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Structure-Reactivity Requirements

with Respect to Nickel-Salen Based Polymers

for Enhanced Electrochemical Stability

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ABSTRACT

Studies revealing general guidance on preparation of electrochemically stable *meso* forms of nickel-salen based polymers as new anode materials for electrochemical devices were performed. Electrochemical performance of these nickel-salen complexes, used as monomers of nickel-salen based polymers, is directly related to the salen ligand structure. Therefore, we

have considered these features in specially designed and synthesized herein new *meso* form of nickel-salen polymer, vis., poly[*meso-N,N'*-bis-(3-methylsalicylidene)-2,3-butanediaminonickel(II)], abbreviated as poly(*meso*-Ni-SaldMe-3dMe). Furthermore, electrochemical conditions suitable for providing the environment appropriate for electropolymerization and charge transfer were optimized. In dependence upon the purpose of the use of the poly(*meso*-Ni-salen) electrodes, it was possible to increase the amount of the charge stored in the polymer conjugated system by proper tuning of both the chemical structure of the polymer and electrochemical conditions. Apparently, the charge transfer through nickel-salen polymers strongly depends upon steric hindrance between polymer layers ensuring efficient counter ions doping. Therefore, this hindrance should carefully be selected. We have defined certain steric requirements with respect to the type and position of moderately electrodonating substituents on the nickel-salen polymers that must be met to achieve high conductivity and stability/durability during potential multi-cycling of the polymer films prepared.

1. INTRODUCTION

Nickel-salen based polymers are Schiff base semiconducting macromolecular compounds composed of multiple monomer units of the same salen metal complex bound in *para* positions of their aromatic rings. Salen-metal complexes are an important class of tetradentate [*O*, *N*, *N*, and *O*] *bis*-Schiff base ligands capable to coordinate cations of different transition metals, e.g., Cr, Ni, Cu, and Co. The undisputed advantage of salen ligands is their relatively easy synthetic preparation by condensation of two equivalents of salicylaldehyde or its derivatives with one equivalent of ethylenediamine or with its derivatives [1]. The metal cation is coordinated through the imine nitrogen atom and the oxygen atom after phenolic proton removal. During

anodic electropolymerization of nickel-salen complexes, electroactive films of conductive nickel-salen based polymers are formed. This electropolymerization proceeds only in moderately electron-donating solvents, including acetonitrile or propylene carbonate [2-4]. However, it does not proceed in electrodonating solvents or in the presence of other electron-donor compounds capable of axial coordination to the nickel metal center of the salen monomer [2, 3, 5, 6]. Then, oxidation of the resulting complex leads to formation of Ni(III) with no polymerization occurring. Besides, the effect of ligand polarization caused by polymer-based nickel-salen modified electrodes interaction with aromatic amines has already been studied [7]. It was proposed that axial coordination of amine to the nickel center of the polymer or its bonding to salen ligand oxygen atoms was responsible for changes observed during electro-oxidation of different nickel-salen polymers in the presence of aromatic amines [7].

For application reasons, it is important to comprehend the difference between nickel-salen based polymers and hybrid polymers with incorporated metal-salen complexes or salen ligands [8]. For instance, electropolymerization of thiophenes substituted with salen metal complexes results in formation of the so-called polythiophene hybrids of transition-metal *bis*(salicylideneimine)s. These hybrids are readily formed via polymerization of thiophene moieties, thus leading to thiophene based polymers with incorporated metal-salen centers [9]. These hybrids were applied as catalysts for heterogeneous asymmetric catalysis [10] and as recognition materials for fabrication of electrochemical sensors [11, 12]. Importantly, electrochemical properties of such polythiophene hybrids of transition-metal *bis*(salicylideneimine)s or any other salen containing hybrid polymers and conductive metal-salen based polymers are markedly different with respect to their both charge transfer and polymerization mechanism.

There is a significant difference between so-called sterically hindered metal-salen complexes [13] and conducting metal-salen polymers with or without steric hindrance on the

imine bridge. That is, the former are unable to polymerize. In the latter, bulky substituents, inserted in *ortho* and *para* positions of the salen ligand of a metal-salen complex, stabilize the one-electron electro-oxidation products [14]. Depending on such factors as the type of these substituents, metal coordination sphere, solvent, and temperature, the electronic structure of these products can be tuned between different forms containing Ni(II) or Ni(III). However, these products are not conducting in a whole continuous potential range because of their valence electrons lack of delocalization in the electric field. Instead, nickel-salen based polymers are electrochemically active in the positive potential range because of the presence of Ni(II)-bridged conjugated electron-donating phenolic moieties.

Nickel-salen based polymer films reveal a mixed redox and π -conjugated conductivity. Their faradic-capacitive charge storage mechanism is attributed to the transfer of delocalized valence electrons in polymer semiconductors, such as nickel-salen based polymers [15]. This transfer occurs in a continuous range of potentials involving two forms of oxidized Ni(II) bridged *bis*-Schiff base ligands, coupled in the polymer chain [16, 17]. The structures of oxidized *bis*-Schiff base ligands bridged with Ni(II) metal centers are responsible for the charge transfer in the nickel-salen based polymers. These oxidized structures were recognized spectroelectrochemically as bisphenolic radical cations and bisphenolic dications [2]. Understanding of the charge transfer mechanism allowed us earlier devising stable and durable unsubstituted in phenyl rings *meso* form of conductive nickel-salen based polymer, vis., poly[*meso*-*N,N'*-*bis*-(salicylidene)-2,3-butanediaminonickel(II)], abbreviated as poly(*meso*-Ni-SaldMe) [2].

The faradaic process engaging a conductive polymer film involves transfer of charges (electrons and ions) across the electrode-electrolyte solution interface. The widely used as charge storage materials derivatives of polypyrrole, polyaniline, or polythiophene, electroactive in the positive potential range, suffer from low charge-discharge cycling stability [18, 19]. This

is because of the polymer volume change accompanying the counter ion shuttling in and out of the polymer during its charging and discharging [20-22]. Therefore, we have recently applied a carbon nanostructure composite of synthesized poly(*meso*-Ni-SaldMe) as an anode material for the asymmetric supercapacitor [2, 23]. Moreover, we emphasized extraordinary stability of this unsubstituted in phenyl rings *meso* Ni-salen polymer analog under electrochemical conditions, the feature uncommon as for nickel-salen based polymers. Hence, high stability of the poly(*meso*-Ni-SaldMe) film upon electrochemical charging and discharging directly arose from reversibility of concomitant viscoelastic and nanomechanical changes [23].

The encouraging results of our former studies focused on unsubstituted in phenyl rings poly(*meso*-Ni-SaldMe) stability and charge transfer mechanism [2, 23, 24] prompted us to find the first structure-reactivity requirement with respect to nickel-salen based polymers ensuring its electrochemical stability. The first structure-reactivity requirement for preparation of electrochemically stable nickel-salen polymer is its *meso* form governed by the two methyl substituents placed on the imine bridge ensuring its electrochemical stability [2, 23, 24].

In order to extend the electroactivity range of *meso* nickel salen polymers (highly desirable for devising and fabricating novel energy storage materials) we synthesized a new analog of *meso* nickel salen polymer, viz. poly[*meso*-*N,N'*-bis-(3-methylsalicylidene)-2,3-butanediaminonickel(II)], abbreviated as poly(*meso*-Ni-SaldMe-3dMe). Then, we compared its electrochemical stability with two known nickel-salen polymers, differing in seemingly negligible structural changes within the substituents placed on the Ni-salen imine bridge. For this comparison we selected earlier synthesized and studied by us unsubstituted in phenyl rings *meso* form of nickel salen polymer, poly(*meso*-Ni-SaldMe) and, nickel-salen polymer containing two dimethyl substituents on the imine bridge, poly[2,3-dimethyl-*N,N'*-bis-(salicylidene)-2,3-butanediaminonickel(II)], abbreviated as poly(NiSaltMe) [25, 26].

Preparation of new poly(*meso*-Ni-SaldMe-3dMe) improved *meso* form of the nickel-salen based polymer with methyl substituents in the 3-positions of each salicylaldehyde moiety was inspired by results of the research focused on electrochromic behavior of nickel-salen polymers behavior, which was different in the presence and absence of two dimethyl substituents on each carbon atom of the imine bridge [27]. Surprisingly, the nickel-salen polymer analog without these substituents, used as the mentioned above electrochromic material, exhibited higher electrochemical stability than its tetra substituted analog. This finding is consistent with the results of our previous [2, 23, 24] and present experimental studies complemented with the literature studies [27, 28] defining and explaining structure-reactivity requirements with respect to electrochemically stable nickel-salen based polymers revealing enhanced charge storage capability.

EXPERIMENTAL SECTION

Chemicals

Tetra(n-butyl)ammonium hexafluorophosphate, (TBA)PF₆, (puriss, electrochemical grade), propylene carbonate (anhydrous, electrochemical grade) were purchased from Sigma-Aldrich and used without further purification. The monomeric nickel-salen based complexes, vis., *meso*-Ni-SaldMe-3dMe, *meso*-Ni-SaldMe, and NiSaltMe, were synthesized in our laboratory according to procedures described earlier [2, 23].

Electrochemical cell configuration and electrodes

The Au coated glass slide, and ITO electrodes with ~0.25 cm² and ~0.78 cm² electrochemically active area, respectively, were used as the working electrodes. A Pt tab and a silver wire were used as the counter and pseudo-reference electrode, respectively.

Apparatus

Electrochemical experiments including polymer deposition by potentiodynamic electropolymerization and multi-scan cyclic voltammetry (CV) measurements were performed with a VSP electrochemistry system of BioLogic (SP 150) Science Instruments controlled by EC-Lab software of the same manufacturer. Surface of the polymer film coated electrodes was imaged with scanning electron microscopy (SEM) using a FEI Nova NanoSEM 450 microscope.

Atomic force microscopy (AFM) images were carried out in PeakForce tapping™ mode in air using a Bioscope Resolve (Bruker Nano Surface, Bruker France SAS, Palaiseau, France). Silicon nitride cantilevers of conical shape were purchased from Bruker (NPG-10, Bruker France SAS, Palaiseau, France) with spring constant of about 0.35 nN/nm. The applied force between the tip and the surface was carefully monitored and minimized at about 0.20 nN and all images were collected with a resolution of 512×512 pixels and a scan rate of 0.5 Hz. These experimental conditions are necessary to prevent mechanical damages of the sample surface due to the lateral scanning and the corresponding shear stress. AFM images with scan size of $2 \mu\text{m} \times 2 \mu\text{m}$ were then analyzed with Nanoscope Analysis for extracting roughness, thickness and textural feature of the polymer films.

Profilometry measurements were carried out using a Detak stylis profiler DetakXT (Bruker Nano Surface, Bruker France SAS, Palaiseau, France).

1. RESULTS AND DISCUSSION

Electrochemical synthesis of nickel-salen based polymer films

Nickel-salen based polymer films were prepared in a three-electrode electrochemical cell by electropolymerization under potentiodynamic conditions on Au coated glass slide and (or) ITO working electrodes (separately). The polymer films were grown oxidatively from propylene carbonate solutions of 1 mM nickel-salen complexes (*meso*-Ni-SaldMe-3dMe, *meso*-Ni-SaldMe, and NiSaltMe) in 0.1 M (TBA)PF₆ by potential multi-cycling between 0.0 and 1.20 V vs. Ag/Ag⁺ at a scan rate of 100 mV s⁻¹, during 50 cycles, under argon atmosphere (Figures 1, 2, and 3, respectively) on Au coated glass slide working electrode substrates, and 0.0 and 1.70 V vs. Ag/Ag⁺ at a scan rate of 100 mV s⁻¹, during 50 cycles, under argon atmosphere on ITO working electrode (Figure S1). For all nickel-salen based polymer films, deposition was pointed out by the current increase in consecutive potential cycles. Moreover, this increase indicated that the deposited films were conductive. After polymer electrodeposition, the resulted film coated electrode was rinsed with the abundant propylene carbonate solvent before further use. The electrochemical responses of the so-fabricated films were recorded, in a three-electrode system, in a monomer-free solution of 0.1 M (TBA)PF₆ in propylene carbonate, this medium being selected from previous observations of stable doping and dedoping of poly(*meso*-Ni-SaldMe) film as performed in such medium over 10 000 times without stability loss [23]. However, in case of the use of, e.g., 0.1 M (TBA)ClO₄ in acetonitrile, the ClO₄⁻ anions were entrapped even in the neutral poly(*meso*-Ni-SaldMe) [2]. Similar entrapment of ClO₄⁻ anions in electro-chemically generated nickel-salen based polymer films was observed by others [27].

For efficient electrodeposition of nickel salen based polymer films, it is crucial to exceed the potential value of nickel-salen complex (monomer) oxidation in the first polymerization cycle. Oxidation of the *meso*-Ni-SaldMe-3dMe on the gold plate electrode occurs at ~0.9 V vs. Ag/Ag⁺ (Figure 1b), while it happens at a more anodic value on the ITO electrode ~1.2 V (Figure S1 a). The same anodic shift when passing from gold to ITO electrode is observed for

the oxidation of *meso*-Ni-SaldMe and NiSaltMe (occurring at ~ 1.0 V vs. Ag/Ag⁺ on gold (Figures 2b and 3b), and at ~ 1.3 V on ITO). The oxidation potential of these nickel-salen monomers depends on its chemical structure (reflected in different electron density distribution). Furthermore, oxidation potential of nickel salen complexes can shift in dependence of working electrode substrate used for its electrodeposition. Electropolymerization of nickel-salen complexes without electrodonating substituent in phenyl rings at too low potential values leads to preparation of unstable nickel-salen polymer films [29].

Electrochemical stability of nickel-salen based polymer films

Chemical structure of nickel-salen based polymers and conditions of their films preparation determine electrochemical stability and the amount of charge that is reversibly stored in these potential-driven π -conjugated polymer redox systems. Hence, studies of their stability under the applied potential conditions are essential for understanding, and then improving their electrochemical properties. Therefore, we herein studied electrochemical stability of carefully selected nickel-salen polymers with different chemical structures, namely, poly(*meso*-Ni-SaldMe-3dMe) (Scheme 1a), poly(*meso*-Ni-SaldMe) (Scheme 1b), and poly(Ni-SaltMe) (Scheme 1c), with respect to potential multi-cycling under CV conditions, from 0.0 to 1.2 V vs. Ag/Ag⁺ for 200 cycles in monomer-free solutions (Figure 4). Furthermore, our previous [2, 23, 24] and present experimental studies of nickel-salen based polymers supplemented with literature [27, 28] studies of their chemical structure modifications were required for preparation of electrochemically stable nickel-salen polymer films indicating extended conductivity in the positive potential range.

In general, the charge transfer mechanism is ultimately ligand-based for all nickel-salen polymers [2, 16, 25, 30]. However, the pathway of charge conduction and delocalization of

charge carriers are affected by differences in the polymer chemical structure [28]. Nickel-salen polymers with no substituents in the 3-position of each salicylaldehyde moiety, like poly(*meso*-NiSaldMe) and poly(NiSaltMe), should conduct charge linearly, i.e., along the -O=Ph=Ph=O-(Ni)-O=Ph=Ph-O- conduction path [2, 16]. Phenolic oxygen atoms, located next to the nickel atom, are redox centers of salen polymers [2] while linearly coupled semi-quinoid and quinoid polymer structures, containing the π -conjugated system, transfer the charge between the redox centers. In nickel-salen polymers with unsubstituted phenyl rings, the redox and electronic conductivity is expected to be balanced. However, this balance can be disrupted either by introduction of substituents in the 3-position of each salicylaldehyde moiety of the polymer or steric hindrance, differing in electron-donor nature, imposed on the imine bridge. A proper way of modification of chemical structure of nickel-salen based polymers for enhancing their conductivity and increasing their electrochemical stability is not obvious. Even small structural changes of these polymers affect their electrochemical stability and the charge storage mechanism [28]. Seemingly, introduction of strongly electrodonating methoxyl substituents into phenyl rings of nickel-salen based polymers should increase the amount of charge that can be reversibly stored in these polymers [29]. Therefore, their electron density increase is expected in the π -conjugated system. However, introduction a strongly electrodonating substituent into 3-position of each salicylaldehyde of the nickel-salen polymer largely inhibits linear coupling [28], which is responsible for effective charge transfer between two neighboring phenolate moieties bridged by the nickel metal center. The presence of strong electron donors in both 3-positions of phenolic rings in the nickel-salen polymer causes ligand-radical localization reflected by disruption of the balance between the redox and electronic conductivity. Therefore, introduction of relatively weak electron donors, such as methyl substituents, in both 3-positions of phenolic rings allows increasing the amount of charge that

can be reversibly stored by these polymers. This is because the balance between redox and electronic conductivity is not disrupted.

Spectroelectrochemical experiments clearly indicated that sterically hindered nickel-salen polymers containing two dimethyl substituents on each carbon atom of the imine bridge of the poly(NiSaltMe) analogs did not allow for substantial charge inter- delocalization [28]. Moreover, the presence of two dimethyl substituents on each carbon atom of the imine bridge strongly influences pathways and delocalization of charge carriers in the poly(NiSaltMe), thus decreasing its electrochemical stability. The charge decrease in each consecutive cycle (Figure 4c and 4d) for the poly(NiSaltMe) under CV conditions confirms that even small chemical structure changes lead to the decrease of electrochemical stability of the nickel-salen based polymer while *meso* forms of nickel-salen polymers, namely, poly(*meso*-Ni-SaldMe-3dMe) (Figure 4a and 4d) and poly(*meso*-Ni-SaldMe) (Figure 4b and 4d) containing two moderately electrodonating methyl substituents located on the imine bridge in the one plane of monomer unit, reveal high electrochemical stability under these conditions.

Introduction of two methyl substituent in the 3-positions of each salicylaldehyde moiety in poly(*meso*-Ni-SaldMe-3dMe) allows extending the conductivity in the positive potential range without decreasing the electrochemical stability (curve 1 in Figure 5). The electroactivity range of ~ 0.3 to ~ 1.20 V vs. Ag/Ag⁺ for the poly(*meso*-Ni-SaldMe-3dMe) is wider than those for the poly(*meso*-Ni-SaldMe) and poly(NiSaltMe) being ~ 0.45 to ~ 1.2 V vs. Ag/Ag⁺ and ~ 0.6 to ~ 1.2 V vs. Ag/Ag⁺, respectively, (Figure 5).

Figure 6 shows CV curves at different potential scan rates for the poly(*meso*-Ni-SaldMe-3dMe) film (Figure 6a) as well as the anodic and cathodic peak currents dependence for this polymer on the potential scan rate (Figure 6b). The linear dependence of the logarithm of both anodic and cathodic peak current on the logarithm of the potential scan rate (Figure 6b) indicates that

the rate of the electrode processes is controlled by the rate of finite diffusion [31]. Apparently, peak potentials are independent of the potential scan rate up to $\sim 30 \text{ mV s}^{-1}$. Moreover, anodic and cathodic peak potentials separation of $\sim 0.05\text{-}0.10 \text{ mV}$ (caused by ohmic resistance) evidences reversibility of the electrode processes (Figure 6c). Figure 6d shows the dependence of the accumulated charge on the potential scan rate for the poly(*meso*-Ni-SaldMe-3dMe) film. The amount of charge decreases with the increase of the potential scan rate because the rate of diffusional permeation of counter ions into the film cannot keep up with high scan rates. Moreover, the volumetric capacitance of the poly(*meso*-Ni-SaldMe-3dMe) film is higher than that for the poly(*meso*-Ni-SaldMe) and poly(NiSaltMe) film (Figure 5b). This advantageous feature favors this methyl-phenyl ring substituted *meso* nickel-salen based polymer as a new anode material for energy storage applications.

Figure 7 presents SEM images of (a) poly(*meso*-NiSaldMe-3dMe), (b) poly(*meso*-NiSaldMe), (c) poly(NiSaltMe) films. Apparently, morphology of poly(*meso*-NiSaldMe) and poly(NiSaltMe) films is similar. These films reveal a non-ordered globular structure (Figure 7b and 7c). However, the full inspection of these films by AFM at high resolution show (Figure S3, S4 and S5) some differences in the graininess size and roughness. Indeed, poly(*meso*-NiSaldMe) exhibits globules of $\sim 138 \text{ nm}$ diameter while for poly(NiSaltMe) the globules size is $\sim 234 \text{ nm}$. Furthermore, the analysis evidenced that the average distance between neighbouring globular structures remains at $\sim 60 \text{ nm}$ for both poly(*meso*-NisaldMe) and poly(NiSaltMe) films. This peculiar surface architecture is governed by continuous counter ions shuttling in and out of the polymer film occurring under potentiodynamic electropolymerization conditions of film deposition (Figures 1 and 2). It can be emphasized that highest roughness is measured for poly(NiSaltMe) and the lowest for poly(*meso*-NisaldMe-3dMe) films. The latter is the most homogeneous/continuous and did not exhibit any globular structures as reported in Figure 8a. Then, the film thickness of each sample was measured by

AFM upon images performed on scratch zones. As reported in figures S3b, S4b and S5b, thicknesses of 53, 83 and 115 nm were measured for poly(*meso*-NiSaldMe-3dMe), poly(*meso*-NiSaldMe) and poly(NiSaltMe) films, respectively. Indeed, the local thicknesses obtained by AFM measurements are in good accordance with macroscopic ones performed by profilometry as reported in tables S1, S2 and S3. The reported values reflect that thinner is the film and the lowest roughness were obtained. Film decrease in both thickness and roughness regarding the polymer because of smaller counter ions entrapment within the matrix and also depending on adapted structure/conformation.

2. CONCLUSIONS

Electrochemical stability improvement in *meso* forms of nickel-salen based polymers results from introduction of moderately electrodonating steric hindrance between polymer layers within the imine bridges, thus ensuring efficient counter ions doping. Two methyl substituents in the *meso* nickel-salen polymer forms repel polymer layers one from the other. That way, space is generated for counter ion movement in and out of the polymer for doping and dedoping, respectively [24]. However, introduction of two dimethyl substituents on each carbon atom of the imine bridge decreases electrochemical stability of the presently and previously studied [27, 28] poly(Ni-salen) films. The poly(*meso*-Ni-SaldMe-dMe) and poly(*meso*-Ni-SaldMe) retains ~96 % of its normalized charge after 200 consecutive CV cycles, while, poly(NiSaltMe) retains only ~30 % of its normalized charge after 200 consecutive CV cycles. Furthermore, introduction of moderately electrodonating methyl substituents in both 3-positions of the salicylaldehyde moieties of *meso*-Ni-salen based polymers affects the polymer electron density distribution, which results in effective charge delocalization. The presence of these two methyl

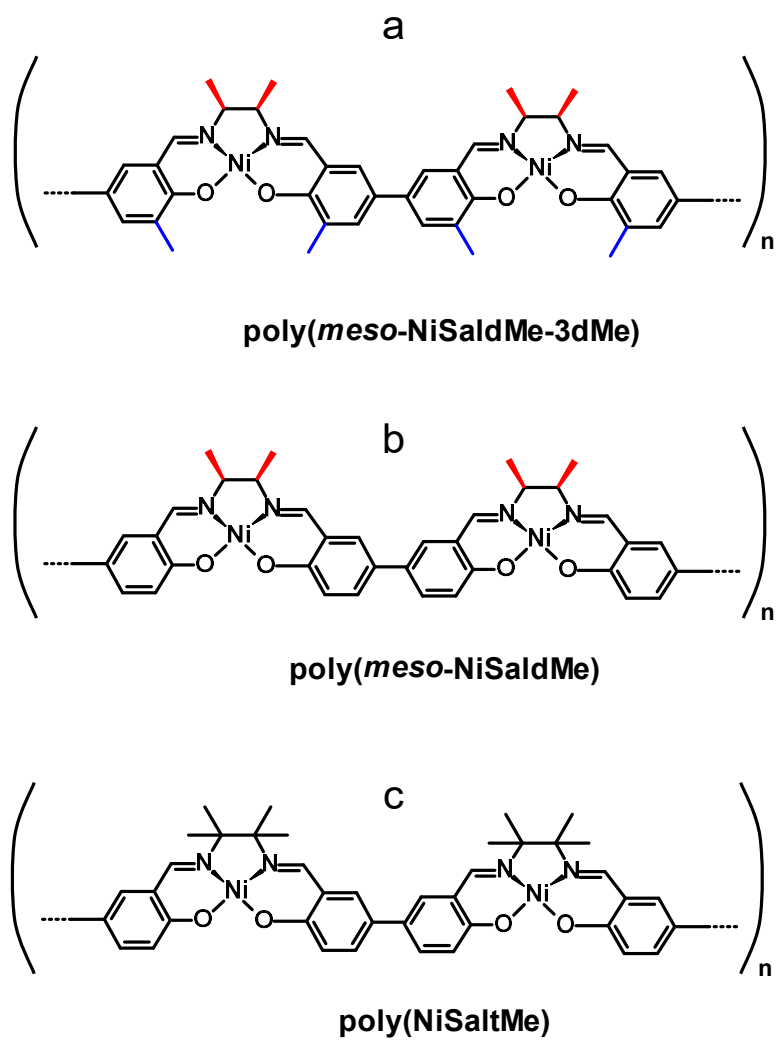
substituents broadens the potential range of the *meso* nickel-salen polymer electroactivity without decreasing its electrochemical stability.

REFERENCES

- [1] P.G. Cozzi, Metal–Salen Schiff base complexes in catalysis: practical aspects, *Chem. Soc. Rev.*, 33 (2004) 410-421.
- [2] K. Łępicka, P. Pieta, A. Shkurenko, P. Borowicz, M. Majewska, M. Rosenkranz, S. Avdoshenko, A.A. Popov, W. Kutner, Spectroelectrochemical Approaches to Mechanistic Aspects of Charge Transport in *meso*-Nickel(II) Schiff Base Electrochromic Polymer, *J. Phys. Chem. C*, 121 (2017) 16710-16720.
- [3] K.A. Goldsby, J.K. Blaho, L.A. Hoferkamp, Oxidation of Nickel(II) bis(salicylaldimine) Complexes: Solvent Control of the Ultimate Redox Site, *Polyhedron*, 8 (1989) 113-115.
- [4] L.A. Hoferkamp, K.A. Goldsby, Surface-Modified Electrodes Based on Nickel(II) and Copper(II) bis(salicylaldimine) Complexes, *Chem. Mater.*, 1 (1989) 348-352.
- [5] B. De Castro, C. Freire, EPR and electrochemical study of nickel(III) complexes of bis(3,5-dichlorosalicylaldehyde) *o*-phenylenediimine. Evidence for adduct formation with pyridines, *Inorg. Chem.*, 29 (1990) 5113-5119.
- [6] C. Freire, B. de Castro, Spectroscopic characterisation of electrogenerated nickel(III) species. Complexes with N₂O₂ Schiff-base ligands derived from salicylaldehyde, *J. Chem. Soc., Dalton Trans.*, (1998) 1491-1498.
- [7] A.A. Vereshchagin, V.V. Sizov, M.S. Verjuzhskij, S.I. Hrom, A.I. Volkov, J.S. Danilova, M.V. Novozhilova, A. Laaksonen, O.V. Levin, Interaction of amines with electrodes modified by polymeric complexes of Ni with salen-type ligands, *Electrochim. Acta*, 211 (2016) 726-734.
- [8] M. Sukwattanasinitt, A. Nantalaksakul, A. Potisatityuenyong, T. Tuntulani, O. Chailapakul, N. Praphairakait, An Electrochemical Sensor from a Soluble Polymeric Ni–salen Complex, *Chem. Mater.*, 15 (2003) 4337-4339.
- [9] R.P. Kingsborough, T.M. Swager, Polythiophene Hybrids of Transition-Metal Bis(salicylidenimine)s: Correlation between Structure and Electronic Properties, *J. Am. Chem. Soc.*, 121 (1999) 8825-8834.

- [10] A. Zulauf, X. Hong, F. Brisset, E. Schulz, M. Mellah, Electropolymerization of chiral chromium–salen complexes: new materials for heterogeneous asymmetric catalysis, *New J. Chem.*, 36 (2012) 1399-1407.
- [11] J.-C. Eloi, L. Chabanne, G.R. Whittell, I. Manners, Metallopolymers with emerging applications, *Mater. Today*, 11 (2008) 28-36.
- [12] B.J. Holliday, T.B. Stanford, T.M. Swager, Chemoresistive Gas-Phase Nitric Oxide Sensing with Cobalt-Containing Conducting Metallopolymers, *Chem. Mater.*, 18 (2006) 5649-5651.
- [13] R.M. Clarke, K. Herasymchuk, T. Storr, Electronic structure elucidation in oxidized metal–salen complexes, *Coord. Chem. Rev.*, 352 (2017) 67-82.
- [14] F. Thomas, Ligand-centred oxidative chemistry in sterically hindered salen complexes: an interesting case with nickel, *Dalton Trans.*, 45 (2016) 10866-10877.
- [15] B. Akinwolemiwa, C. Wei, G.Z. Chen, Mechanisms and Designs of Asymmetrical Electrochemical Capacitors, *Electrochim. Acta*, 247 (2017) 344-357.
- [16] M. Vilas-Boas, C. Freire, B. de Castro, P.A. Christensen, A.R. Hillman, New Insights into the Structure and Properties of Electroactive Polymer Films Derived from [Ni(salen)], *Inorg. Chem.*, 36 (1997) 4919-4929.
- [17] V.V. Sizov, M.V. Novozhilova, E.V. Alekseeva, M.P. Karushev, A.M. Timonov, S.N. Eliseeva, A.A. Vanin, V.V. Malev, O.V. Levin, Redox transformations in electroactive polymer films derived from complexes of nickel with Salen-type ligands: computational, EQCM, and spectroelectrochemical study, *J. Solid State Electrochem.*, 19 (2015) 453-468.
- [18] T. Liu, L. Finn, M. Yu, H. Wang, T. Zhai, X. Lu, Y. Tong, Y. Li, Polyaniline and Polypyrrole Pseudocapacitor Electrodes with Excellent Cycling Stability, *Nano Lett.*, 14 (2014) 2522-2527.
- [19] G. Zotti, G. Schiavon, S. Zecchin, Irreversible processes in the electrochemical reduction of polythiophenes. Chemical modifications of the polymer and charge-trapping phenomena, *Synth. Met.*, 72 (1995) 275-281.
- [20] E. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota, F. Béguin, Supercapacitors based on conducting polymers/nanotubes composites, *J. Power Sources*, 153 (2006) 413-418.
- [21] M.A. Vorotyntsev, E. Vieil, J. Heinze, Ionic exchange of the polypyrrole film with the PC lithium perchlorate solution during the charging process, *Electrochim. Acta*, 41 (1996) 1913-1920.

- [22] M.A. Vorotyntsev, E. Vieil, J. Heinze, Charging process in polypyrrole films: effect of ion association, *J. Electroanal. Chem.*, 450 (1998) 121-141.
- [23] K. Łepicka, P. Pieta, R. Gupta, M. Dabrowski, W. Kutner, A redox conducting polymer of a meso-Ni(II)-SaldMe monomer and its application for a multi-composite supercapacitor, *Electrochim. Acta*, 268 (2018) 111-120.
- [24] K. Łepicka, M. Majewska, R. Nowakowski, W. Kutner, P. Pieta, High Electrochemical Stability of meso-Ni-Salen Based Conducting Polymer Manifested by Potential-Driven Reversible Changes in Viscoelastic and Nanomechanical Properties, *Electrochim. Acta*, 297 (2019) 94-100.
- [25] M. Vilas-Boas, C. Freire, B. de Castro, P.A. Christensen, A.R. Hillman, Spectroelectrochemical Characterisation of poly[Ni(saltMe)]-Modified Electrodes, *Chem. Eur. J.*, 7 (2001) 139-150.
- [26] M. Vilas-Boas, C. Freire, B. de Castro, A.R. Hillman, Electrochemical Characterization of a Novel Salen-Type Modified Electrode, *J. Phys. Chem. B*, 102 (1998) 8533-8540.
- [27] M. Nunes, M. Araújo, J. Fonseca, C. Moura, R. Hillman, C. Freire, High-Performance Electrochromic Devices Based on Poly[Ni(salen)]-Type Polymer Films, *ACS Appl. Mater. Interfaces*, 8 (2016) 14231-14243.
- [28] E. Dmitrieva, M. Rosenkranz, J.S. Danilova, E.A. Smirnova, M.P. Karushev, I.A. Chepurnaya, A.M. Timonov, Radical formation in polymeric nickel complexes with N2O2 Schiff base ligands: An in situ ESR and UV-vis-NIR spectroelectrochemical study, *Electrochim. Acta*, 283 (2018) 1742-1752.
- [29] E.V. Alekseeva, I.A. Chepurnaya, V.V. Malev, A.M. Timonov, O.V. Levin, Polymeric nickel complexes with salen-type ligands for modification of supercapacitor electrodes: impedance studies of charge transfer and storage properties, *Electrochim. Acta*, 225 (2017) 378-391.
- [30] J. Tedim, S. Patrício, J. Fonseca, A.L. Magalhães, C. Moura, A.R. Hillman, C. Freire, Modulating spectroelectrochemical properties of [Ni(salen)] polymeric films at molecular level, *Synth. Met.*, 161 (2011) 680-691.
- [31] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley 2000.



Scheme 1. Structural formulas of (a) poly(*meso*-NiSaldMe-3dMe), (b) poly(*meso*-NiSaldMe), (c) poly(NiSaltMe).

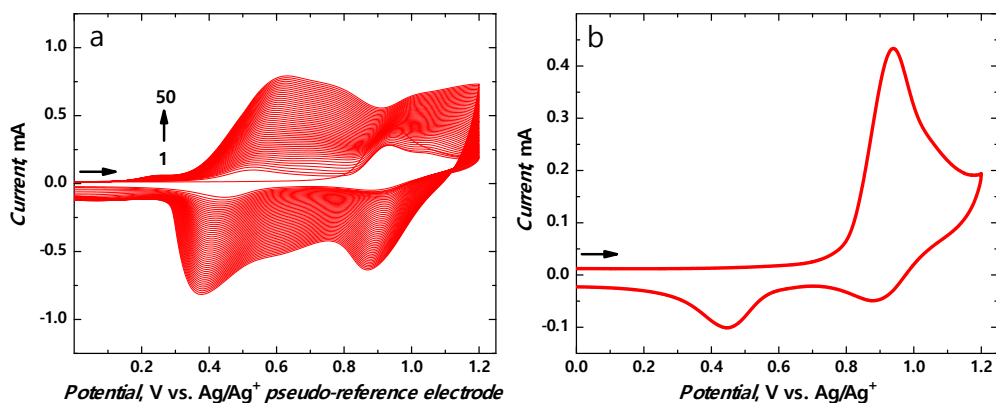


Figure 1. (a) Multicyclic potentiodynamic curves of oxidative electropolymerization of 1 mM *meso*-NiSaldMe-3dMe in a propylene carbonate solution of 0.1 M (TBA)PF₆. A potential scan rate was 100 mV s⁻¹. (b) The first electropolymerization cycle.

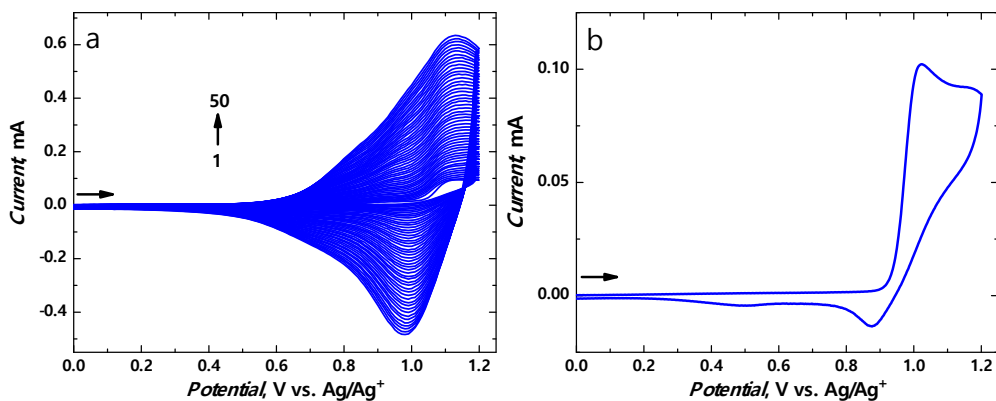


Figure 2. (a) Multicyclic potentiodynamic curves of oxidative electropolymerization of 1 mM *meso*-NiSaldMe in a propylene carbonate solution of 0.1 M (TBA)PF₆. A potential scan rate was 100 mV s⁻¹. (b) The first electropolymerization cycle.

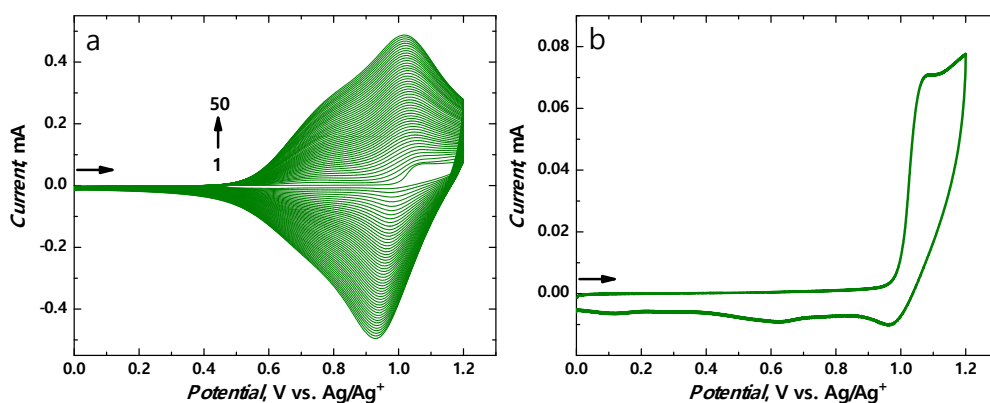


Figure 3. (a) Multicyclic potentiodynamic curves of oxidative electropolymerization of 1 mM NiSaltMe in a propylene carbonate solution of 0.1 M (TBA)PF₆. A potential scan rate was 100 mV s⁻¹. (b) The first electropolymerization cycle.

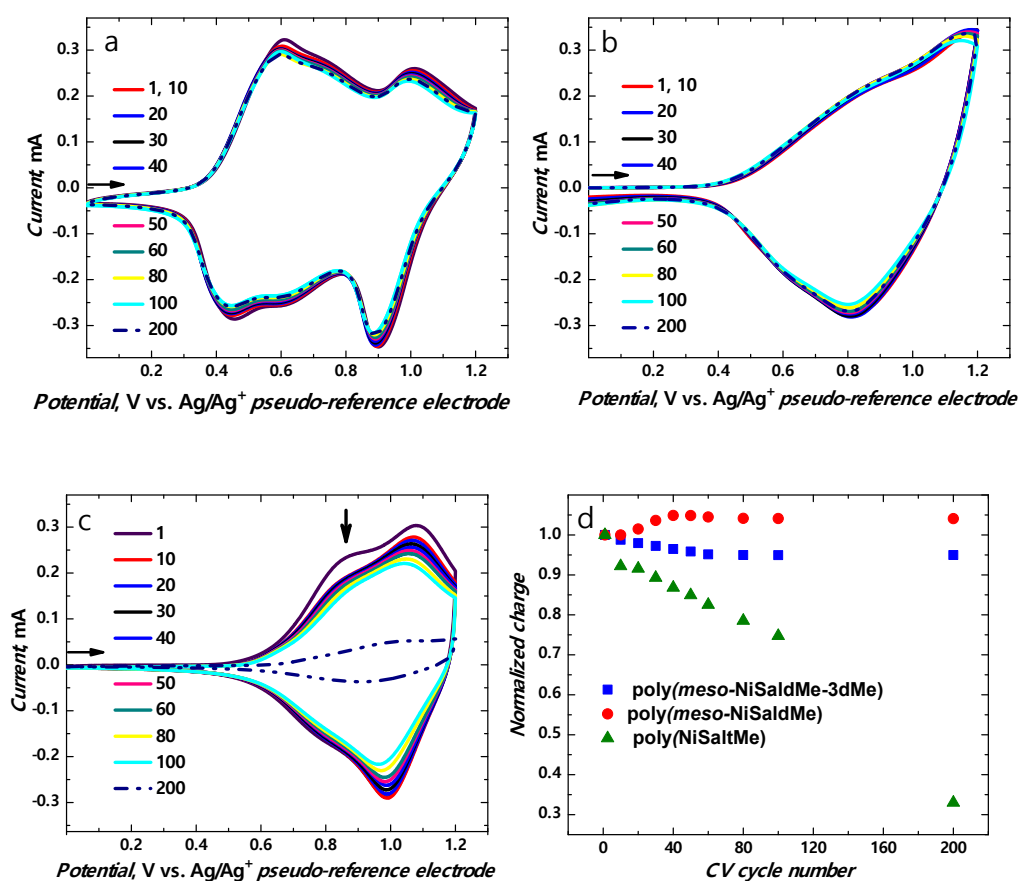


Figure 4. Multi-cycle CV curves for (a) poly(*meso*-NiSaldMe-3dMe), (b) poly(*meso*-NiSaldMe), and (c) poly(NiSaltMe) film coated Au electrodes in 0.1 M (TBA)PF₆,

in propylene carbonate, at a scan rate of 50 mV s^{-1} ; cycle numbers are indicated at curves. (d) The normalized charge stored in each cycle versus the cycle number.

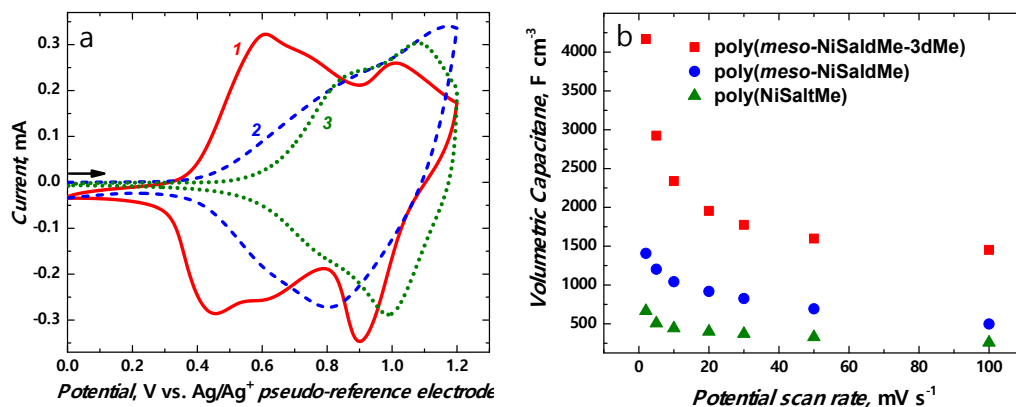


Figure 5. (a) CV curves, recorded for (1) poly(*meso*-NiSaldMe-3dMe), (2) poly(*meso*-NiSaldMe) and (3) poly(NiSaldMe) films in 0.1 M (TBA)PF₆, in propylene carbonate, at a scan rate of 50 mV s^{-1} . (b) The dependence of the volumetric capacitance of (1), (2), (3) on the potential scan rate.

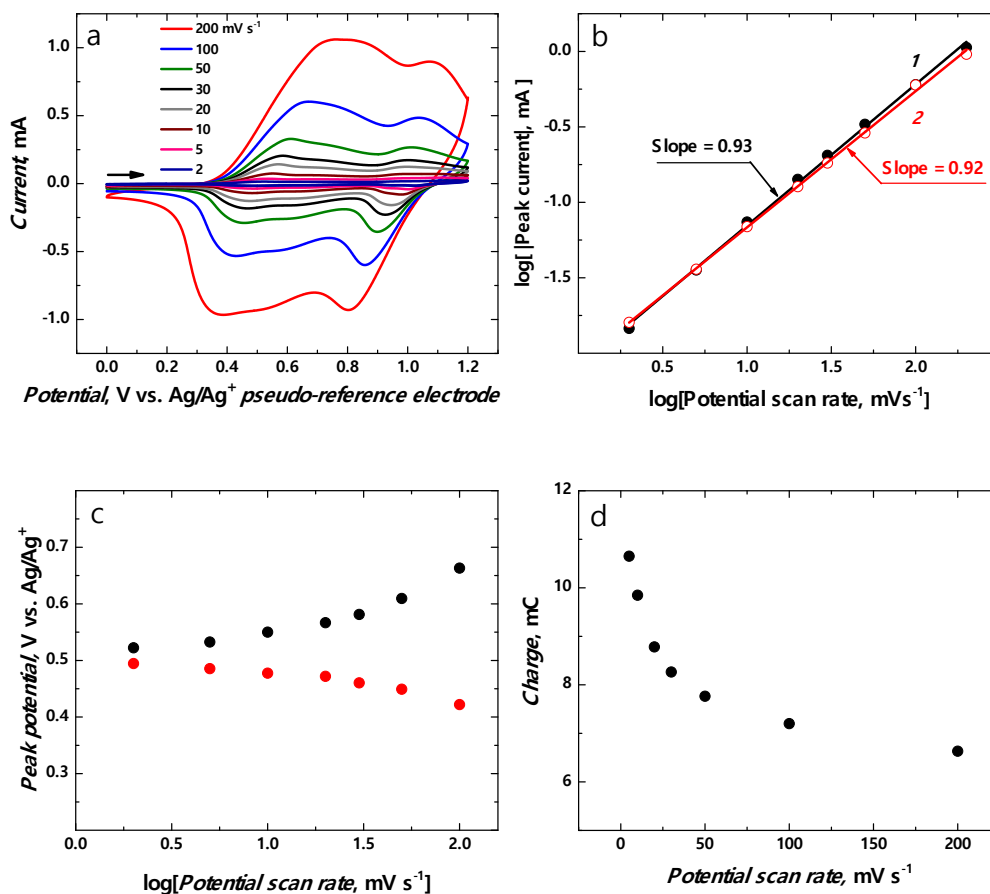


Figure 6. (a) CV curves for the poly(*meso*-NiSaldMe-3dMe) film in 0.1 M (TBA)PF₆, in propylene carbonate for different potential scan rates. (b) The logarithm of the (1) anodic and (2) cathodic peak current dependence on the logarithm of the potential scan rate. (c) The anodic and cathodic peak potential dependence on the logarithm of the potential scan rate. (d) The dependence of the accumulated charge on the potential scan rate calculated from the CV measurements depicted in Panel a.

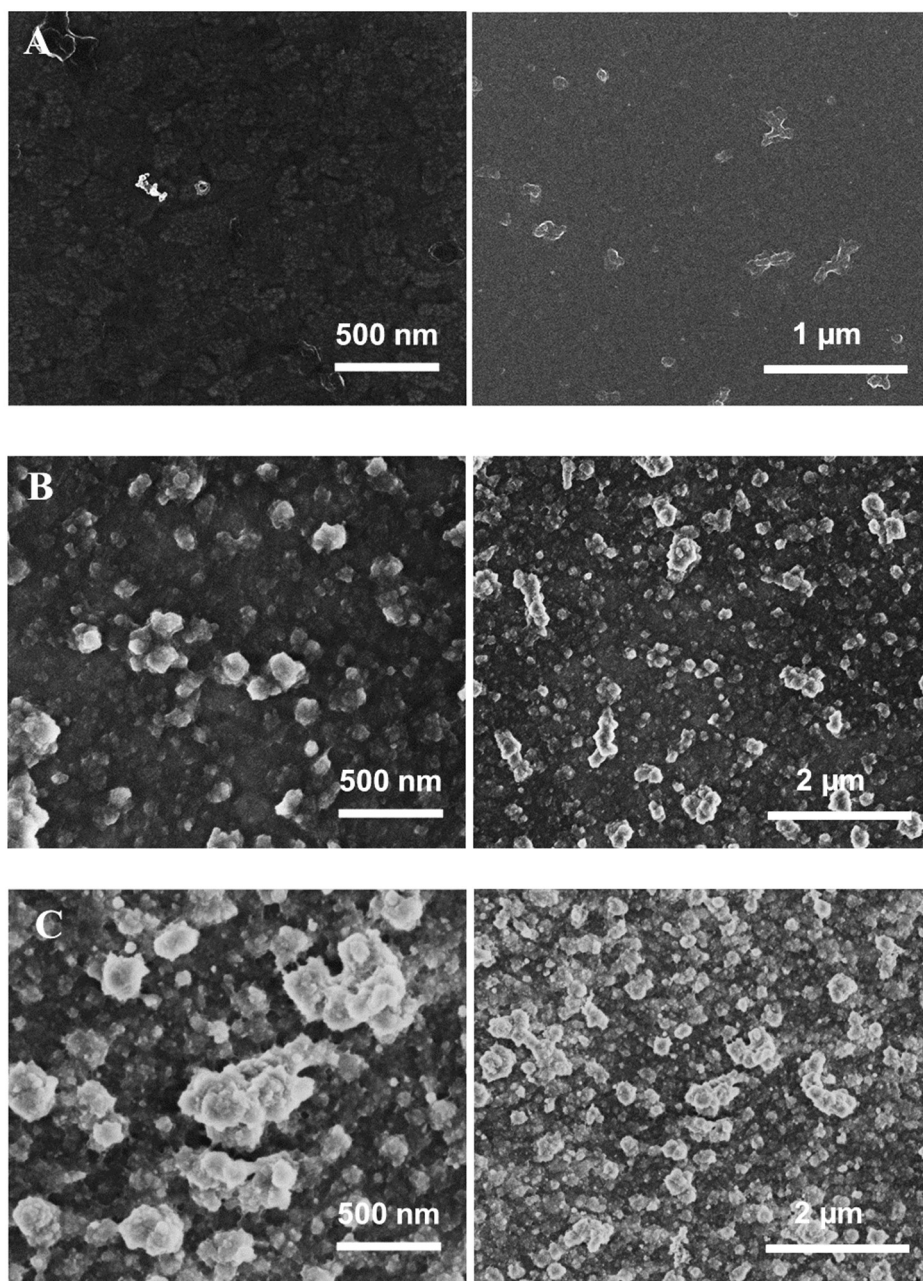


Figure 7. SEM images at two different magnifications of (a) poly(*meso*-NiSaldMe-3dMe), (b) poly(*meso*-NiSaldMe), (c) poly(NiSaltMe).

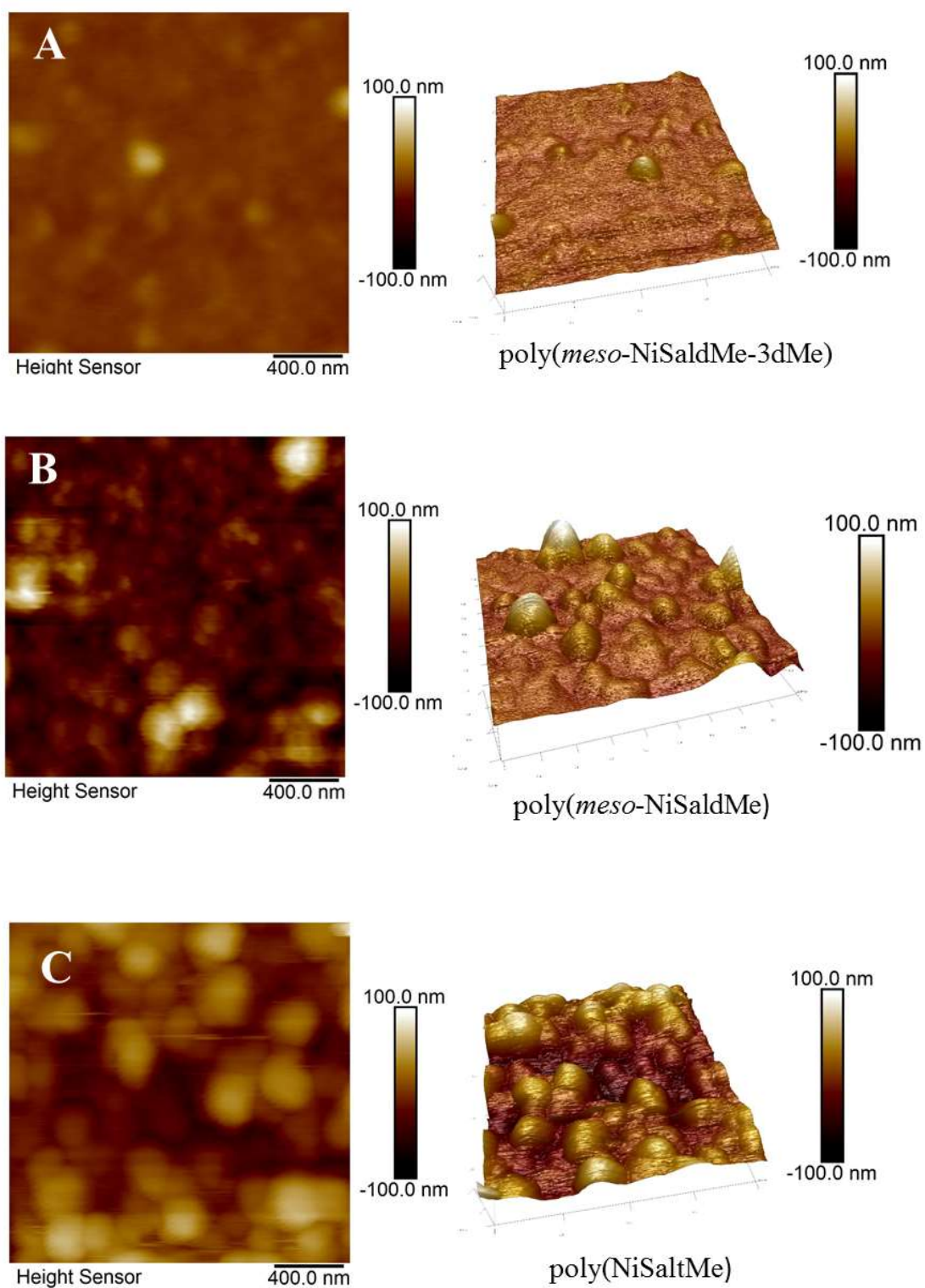


Figure 8. Topographical AFM images of $2\mu\text{m} \times 2\mu\text{m}$ scan size. (a) poly(*meso*-NiSaldMe-3dMe), (b) poly(*meso*-NiSaldMe), (c) poly(NiSaltMe).