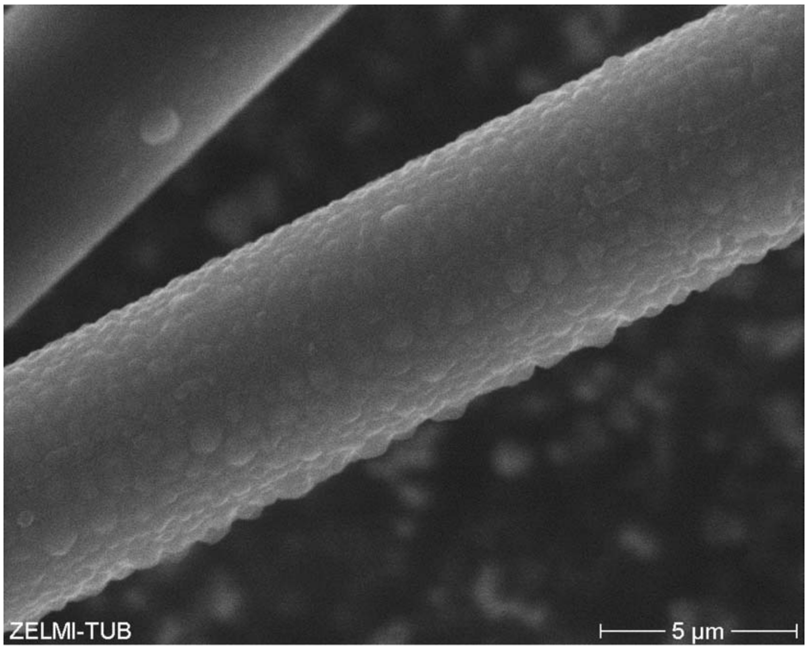


Figure 5 NVCzMeTh4 (increase in radius compared to ungrafted fiber is 380 ± 30 nm).

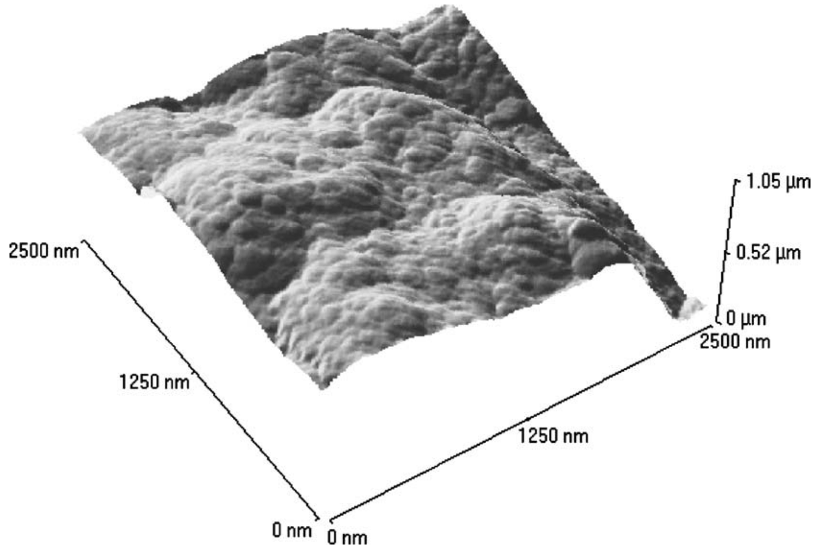


Figure 6 AFM 3D image of sample NVCzMeTh4.

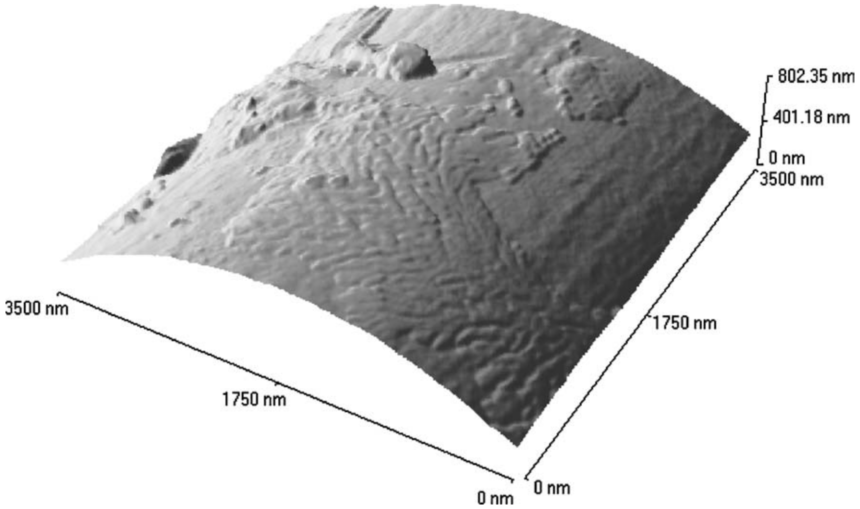


Figure 7 AFM of electrografted poly(3-MeTh) onto carbon fiber.

seems to initiate from a defect on the carbon surface and proliferate with a fractal structure.

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