*Article*

# Corrosion Inhibition studies of poly (N-tert-amylacrylamide -co- N-phenyl acrylamide) copolymers by EIS and PDP methods

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### Abstract

Herein, we reported the synthesis and corrosion inhibition studies of poly (N-tert- amylacrylamide-co-N-phenyl acrylamide) copolymers. The copolymers are synthesized by free radical polymerization using NTA and NPAM monomers . The synthesized copolymers are subjected to corrosion inhibition behavior by EIS and PDP methods. Both the methods showed same results of 85.0 percentage of inhibition.

**Keywords:** copolymerization, corrosion inhibition, N-phenylacrylamide, EIS study

## 1. Introduction

The study of corrosion on stainless steel and its prevention in aggressive media has more technological values in the field of applied electrochemistry [1]. Generally acidic solutions are used as picking agent of iron and steel, chemical cleaning of scale in metallurgy, acidizing in oil recovery and other petrochemical processes. The main combating corrosion in acidic environment is the application of corrosion inhibitors or coating. However, nearly all-powerful corrosion inhibitors may affect both environment and health due to their toxic and carcinogenic substances. Thus, in order to ensure the protective properties of the coatings needed, of the various types of protective coatings there are in use, organic polymer coatings play an important role in the prevention of corrosion on mild steel [2 ]. Among the organic coating, recently, the methacrylic polymer coatings have found wide applications in several industries [3]. Methacrylic coating based copolymers for its application in the corrosion

protection of mild steel. They simply constitute a physical barrier against to attack the corrosive environment and reduce the corrosion rate of the substrate. This serves as an efficient way to protect metallic substrates from corrosion. Methacrylic coatings are fast setting adhesives, having high impact strength, capable of making excellent bonding with metals, show resistance to chemical fumes, alkalis, acids and exhibit high tolerance to contaminated surfaces [4] [5] [6]. In this study, we aimed to evaluate the corrosion protection properties of these copolymers, potentiodynamic polarization study was carried out with mild steel samples dip coated with different compositions of the copolymers in 0.05 M $H_2SO_4$.

## 2. Material and Method

The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene [7]. The white crystals have tmp.91° C (Lit.91-92° C) and the

yield was -87%. Appropriate quantities of the monomers NTA and N-phenyl acrylamide[8], 50mg of the free radical initiator AIBN and 25ml of the polymerization solvent are placed in a standard reaction tube to obtain a homogenous solution. The mixture was flushed with oxygen free dry nitrogen gas. The inlet and outlet of the reaction tube were closed by means of rubber tubing's and pinch cock. The reaction vessel is then immersed in a thermostatic water bath maintained at 60°C. The copolymerization reaction was allowed to proceed for an appropriate duration that would give a conversion below 10%. After the reaction vessel was removed from the thermostat and cooled under the tap. The solution poured in ice cold water to precipitate the copolymer and the copolymer washed with methanol. It was then dried in vacuum oven for 24 hrs. The $^1$H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer (JEOL,Tokyo,Japan) operating at 400 MHz in $CDCl_3$ .DSC - Q200 V23 , Differential scanning calorimeter was used to study the thermal behavior of copolymers at a heating rate of 20°C /min under nitrogen atmosphere. Thermogravimetric analysis was carried out using TGA Q500 V-20 at a heating rate of 20°C/min under nitrogen atmosphere. The electrode of 1cm$^2$ area were cut from the mild steel sheet and one side of the electrode and stem was masked with epoxy resin. The electrode was polished with 400-1200 grit emery papers and degreased with acetone. 100 ml of the test solution was taken in a three-electrode polarization cell and the electrode was introduced into the test solution in the polarization cell and allowed to attain a steady potential value for 20 min. A constant potential was applied and the resultant current was measured. The experiments were carried out ± 200 mV from corrosion potential. Polarization measurements were carried out using Electrochemical work station CHI 660 USA.The potential of the working electrode was measured with respect to SCE and the platinum electrode was used as an auxiliary electrode. Then the applied potentials were plotted against resultant current density. The current density and Tafel slopes (ba and bc) values were obtained from the polarization curves by extrapolation of anodic and cathodic curves back to the corrosion potential. The experiments were performed with and without addition of inhibitors at different temperature. The inhibition efficiency of these systems was calculated by using the following equation.

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

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$I_{corr}$ = Corrosion current density in the absence of inhibitor

$I_{corr(i)}$ = Corrosion current density in the presence of inhibitor.

A well-polished mild steel electrode was introduced into 100ml of test solution and allowed to attain a steady potential value. An A.C. signal of amplitude of 10mV was applied and the frequency was varied from 10 MHz to 10 KHz using electrochemical work station CHI 660USA. The real and imaginary parts of the impedance were plotted in the form of Nyquist plots. From the Nyquist plot, the charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) values were calculated.The charge transfer resistance values were obtained from the plots of Z' vs Z". The values of ($R_s + R_{ct}$) correspond to the point where the plots cuts Z' axis at low frequency and $R_s$ corresponds to the point where the plot cuts Z' axis at high frequency. The difference between $R_{ct}$ and $R_s$ values give the charge transfer resistance ($R_{ct}$) values. The $C_{dl}$ values were obtained from the relationship

$$C_{dl} = \frac{1}{2\pi f_{max} \times R_{ct}}$$

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where $C_{dl}$ = double layer capacitance; $R_{ct}$ = Charge transfer resistance
$f_{max}$ = frequency at Z" value maximum.

The inhibition efficiencies were obtained from $R_{ct}$ values as follows

$$IE\% = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

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where $R_{ct}$ = Charge transfer resistance in the absence of inhibitor

$R_{ct(i)}$ = Charge transfer resistance in the presence of inhibitor.

## 3. Results and Discussion

### 3.1 Copolymerization of NTA and NPAM

Copolymers of N-tert-amylacrylamide (NTA) and N-phenyl acrylamide (NPAM) were prepared by free radical polymerization in DMF at 60°C using AIBN as initiator (Scheme)
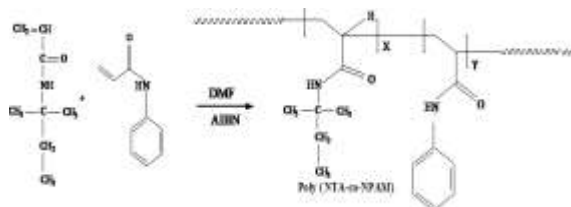


Scheme : Copolymerization of NTA and NPAM

### 3.2 Characterization of Copolymer spectra of Poly (NTA-co-NPAM)

The $^1$H-NMR spectra of copolymer, is shown in Figure 1. The following peaks appear in the copolymer spectrum : at 1.4 -2.9 ppm for CH$_2$ group , at 3.0 ppm for backbone CH$_2$ , at 6.9-7.8 ppm due to NPAM aromatic protons and at 8.0 ppm for NH proton of NTA.
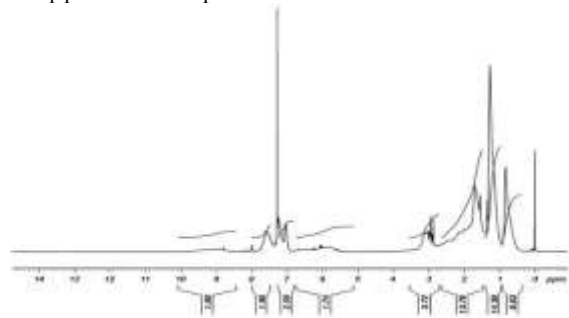


Figure 1: $^1$H NMR spectra of Poly (NTA-co-NPAM) 0.5 :0.5

### 3.3 Determination of copolymer composition of Poly (NTA-co-NPAM)

The phenyl area is used to determine the copolymer composition. Resonance signal at 6.8-7.8 ppm corresponds to aromatic proton, and their integrated intensity of this peak is compared to the total intensities of all the peaks in the copolymer spectrum, which is a measure of their relative areas. The copolymer compositions (Table 1) can be obtained using

$$X_{NPAM} = \frac{15A\,(aryl)}{5A_{total} + 6A(aryl)} \quad \text{--------- (4)}$$

Where X= mole fraction and A= peak area.

Table 1: Mole fraction of the Copolymers of N-tert-amylacrylamide and NPAM

| Mole fraction of NTA in feed, $M_1$ | Mole fraction of NPAM in feed , $M_2$ | Mole fraction of NTA in copolymer, $m_1$ | Mole fraction of NPAM in copolymer , $m_2$ |
|---|---|---|---|
| 0.3 | 0.7 | 0.3573 | 0.6427 |
| 0.5 | 0.5 | 0.5497 | 0.4503 |
| 0.7 | 0.3 | 0.7229 | 0.2771 |

### 3.4 Thermal studies of Poly (NTA-co-NPAM)

The TGA data for the copolymers of NTA with NPAM are shown in Figure 2 and given in Table 2. From the Table 2 , it was observed that the copolymers undergoes double stage decomposition . The initial weight loss is due to moisture content. Weight loss at stage 1 around 200°C is due to scission in amide linkage. Weight loss at 350-450°C is the second stage decomposition where maximum weight loss of 99.54% occurs because of main chain degradation. The increase in $T_g$ is observed as the fraction of NPAM increases in the copolymer.

Table 2 : TGA and DSC data for Poly (NTA-co-NPAM)

| Copolymers | Mole fraction of NTA, in feed | Mole fraction of DCPMA, in feed | Mole fraction of DCPMA ,in copolymer | IDT (°C) | T50 (°C) | $T_f$ (°C) | $T_g$ (°C) |
|---|---|---|---|---|---|---|---|
| NTA-NPAM | 0.70 | 0.30 | 0.2771 | 124 | 386 | 652 | 140 |
| NTA-NPAM | 0.50 | 0.50 | 0.4505 | 128 | 395 | 676 | 150 |
| NTA-NPAM | 0.30 | 0.70 | 0.6427 | 136 | 398 | 702 | 156 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Poly-NTA | | - | - | - | - | 86.2 |

IDT: Initial Decomposition Temperature; $T_{50}$: decomposition temperature at 50% weight loss ;$T_f$: final decomposition temperature
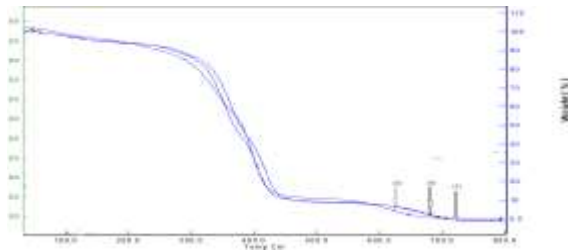


Figure 2 : TGA curves of Poly (NTA-co-NPAM);(3) Mole fraction NTA(0.3);(5) Mole fraction NTA(0.5);(7)    Mole fraction NTA(0.7)

### 3.5 Corrosion inhibition studies of poly (NTA-NPAM) copolymer by EIS and PDP methods

Polarization curves of mild steel in 0.05M $H_2SO_4$ with and   without presence of copolymers are shown in Figure 3. From the figure it is seen that the anodic and cathodic curves for mild steel in the presence of copolymers were shifted towards negative direction compared to the absence of copolymer metal immersed in 0.05M $H_2SO_4$. The polarization parameters such as corrosion potential (Ecorr) and corrosion current density(Icorr) obtained by extrapolation of tafel lines are listed in Table 3. It is observed from the table that Ecorr values increased significantly for mild steel in the presence of copolymers. The tafel plots of all the studied mole ratios of poly(NTA-co-NPAM) have good corrosion protective behavior. As can be seen, the corrosion current density in the presence of copolymer was lower than that of  absence of copolymer in mild steel. Moreover both the anodic and cathodic current density was slight shift in the corrosion potential for all the studied copolymer in mild steel and it suggested that the coating exhibit mixed type of corrosion protection. However, mild steel in the presence polymer shows that the lowest corrosion current density was detected in the range of equal (0.5-0.5) mole ratio of NTA and NPAM and it was increased  with increase of any one monomer unit. Hence mild steel in the presence of 0.-0.5 mole ratio of copolymer showed excellent resistance than in the presence of other copolymer. Hence the copolymer coated on mild steel restricts the interaction between the metal and the electrolyte

[9] [10].

The electrochemical impedance plots for in the presence and absence of various mole ratios of Poly(NTA-co-NPAM) with mild steel shown in Figure 4. The copolymer shows changes in both charge transfer resistance and capacitance. The charge transfer resistance increases much in consequence of the presence of copolymer film, it avoids the electrolyte. The film resistivity reduces the value of capacity of copolymer. As the NPAM composition decreases, the adhesiveness of the copolymer on mild steel decreases, this in turn decreases the corrosion resistance. The decrease in the CdI resulting from a decrease in local dielectric constant and/or increase in the thickness of double layer, suggested that in the copolymer molecules function by strong adhesion at the metal/solution interface. From the Table   4 poly(NTA-co-NPAM) of equal mole ratio exhibit high Rct value. This shows high corrosion protection efficiency. Hence, all the mole ratio of this polymer showed good protection against corrosion. This behavior due the uniform and adherent of copolymer on mild steel, which effectively prevent the penetration of corrosive ion.
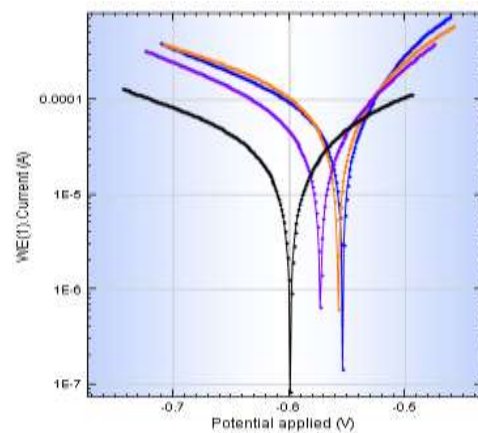


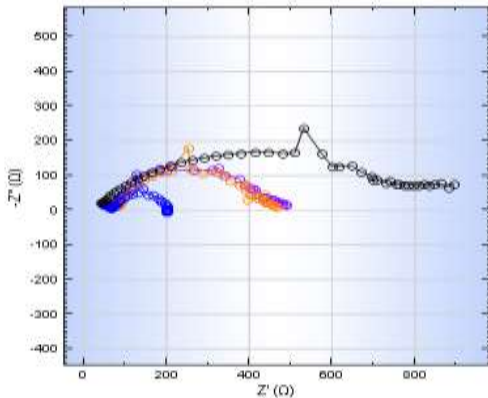Figure  3: Tafel plots of poly(NTA-NPAM)

Figure 4. : Nyquist plots for uncoated and various mole ratio of poly (NTA-NPAM) mild steel in 0.05M $H_2SO_4$

Table 3. Potentiodynamic polarization parameters of poly (NTA-NPAM) in absence and presence of various mole ratios of copolymer with mild steel in 0.05M $H_2SO_4$

| Polymer Sample | $E_{corr}$ (mV) | $\beta a$ (V/dec) | $\beta c$ (V/dec) | $I_{corr}$ ($10^{-4}$ A cm$^{-2}$) | $E_b$ (mV) | $R_p$ ($\Omega$) | Rate (mpy) | IE(%) |
|---|---|---|---|---|---|---|---|---|
| Uncoated | -481 | 0.2 | 0.04 | 1.62 | -589 | 86.92 | 1.88 | |
| 0.3-0.7 | -558 | 0.29 | 0.13 | 0.4450 | -705 | 334.71 | 1.35 | 72 |
| 0.5-0.5 | -573 | 0.2 | 0.12 | 0.2445 | -711 | 540.19 | 0.71 | 85 |
| 0.7-0.3 | -599 | 0.48 | 0.3 | 0.4405 | -723 | 1108 | 0.84 | 75 |

Table 4. Electrochemical impedance parameters of poly(NTA-co-NPAM) mild steel in 0.05M $H_2SO_4$

| Polymer Sample | $R_{ct}$ ($\Omega$) | $C_{dl}$ ($\mu$ F cm$^{-2}$) x $10^{-5}$ | IE(%) |
|---|---|---|---|
| Uncoated | 69.565 | 1.92 | |
| 0.3-0.7 | 249.89 | 0.845 | 72 |
| **0.5-0.5** | **475.17** | **0.055** | **85** |
| 0.7-0.3 | 275.91 | 0.81 | 75 |

Both the polarization and impedance study showed almost same inhibition efficiency (IE%) of 85.0 percentage.

## 4. Conclusions

The poly (NTA-co-NPAM) was successfully synthesized by free radical polymerization using N-tert-amylacrylamide (NTA) and N-phenylacrylamide monomers .The formation of copolymers was characterized by ^{1}H-NMR spectroscopy. The synthesized copolymers exhibited IE (%) of 85.0 percentage and it behaves as good anti-corrosive material on metal surfaces.

## Acknowledgement

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