

# Corrosion inhibition studies of poly (N-tert-amylacrylamide -co-8-quinolinyl acrylate ) copolymers

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## ABSTRACT

This paper describes the synthesis and corrosion inhibition efficiency of poly (N-tert-amylacrylamide -co-8-quinolinyl acrylate) copolymers. The copolymers were synthesized by free-radical copolymerization procedure using N-tert-amylacrylamide and 8-quinolinyl acrylate monomers. Both the Potentiodynamic polarization and Electrochemical Impedance Spectroscopy Studies showed the corrosion inhibition efficiency about 88.0%

**Key words:** Corrosion inhibitors; NMR spectroscopy; copolymers

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## 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 [4-6].

## 2. EXPERIMENTAL

### Materials

#### N,N'-Dimethylformamide

Oneliter of DMF was mixed with 120g of benzene and 36g of water and distilled at 140°C to remove the impurities together with water and benzene.

#### 2,2'-Azobisisobutyronitrile (AIBN)

AIBN was recrystallized from methanol at 0 - 10°C.

#### Acrylonitrile

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous CaCl<sub>2</sub>. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber coloured bottle and kept in the refrigerator at 5 °C.

#### <sup>1</sup>H-NMR spectroscopy

The <sup>1</sup>H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz in CDCl<sub>3</sub>.

### Thermal Analysis

A 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.

### Preparation of N-tert-amylacrylamide (NTA)

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 mp.91° C (Lit.91-92° C) and the yield was -87%.

### Preparation of 8-quinolinyl acrylate(8QA)

The 8-quinolinyl acrylate comonomer was prepared by esterification of 8- hydroxy quinoline and acryloyl chloride. Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride<sup>5</sup>. Absolute ethanol(400ml) and NaOH(0.2 mol, 8g)were added to a three-necked flask that was equipped with stirrer, condenser and thermometer. The flask was placed in a water bath and the contents were stirred until all the NaOH was dissolved. Next, 8-hydroxy quinoline (0.2 mol) was added to the reaction mixture, which was then heated to room temp. and then cooled to 0-5°C with ice. Freshly prepared acryloyl chloride (0.2 mol) was added in a dropwise manner to the cooled reaction mixture and stirred for 90 min. The mixture was then poured in to a crushed-ice-water mixture where a white colored product was separated out. The product was filtered, washed thoroughly with cold water and recrystallized frommethanol[8].

### Preparation of copolymers

Appropriate quantities of the monomers NTA and 8-QA , 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.

**Table 1: Copolymerization ofN-tert-amylacrylamideand8-quinolinyl acrylate**

S.No	Mole fraction of NTA ( M <sub>1</sub> )	Mole fraction of 8-QA ( M <sub>2</sub> )	Reaction Time ( Min)	Weight of Copolymer (mg)	Copolymer Conversion %
1	0.2	0.8	360	124	2.5
2	0.3	0.7	360	125	2.5
3	0.4	0.6	360	131	2.6
4	0.5	0.5	360	144	2.9
5	0.6	0.4	360	155	3.1
6	0.7	0.3	360	184	3.7
7	0.8	0.2	360	194	3.9

### Electro chemical analysis

#### Potentiodynamic polarization

The electrode of 1cm<sup>2</sup> 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.

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad \text{-----1}$$

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

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

### Electrochemical Impedance Spectroscopy Studies

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

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

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

$$IE\% = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100 \quad \text{----- 3}$$

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

#### <sup>1</sup>H-NMR spectrum of N-tert-amylacrylamide (NTA)

<sup>1</sup>H-NMR(CDCl<sub>3</sub>),6(ppm) : The <sup>1</sup>H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer(JEOL, Tokyo, japan) opwrating at 400 MHz respectively in CDCl<sub>3</sub>. The following peaks appear in NTA spectrum: at 0.78ppm for-CH<sub>3</sub> , at 1.2ppm for-(CH<sub>3</sub>)<sub>2</sub>, at 1.7 ppm for- CH<sub>2</sub>, at5.49 ppm for =CH vinylic proton and at 6.1ppm for vinylic =CH<sub>2</sub> proton (Figure 1)

#### <sup>13</sup>C-NMR(CDCl<sub>3</sub>),6(ppm) : (Figure 2)

The  $\delta$  163.90(CH<sub>2</sub> = C(H)-CO-NH...);132.93(CH<sub>2</sub> =C(H)-CO-NH...);123.87(CH<sub>2</sub>=C(H)-CO-NH..) ; 52.82(-CO-NH-C(CH<sub>3</sub>)-CH<sub>2</sub>); 31.87(-CO-NH-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>);26.19(-CO-NH-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>) 8.26(-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>).

#### <sup>1</sup>H-NMR spectrum of 8-quinolinyl acrylate (8-QA)

The 8-quinolinyl acrylate comonomer was prepared by esterification of 8-hydroxy quinoline and acryloylchloride.The following peaks appear in 8-QA spectrum; at 7.1 – 8.9 ppm for quinolinyl aromatic protons,at 5.5 – 6.6ppm for vinyl protons (Figure 3).

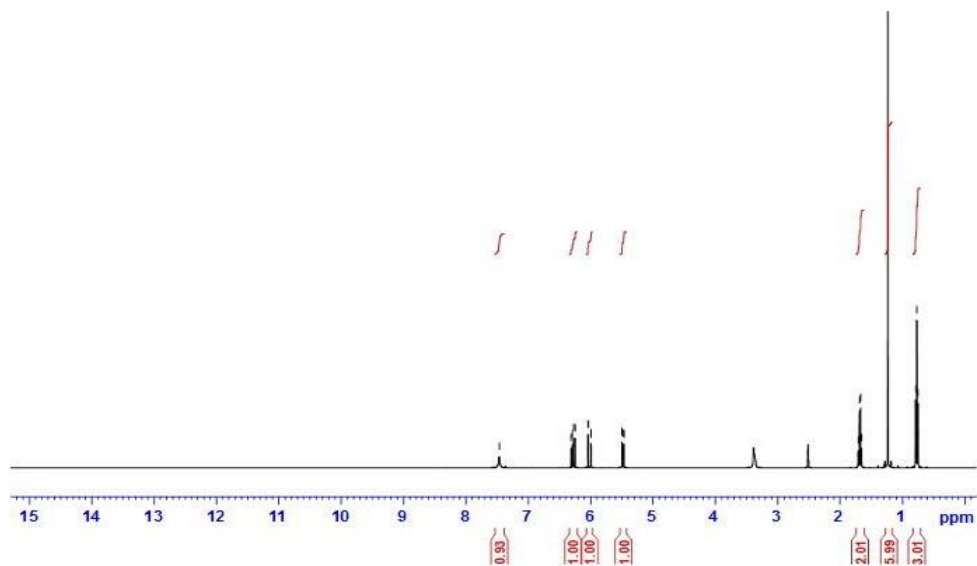


Figure 1 :<sup>1</sup>H-NMR spectrum of N-tert-amylacrylamide (NTA)

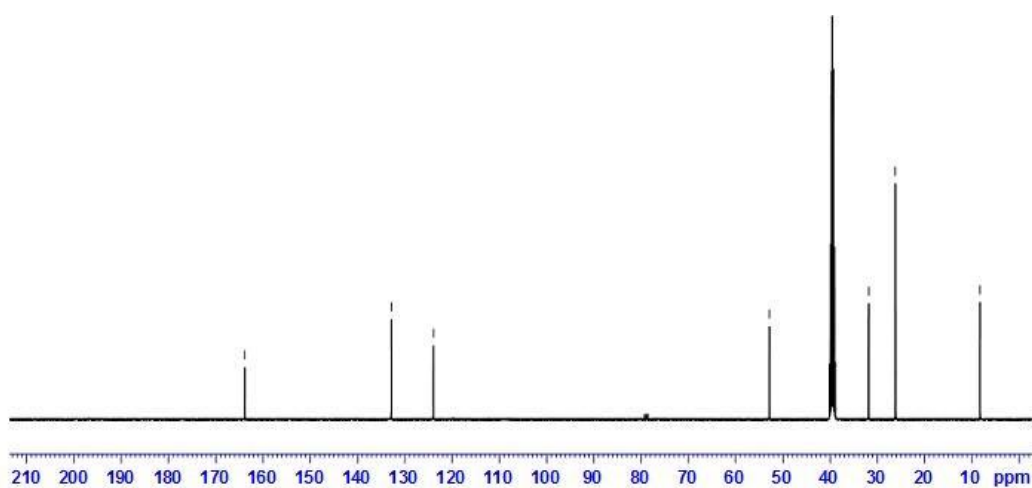


Figure 2 .<sup>13</sup>C-NMR spectrum of N-tert-amylacrylamide

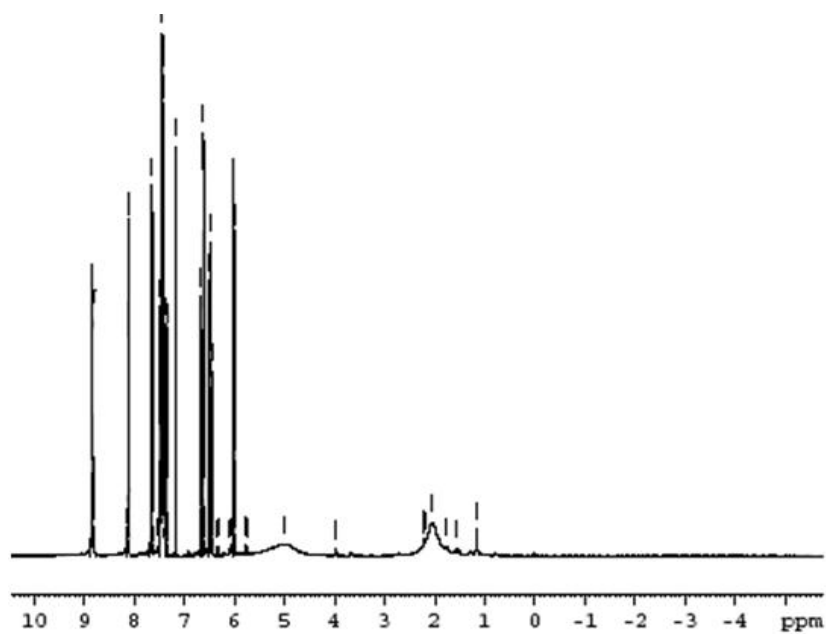
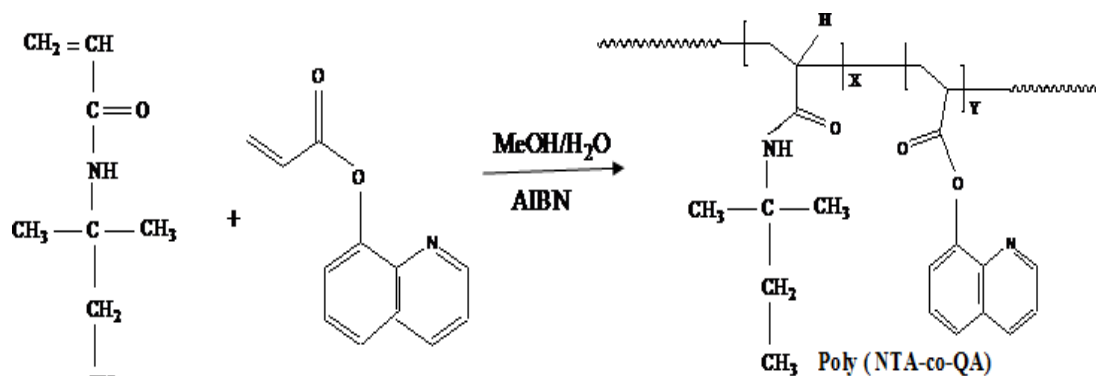


Figure 3 :<sup>1</sup>H-NMR spectrum of 8-quinolinyl acrylate (8-QA)

### Copolymerization of NTA and 8-QA

A series of copolymers of N-tert-amylacrylamide (NTA) and 8-quinolinyl acrylate (8-QA) were prepared. The schematic representation of the copolymer is given in Scheme 1.



Scheme 1 : Copolymerization of NTA and 8-QA

### Characterization of Copolymer spectrum of Poly(NTA-co-8-QA)

The  $^1\text{H-NMR}$  spectrum of copolymer, poly (NTA-co- 8-QA) ( 0.5 : 0.5) is shown in Figure 4 . The following peaks appear in the copolymer spectrum : at 1.03 -1.89 ppm for  $\text{CH}_2$  group , at 3.57 ppm for backbone  $\text{CH}_2$  , at 7.1-8.2 ppm due to quinolinyl aromatic protons and 8.7ppm due to NH Proton.

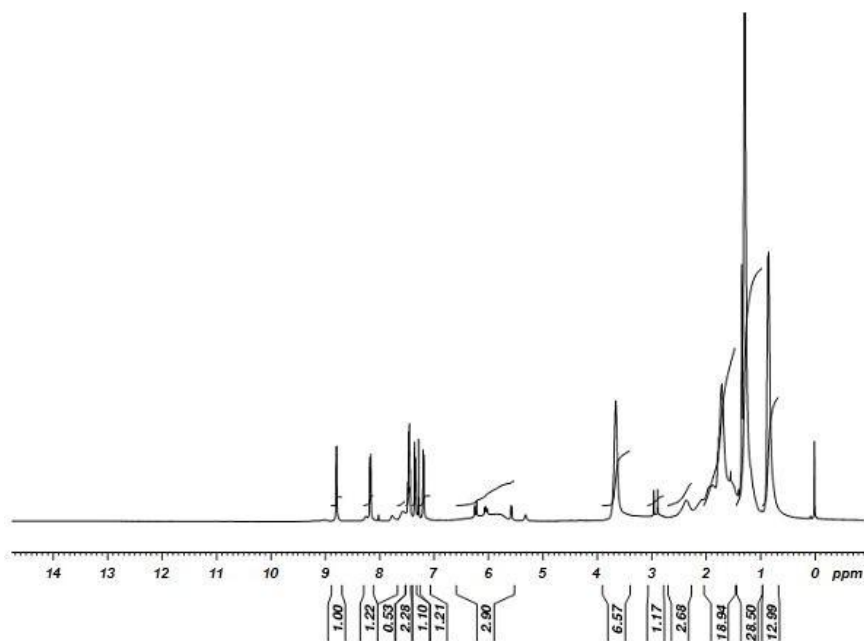


Figure 4 : $^1\text{H-NMR}$  spectrum of poly (NTA-co-8-QA) ( 0.5 : 0.5)

### Determination of copolymer composition of Poly (NTA-co-8-QA)

The copolymer composition was determined by  $^1\text{H-NMR}$  spectral analysis of the copolymer. The assignment of the resonance peaks in the  $^1\text{H-NMR}$  spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain. The quinolinyl peak area is used to determine the copolymer composition. Resonance signal at 7.1-8.2 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 can be obtained using

$$X_{8QA} = \frac{15 A(\text{aryl})}{\sum A(\text{aryl})} \quad \text{-----} 4$$

where X= mole fraction and A= peak area.

**Table 2: Mole fractions of the copolymers of N-tert-amylacrylamide (NTA) and 8-quinolinyl acrylate(8-QA)**

Mole fraction of NTA in feed, M <sub>1</sub>	Mole fraction of 8-QA in feed, M <sub>2</sub>	Mole fraction of NTA in copolymer, m <sub>1</sub>	Mole fraction of 8-QA in copolymer, m <sub>2</sub>
0.3	0.7	0.3362	0.6638
0.5	0.5	0.6680	0.3320
0.7	0.3	0.8067	0.1933
0.8	0.2	0.9014	0.0986

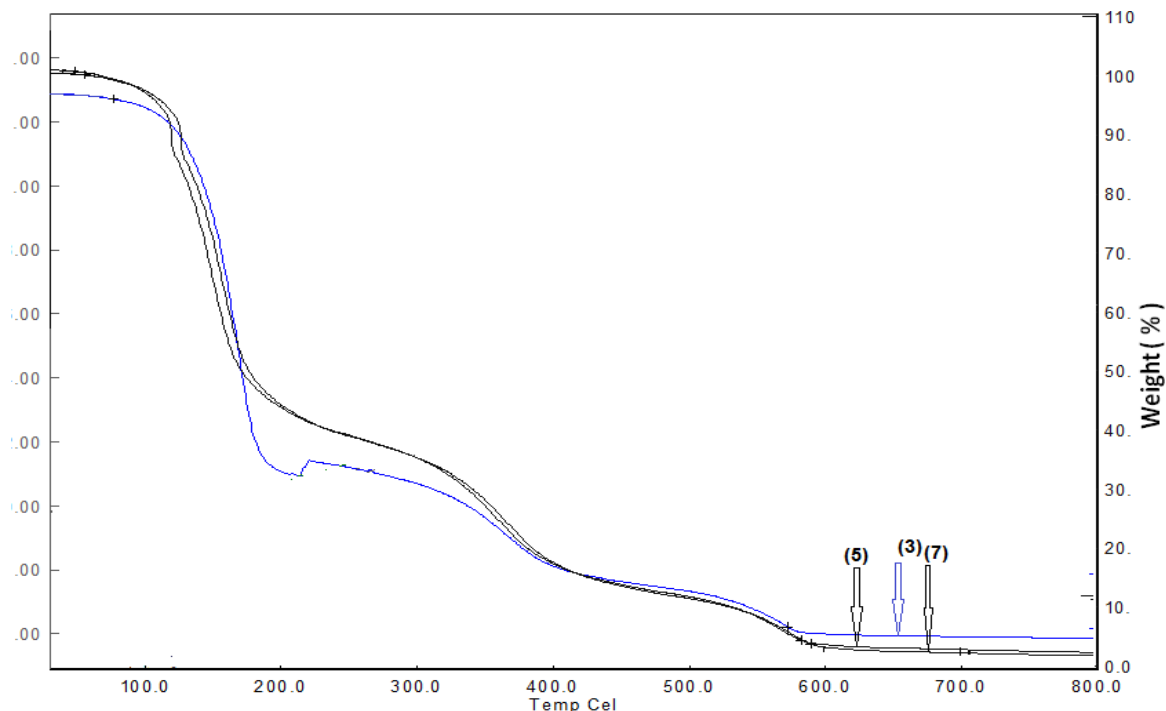
**Thermal analysis of Poly (NTA-co-8-QA)**

The glass transition temperature (T<sub>g</sub>) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The T<sub>g</sub> depends on the morphology of the polymer. The T<sub>g</sub> of poly(N-tert- amylacrylamide) homopolymer is 86.2°C. The T<sub>g</sub> of corresponding copolymers increases with increasing feed content of 8-QA. The increase in T<sub>g</sub> may be due to a reduction in segmental mobility. The TGA data for the copolymers of NTA with 8-QA are given in Table-3. From the table, it was observed that all the copolymers undergo two stage decomposition. The initial weight loss is due to moisture content. The weight loss at stage 1 is associated with the scission of amide linkage and decarboxylation of side chain units. The weight loss at stage 2 due to breakdown of polymer main chain. The T<sub>f</sub> value indicates that the thermal stability of copolymers increases with increasing amount of 8 QA.

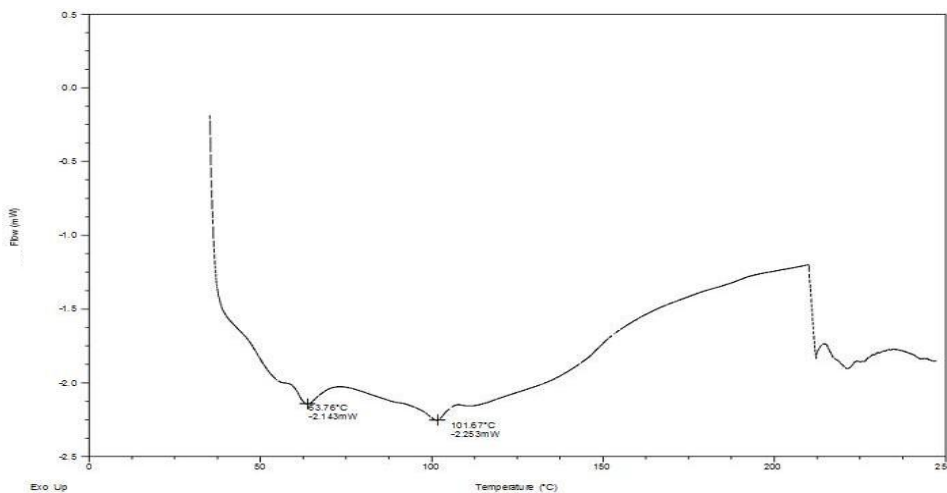
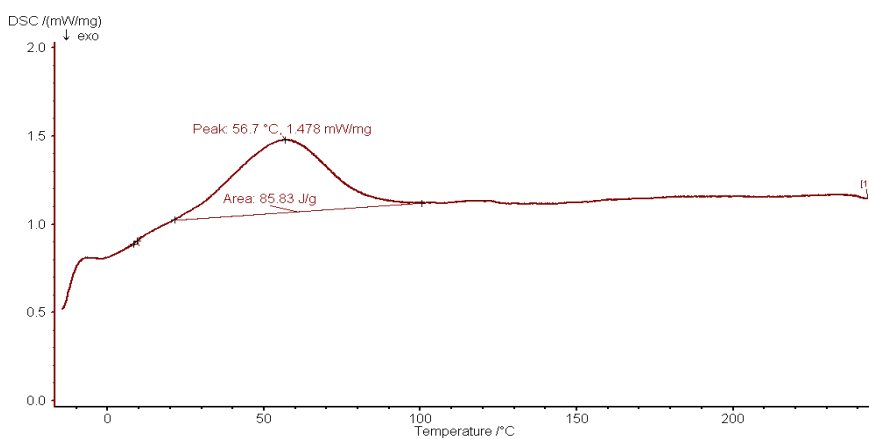
**Table 3 : TGA and DSC data for Poly (NTA-co-8-QA)**

Copolymers	Mole fraction of NTA, in feed	Mole fraction of 8-QA, in feed	Mole fraction of 8-QA, in copolymer	IDT (°C)	T50 (°C)	T <sub>f</sub> (°C)	T <sub>g</sub> (°C)
NTA-8QA	0.70	0.30	0.1933	120	164	625	110
NTA-8QA	0.50	0.50	0.3320	140	169	650	120
NTA-8QA	0.30	0.70	0.6638	150	176	675	130
Poly-NTA		-	-	-	-	-	86.2

IDT : Initial Decomposition Temperature; T<sub>50</sub> : decomposition temperature at 50% weight loss  
 T<sub>f</sub>: final decomposition temperature; T<sub>g</sub>: glass transition temperature



**Figure 5 : TGA curves of Poly (NTA-co-QA) ,(3)Mole fraction of NTA (0.3)  
(5)Molefractin of NTA (0.5), (7) Mole fractin of NTA (0.7)**



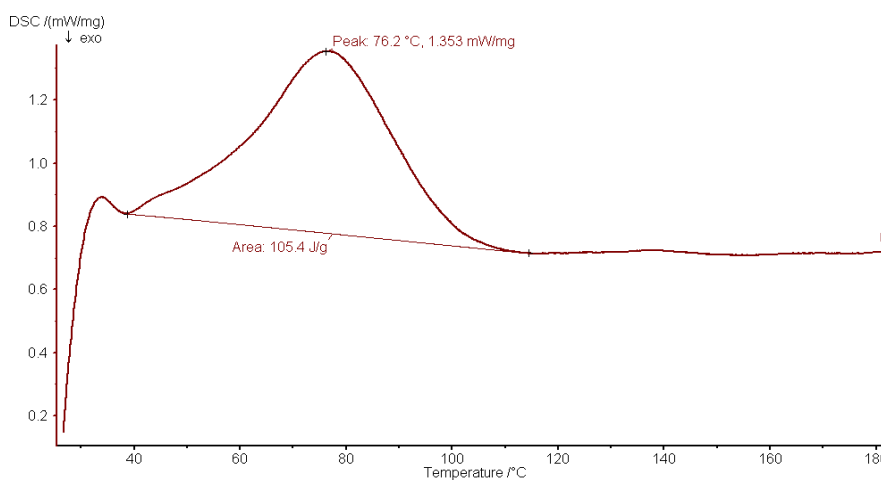


Figure 6 : DSC curves of Poly (NTA-co-8-QA) (0.3:0.7, 0.5:0.5 , 0.7:0.3)

## ELECTROCHEMICAL ANALYSIS

### Potentiodynamic Polarization

Polarization curves of mild steel in 0.05M H<sub>2</sub>SO<sub>4</sub> with and without presence of copolymers are shown in fig. 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<sub>2</sub>SO<sub>4</sub>. The polarization parameters such as corrosion potential (E<sub>corr</sub>) and corrosion current density (I<sub>corr</sub>) obtained by extrapolation of tafel lines are listed in Table. It is observed from the table that E<sub>corr</sub> values increased significantly for mild steel in the presence of copolymers. The tafel plots of all the studied mole ratios of poly(NTA-co-QA) 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 QA and it was increased with increase of any one monomer unit. Hence mild steel in the presence of 0.5: 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.

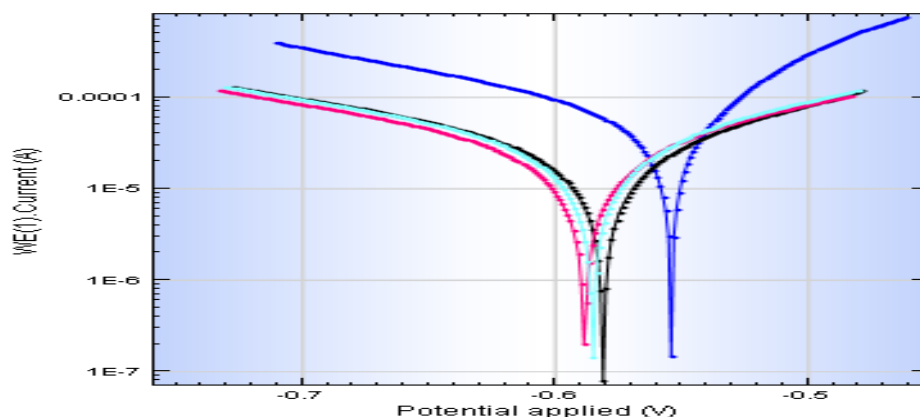


Figure 7: Potentiodynamic Polarization curves of poly(NTA-co-8QA)

Table 4. Potentiodynamic polarization parameters of poly(NTA-co-8-QA) in absence and presence of various mole ratios of copolymer with mild steel in 0.05M H<sub>2</sub>SO<sub>4</sub>

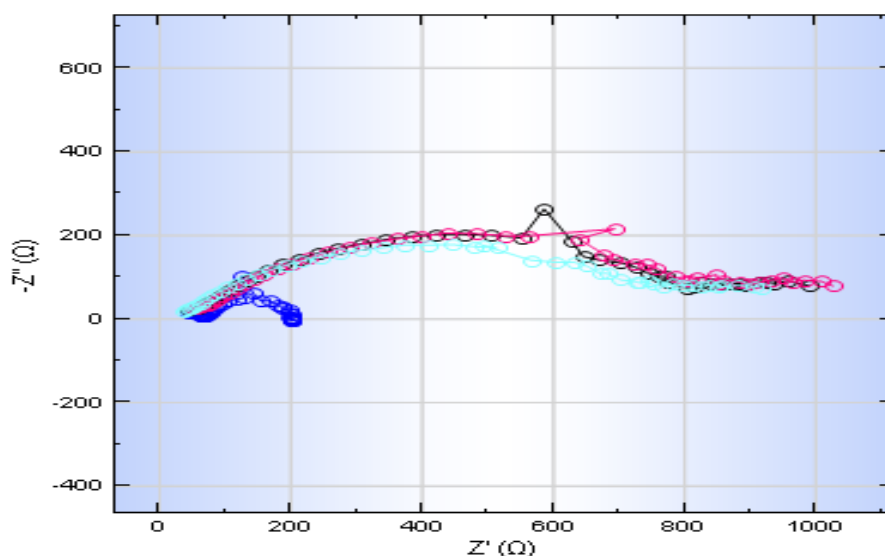


Polymer sample	$E_{corr}$ (mV)	Ba (V/dec)	Bc (V/dec)	$I_{corr}$ ( $10^{-4}$ A $cm^{-2}$ )	Eb (mV)	$R_p$ ( $\Omega$ )	Rate(mpy)	IE(%)
Uncoated	-481	0.2	0.04	1.62	-589	86.92	1.88	
0.3-0.7	-581	0.33	0.23	0.210	-724	1304.3	0.53	87
0.5-0.5	-580	0.31	0.22	0.194	-715	1224.6	0.52	88
0.7-0.3	-585	0.35	0.23	0.220	-716	1166.6	0.61	86

**Electrochemical impedance plots for in the presence and absence of various mole ratios of Poly(NTA-co-QA)**

The electrochemical impedance plots for in the presence and absence of various mole ratios of Poly(NTA-co-QA) with mild steel shown in figure. 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 QA composition decreases, the adhesiveness of the copolymer on mild steel decreases, this in turn decreases the corrosion resistance. The decrease in the  $C_{dl}$  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[9,10 ].

From the table it is noticed that, the poly(NTA-co-8QA) of equal mole ratio exhibit high  $R_{ct}$  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. Both the polarization and impedance study showed almost same inhibition efficiency (IE%)



**Figure 8 :Nyquist plots for uncoated and various mole ratio of poly (NTA-co-8QA) mild steel in 0.05M  $H_2SO_4$**

**Table 5. Electrochemical impedance parameters obtained for various mole ratio of poly(NTA-co-8-QA) mild steel in 0.05M  $H_2SO_4$**

Polymer Sample	$R_{ct}$ ( $\Omega$ )	$C_{dl}$ ( $\mu$ F $cm^{-2}$ ) $\times 10^{-5}$	IE(%)
Uncoated	69.565	1.92	
0.3-0.7	559.61	0.078	87
0.5-0.5	551.35	0.081	88
0.7-0.3	493.68	0.064	86

#### 4. CONCLUSIONS

The poly (NTA-co-8-QA) was successfully synthesized by free radical polymerization using N-tert-acylacrylamide(NTA) and 8-quinolinyl acrylate monomers. The formation of copolymers was characterized by <sup>1</sup>H-NMR spectroscopy. The synthesized copolymers exhibited IE (%) of 88.0 percentage and it behaves as good anti-corrosive material on metal surfaces.

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