

Novel Electro Polymerization Method to Synthesized Anti-corrosion Coated Layer on Stainless Steel Surface from (N-Benzothiazolyl Maleamic Acid) and Study its Biological Activity

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ABSTRACT

Electro polymerization of N-benzothiazolyl maleamic acid (NBM) was carried out on stainless steel plate electrode in a protic medium of monomer aqueous solution using electrochemical oxidation procedure in electrochemical cell. Spectroscopic characterization techniques were investigated to obtain information about the chemical structure of polymer. The anti-corrosion action of polymer was investigated on stainless steel by electrochemical polarization method. In addition, the effect of adding nanomaterial (TiO₂, ZnO (bulk-nano)) to monomer solution on the corrosion behavior of stainless steel was investigated. The results obtained showed that the corrosion rate of S-steel increased with temperature increase from 293K to 323K and the values of inhibition efficiency by coating polymer increase with nanomaterial addition. Apparent energies of activation have been calculated for the corrosion process of S-steel in acidic medium before and after polymeric coating. Furthermore were studied the effect of the preparing polymer on some strain of bacteria.

Keyword: electro polymerization, N-benzothiazolyl maleamic acid, anti-corrosion, antibacterial.

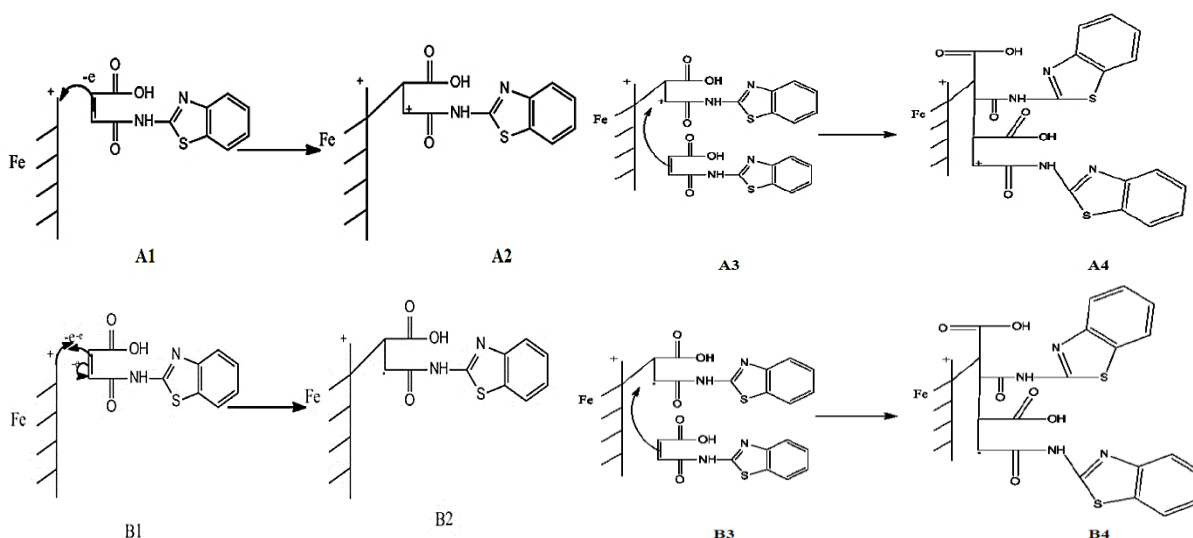
INTRODUCTION

By an unexpected discovery of poly acetylene in the late seventies, later awarded by the Nobel Prize in Chemistry in 2000, the field of electro-conducting polymers is still expanding. Conducting polymers have a many application for different technical products and processes. They was used it for antistatic layers¹ and in through-hole plating of printed circuit boards². They can be applied in anticorrosive surfaces³⁻⁵, electro-optical devices⁶, electrochemical sensors⁷⁻⁸ or electro-active membranes⁹. The classical method of polymer deposition is chemical or electrochemical synthesis in organic solvents¹⁰. Based on the chemical structures, conducting polymers exists in different forms, which are aromatic, heterocyclic, benzenoid, or nonbenzenoid. Electrical conductivity of organic polymer layer at the electrode surface because of the oxidation or reduction of these molecules. Conducting polymers are electrically conductive due to their extensively π - conjugated backbone. The conductivity's degree are effective by the density and mobility of electrons¹². Conductivity is according to the charge transfer along the chain or between the different conjugated segments (domains) in the same chain. The hopping of electron between different chains also results in the polymer conductivity. It stated that the structure defects in the polymer backbone causes alternating change in single and double bonds¹³. Electrochemical polymerization techniques is an interesting method for synthesis of coating polymer film electrodes. The most widely used process involves the electrochemical

oxidation of a suitable monomer species at the working electrode, to form a conducting or non-conducting polymer film^{14,15}. The development of chemically modified electrodes (CMEs) based on coating an electrode substrate with a polymeric film which has been subject of considerable attention in last year's¹⁶⁻²⁰. This approach can be simpler, more effective and more versatile than derivatization techniques, such as covalent attachment or chemisorption, which produce no more than monolayer coverage of the modifier at the electrode surface film. From the beginning, the electroconducting polymers were preparation chemically²¹, with deeper look into the polymerization mechanism; it become clear that electro-conducting polymers can be obtain by electrochemical methods²². Although appropriate for smaller quantity of the desired electro-conducting polymer, the electrochemical synthesis have some advantages. The electrochemical synthesis includes the direct oxidation of monomer at the anode surface, thus there is no need for an oxidizing agent. However, in most cases, the polymer grafting on electrode facilitating further analysis. Electro-polymerization doesn't give neutral non-conducting polymer but its oxidized form. Anion and electron transport are essential for polymer film formation²³. Electrochemical polymerization is a suitable way for synthesis of polymer coating films.

Experimental

The electrochemical polymerization of NBM onto the S-steel (anode) electrode surface was carried out in a potentiostat using a regulated DC power supply. The



Scheme 1: Proposed Cationic (A) and Radical (B) Mechanisms for the Grafting and the Growth of PBM Films.

Table 1: Corrosion data of S-steel in 0.2M HCl with and without coating.

coating	T/K	$-E_{corr}$ mV	i_{corr} $\mu\text{A}/\text{cm}^2$	$-b_c$ mV/Dec	b_a mV/Dec	%I	Weight loss $\text{g}/\text{m}^2.\text{d}$	Penetration loss[mm/a]
Blank 0.2M HCl	293	364.1	16.00	109.1	179.5	-	4.01	0.1780
	303	368.4	22.45	131.8	349.8	-	5.63	0.2500
	313	369.0	25.35	141.1	274.0	-	6.35	0.2830
	323	371.1	27.15	123.0	242.4	-	6.81	0.3030
PBM	293	267.9	2.50	137.0	164.5	84.37	6.28	0.0279
	303	282.5	3.81	126.0	210.6	83.02	9.55	0.0425
	313	306.6	4.57	104.1	231.5	81.97	1.14	0.0509
	323	316.9	5.64	84.8	115.7	79.22	1.41	0.0629
TiO_2 & PBM	293	221.0	1.33	136.3	146.0	91.68	0.334	0.0148
	303	224.1	2.45	117.1	151.9	89.08	0.613	0.0273
	313	231.5	3.39	147.0	185.8	86.62	0.851	0.0379
	323	236.5	4.38	159.3	194.6	83.86	1.1	0.0489
ZnO_b & PBM	293	233.2	1.07	96.4	164.9	93.31	2.68	0.0119
	303	235.1	1.84	86.2	88.2	91.8	4.62	0.0205
	313	243.3	2.97	99.3	168.6	88.28	7.44	0.0331
	323	255.0	3.91	103.2	250.1	85.23	0.980	0.0436
ZnO_n & PBM	293	201.9	0.705	176.0	214.1	95.59	0.177	0.00787
	303	212.9	1.64	135.2	119.5	92.69	4.11	0.0183
	313	219.3	2.66	84.4	124.3	89.5	6.66	0.0296
	323	237.8	3.40	146.3	152.5	87.47	0.853	0.0380

electrodes were cleaned and washing by acetone. The solutions employed for polymerization were 0.1g of N-benzothiazolyl maleamic acid (monomer)²⁴ in 100ml DMSO with three drop of H_2SO_4 concentration (37%). The polymerization was carried out at 1.1V and at 293K. The polymer film was deposited at the anode surface.

For corrosion measurements, the cell used was a conventional three electrodes: the working electrode (WE) (that is the metal coated and non-coated), the reference electrode (the potential of the WE is measured relative to this potential), and counter or auxiliary electrode (that the majority of the current passes through). Anodic and cathodic polarization of s. steel was carried out under potentiostatic conditions in 0.2M HCl in the absence as well as in the presence-coated layer at different temperature (293-323) K. In addition, in presence of 0.05g

of ZnO (bulk-nano) and TiO_2 nanomaterial which add to improve the coated layer against corrosion and bacteri.

RESULT AND DISCUSSION

Mechanism of Polymerization

Based on the published literature, a cationic^{25,26} or a radical mechanism²⁷⁻³⁴ can be proposed to explain electro polymerization reactions and, in particular, the grafting and the growth of the PBM films. The first consider is the cationic mechanism (Scheme 1): the application of an anodic potential to an NBM solution implies the transfer of one electron from the monomer to the working electrode (A1). This transfer leads to the formation of a radical cation adsorbed on the electrode surface which is represented in A2. Alternatively, if the lifetime of A2 is long enough compared to the mean time for a NBM molecule to diffuse toward the electrode, then the NBM molecules can add on

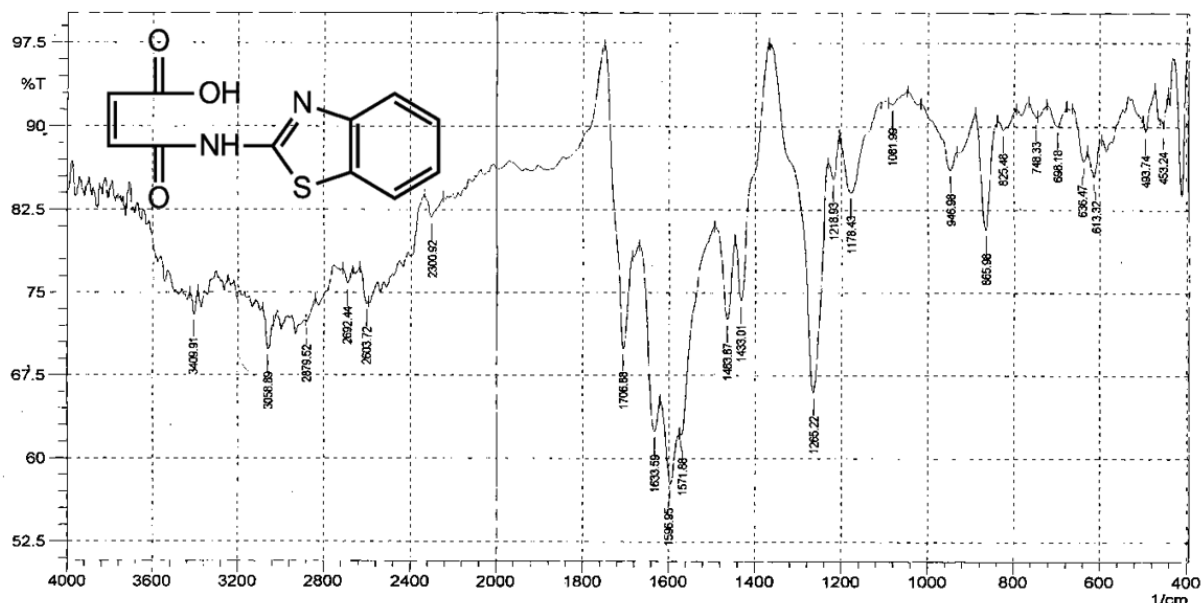


Figure 1: FT-IR spectrum of NBM.

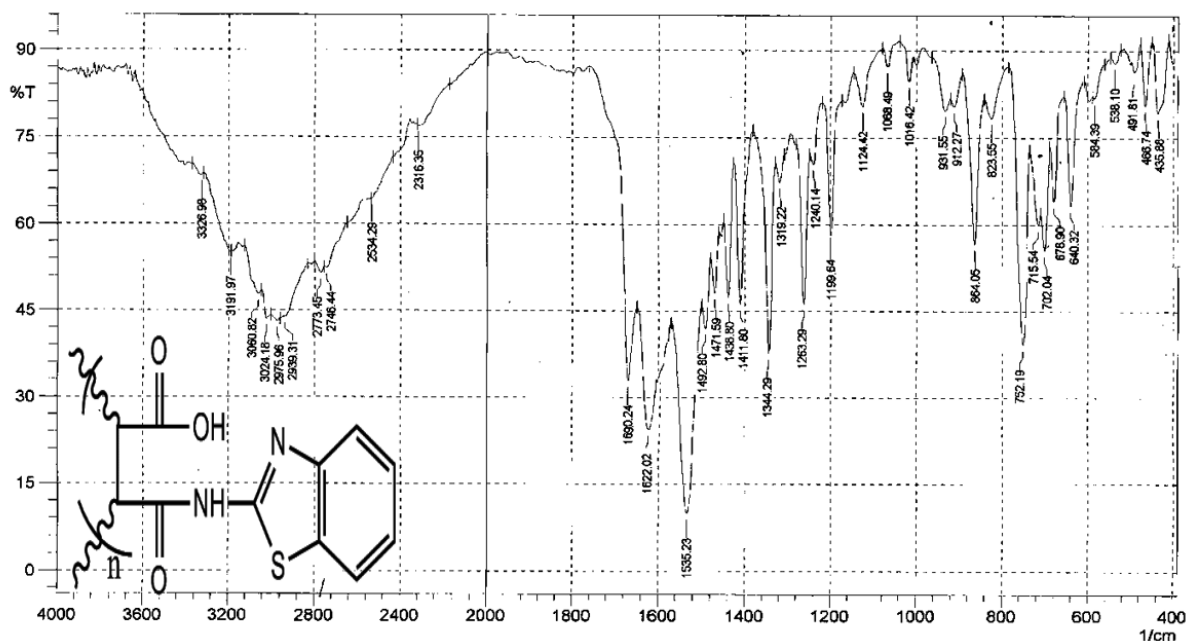


Figure 2: FT-IR spectrum of polymer.

Table 2: Activation parameters E_a , ΔH^* and ΔS^* for the coated and non-coated S-steel dissolution in 0.2M HCl.

Coating	R^2	E_a kJ.mol ⁻¹	A/Molecule. Cm ⁻² .S ⁻¹	R^2	ΔH^* KJ. K ⁻¹ . mol ⁻¹	$-\Delta S^*$ J.K ⁻¹ . mol ⁻¹
HCl Blank	0.899	13.565	4.482 x 10 ³	0.852	11.013	183.600
PBM	0.968	20.732	1.3106 x 10 ⁻⁴	0.958	18.178	174.683
PBM & TiO ₂	0.968	30.853	4.56667 x 10 ⁻⁵	0.961	28.299	145.154
PBM & ZnO _b	0.987	34.474	1.559552 x 10 ⁻⁶	0.963	31.060	137.494
PBM & ZnO _n	0.950	41.206	1.7831997 x 10 ⁻⁷	0.811	45.390	94.984

via a cationic mechanism at the charged ends of the adsorbed oxidized NBM (A4). This process by propagation leads to the formation of a grafted polymer. Let us now consider a radical mechanism³⁵ (Scheme 1B). The radical counterpart of A2 is B2. First, the chemisorbed

radical depicted in B2 cannot be the result of an electrochemical process. If we assume that the grafting step is disconnected from the electrochemical process, we are nevertheless faced with the fact that the radical mechanism is not particularly favored under the

Table 3: Antimicrobial activity of the tested polymer and polymer with nanomaterial.

compound	<i>Staph. Aure</i>	<i>E. Coli</i>	<i>Pseud.</i>
PIM	24	26	27
PBM & TiO ₂	21	25	23
PBM & ZnO _(B)	16	24	18
PBM & ZnO _(n)	16	21	16

Solvent: DMSO; [C]: 800µg/ml.

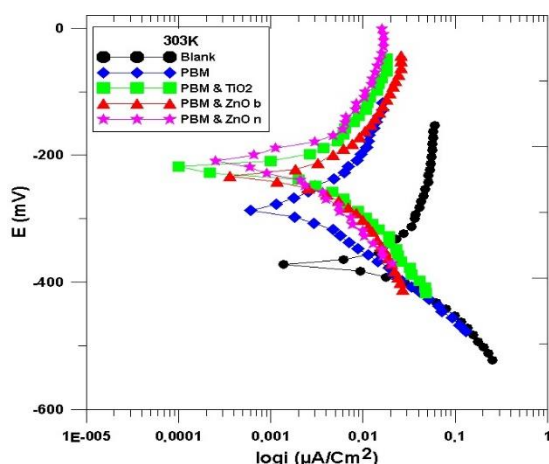


Figure 3: Polarization plots of S-steel coated with polymer and nanomaterial in 0.2M HCl at 293K.

present electrochemical conditions. Indeed, the radical mechanism proceeds via a hemolytic scission of the double bond (Scheme 1B). However, homolytic rupture of the C=C bond is highly improbable considering the initial polarization of the bond which is further enhanced under the field created by the electric double layer³⁶. Moreover, this electric field induces a reorientation of the molecule³⁷. This all together makes the radical mechanism rather unlikely to account for the grafting and the growth of PBM films under anodic electrochemical conditions.

Polymer Characterization

Fourier Transform Infrared (FT-IR) Spectroscopy

A typical PBM coating formed under the conditions described previously has been examined by FT-IR spectroscopy. The resulting spectrum of monomer (Figure 1) was compared with FT-IR spectrum of polymer (Figure 2) and a good result has been found. In this spectra, the characteristic bands of the monomers double bond C=C (1596 cm⁻¹ for NBM) are disappear and confirm the formation of PBM.

The band appeared at 1710 cm⁻¹ that confirmed the presence of C=O carboxyl groups, the absorption of imide group was appeared at 1643 cm⁻¹, the absorption bonds of N-H and O-H carboxylic group make overlap and appeared at 2700-3300 cm⁻¹ 38-40.

Potentiostatic polarization measurements

The effect of polymeric coating film on the anodic and cathodic polarization curves of S-steel in 0.2M HCl solution at different temperature (293-323)K was studied. The effect of adding different nanomaterial compound

(TiO₂ and ZnO (bulk-nano)) is represented in Fig. 3. The corrosion current density (I_{corr}) was calculated by the extrapolation of anodic and cathodic Tafel lines. Table 1 represents the effect of polymer coating with and without nanomaterial on the corrosion parameters of S-steel electrode in 0.2M HCl solution. These parameters are anodic Tafel slope (ba), cathodic Tafel slope (bc), corrosion potential (E_{corr}), corrosion current (I_{corr}), IE, weight and penetration loss. Inhibition efficiency was calculated from corrosion current densities using the following equation (1)⁴¹:

$$\% I = \left(\frac{I_{corr}}{I_{corr}^0} \right) 100 \tag{1}$$

where I_{corr} and I⁰_{corr} are the corrosion rates of S-steel electrode in the presence and in the absence of coating, respectively.

The corrosion potential shifted to more positive values and I_{corr} decreased when the nanomaterial compound adding to the monomer solution indicating the inhibiting effect of these compounds. When the polymer film crafted with nanomaterial coated on the S-steel the corrosion potential shifted to the noble side. This indicates that a film formed on anodic sites of the metal surface⁴².

Kinetic and thermodynamic of activation parameters

The effect of temperature on the corrosion rate of S-steel in free acid 0.2M HCl in the presence of different coating of polymer was studied in the temperature range of (293–323)K using potentiostatic measurements. In examining the effect of temperature on the corrosion process in the presence of the polymer coating, the Arrhenius equation below eq. (2 and 3) was used in figure (4) to calculate apparent effective activation energies (E_a). Inspection of Table (2) and showed that the value of E_a determined in 0.2M HCl with coating S-steel is higher than that for uncoated S-steel⁴³:

$$C.R = A \exp(-E_a/RT) \tag{2}$$

$$\log C.R = \log A - E_a/2.303RT \tag{3}$$

The values of enthalpy of activation ΔH* and entropy of activation ΔS* were obtained from (fig.5) from the transition state eq. (4 and 5):

$$C.R = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \tag{4}$$

$$\log (C.R/T) = \log R/Nh + \Delta S^* /2.303R - \Delta H^* /2.303RT \tag{5}$$

Where C.R is the corrosion rate, R the gas constant, T the absolute temperature, A the pre exponential factor, h the blank's constant and N is Avogadro's number, E_a* the activation energy for corrosion process, ΔH* the enthalpy of activation and ΔS* the entropy of activation. The calculated kinetic and thermodynamic values are given in tables (3.5) – (3.7). The results in the tables indicate positive values of enthalpy changes (ΔH*) of the corrosion transition state reaction of S-steel in 0.2M HCl with different coating film at temperatures range 293- 323 K indicating the endothermic nature for this reaction. The negative values of entropy (ΔS*) for the S-steel corrosion mean loss in the degrees of freedom and the consequent restriction of the corrosion products⁴⁴.

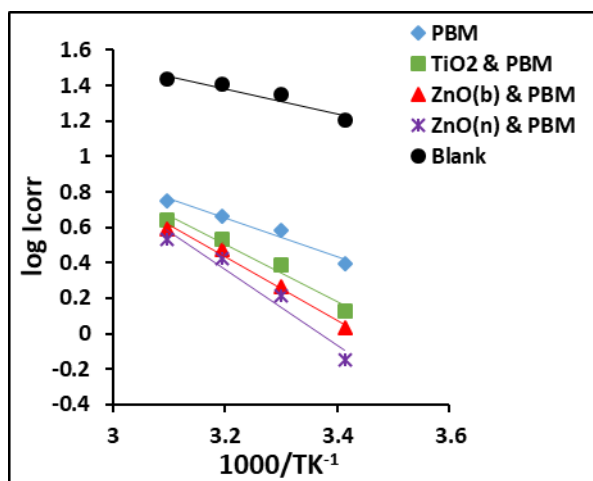


Figure 4: Arrhenius Plot of log C.R versus 1/T for S-steel in 0.2M HCl in the absence and presence coating

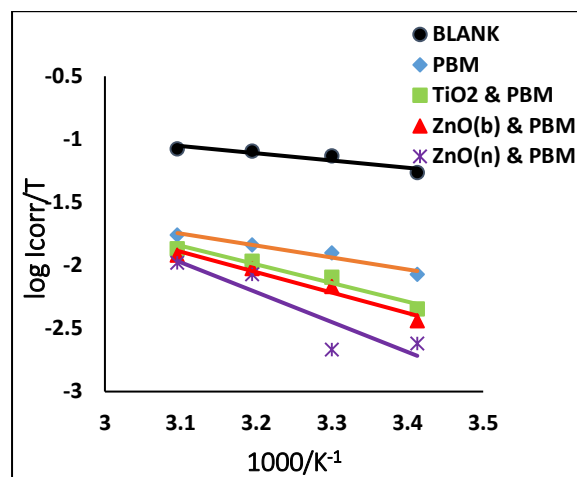


Figure 5: Arrhenius plots of log C.R/T vs. 1/T for S-steel in 0.2M HCl in the absence and presence coating

The inhibition efficiency of coating decreases with temperature increase and its decrease leads to increase the apparent activation corrosion energy. The positive sign of the ΔH^* reflects the endothermic nature of the S-steel dissolution process in the presence and absence of the coating film, while the negative sign of ΔS^* shows an increase in the system order^{45,46}.

Antibacterial study

nanotechnology has become increasingly important in the biomedical and pharmaceutical areas as alternative antimicrobial strategy due to reemergence infectious diseases and the appearance of antibiotic resistant strains⁴⁷. Nanoparticles (NPs) are biocidal effectiveness is suggested to be owing to a combination of their small size and high surface to volume ratio, which enable intimate interactions with microbial membranes⁴⁸. The results of antibacterial activity of polymer and polymer with nanomaterial are listed in table 3. The result refer that the polymer and polymer with nanomaterial compounds possess strong activity against *Staphylococcus aureus*, *pseudomonas* and *Escherichia coli*. Among these metal oxides, ZnO has attracted a special attention as antibacterial agent. For instance, ZnO inhibits the adhesion and internalization of *Staphylococcus aureus*, *pseudomonas* and *Escherichia coli*⁴⁹.

CONCLUSION

Electro polymerization of NBM on S-steel surface was found to inhibit the corrosion rate in 0.2M HCl solution. The inhibition efficiency of polymer will increases with adding nonmaterial to monomer solution especially with ZnO(n), and decreases with temperature increase(293-323)K. Beside the resistance to corrosion, polymer coating can also provide antimicrobial activity against *Staphylococcus aureus*, *pseudomonas* and *Escherichia coli* bacteria. With the further studies of Electro polymerization technique and related characterization technologies, Electro polymerization protective coatings will have wider and more practical applications.

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