2,4-Dichlorophenylacrylate Copolymers as Corrosion Inhibitor for Mild Steel in 0.5M H₂SO₄ solution

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Abstract

Herein we report, the poly (NTA-2,4-Dichlorophenylacrylate) copolymers were synthesized using N-tert-amylacrylamide and 2,4-Dichlorophenyl acrylate monomers by Free-radical polymerization at $60^{\circ}C$. The synthesized copolymers were subjected to corrosion inhibition studies on Mild steel using 0.5M H₂SO₄ solution. These copolymers are showed the corrosion inhibition efficiency of 86.0%

Introduction

Corrosion of metals in acidic solutions is one of the major problems   in many industries. Acids are widely used in industries for purpose of acid pickling, acid cleaning and oil well acidizing. Because of general aggressiveness of acid solution, the metals are being corroded easily. It is necessary to add corrosion inhibitors to prevent metal dissolution and minimize the acid consumption [1-10]. An inhibitor is a chemical compound that effectively reduces the corrosion rate of a metal when added   to a aggressive medium or environment. Well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The inhibiting action exercised by organic compounds on the dissolution of metallic species is normally related to interactions by adsorption between the inhibitors and the metal surface. The good inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production. Polymers are very large molecules that are formed by the combination of a number of relatively small molecules called monomers. Polymers can be made   from inorganic or organic molecules. In the last two decades, the uses of polymeric compound as corrosion inhibitors have been increased.

In the past years, there has been increased emphasis on applications of polymers, copolymers, grafted polymers and polymer composites as green corrosion inhibitors. Umoren et al [11, 12] reviewed the polymers for corrosion prevention applications. The prime controlling factors influencing the corrosion inhibitive performance of polymeric compounds on the corrosion of metals in various corrosive environments have been discussed. The high performances of the polymeric corrosion inhibitors are due to their larger size and numerous functional anchoring groups. Through the anchoring groups the polymers are easily got adsorbed on the metal surface and protect considerably more surface than the corresponding monomers. Molecular size, weight, composition and nature of the anchoring groups in a polymer are influencing the corrosion inhibition. The solution pH, concentration, exposure time and temperature also find their role in influencing the inhibition performance.

Quaternary ammonium chloride-based copolymers having unique properties attracted great attention to apply as anti- corrosive materials in various industrial processing for preventing corrosion of iron and steel in acidic media [13-15]. Atta et al., tested the corrosion inhibition efficiencies of crosslinked poly (Acrylamidopropyl) trimethylammonium chloride –co-Acrylamide) on mild steel in acidic medium and reported as the polymeric material showed mixed type inhibitor [16,17]. The corrosion inhibition study of polyacrylamide in 1.0M HCl medium showed 62.35 % of inhibition and acted as mixed type of inhibitor [18,19]. Based on the above literature survey, the anti-corrosion studies of N-substituted acrylamide are scanty. Therefore, we planned to synthesize poly (N-tert-amylacrylamide-co-2,4-dichlorophenyl acrylate) in order to investigate the anti-corrosive property. Herein we reported the synthesis of poly (N-tert-amylacrylamide-co-2,4-dichlorophenylacrylate) via free radical polymerization using AIBN initiator at 60 ^{O} C. The synthesized copolymer was characterized by NMR spectroscopy and corrosion inhibition study was carried out in 0.5M H_2SO_4 medium.

Experimental

2,2'-Azobisisobutyronitrile (AIBN) initiator
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 $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber colored bottle and kept in the refrigerator at 5°C.

Preparation of N-tert-amylacrylamide
N-tert-amylacrylamide(NTA) was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide formed was recrystallized in warm dry benzene [20] .

Preparation of 2,4-dichlorophenyl acrylate(2,4-DCPA)

2,4-dichlorophenyl acrylate was prepared by the reaction of 2,4-dichlorophenol with Acryloyl chloride. Absolute ethanol (400ml) and NaOH (0.2 mol) 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. 2,4-dichlorophenol (0.2 mol) was added to the reaction mixture, which was then heated to room temperature and then cooled to 0-5°C by ice. Freshly prepared acryloyl chloride (0.2 mol) was added drop wise to the cooled reaction mixture and stirred for 90 min. The mixture was then poured in to a crushed-ice. Light yellow colored precipitate was separated out. The product was filtered, washed thoroughly with cold water and recrystallized from petroleum ether.

Preparation of copolymers

Appropriate quantities of the monomers, 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 $60°C$.

Table -1: Copolymerization of N-tert-amylacrylamide and 2,4-dichloro phenylacrylate

Mole fraction of NTA (M_1)	Mole fraction of 2,4-DCPA (M_2)	Reaction Time (Min)	Weight of Copolymer(mg)	Copolymer Conversion %
0.2	0.8	360	140	2.8
0.3	0.7	360	140	2.8
0.4	0.6	360	135	2.7
0.5	0.5	360	155	3.1
0.6	0.4	360	175	3.5
0.7	0.3	360	130	2.6
0.8	0.2	360	130	2.6

Characterization of Copolymers

^{1}H-NMR spectrum of copolymers were recorded on the GSX-400 spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz in $CDCl_3$. 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 the specimen

Mild steel specimens (Fe: 98.7; C: 0.033; Mn: 0.235; Si: 0.005; S: 0.005, etc.) of dimension 2cmx1cm were polished to a mirror finish, degreased with acetone and alcohol followed by double distilled water, and used for the surface examination studies

Corrosion Inhibition studies

Weight Loss Method

The weight Loss method is the best known and simplest of all corrosion monitoring techniques. This method involves exposing a specimen of material to a process environment for a given duration, then removing the specimen for analysis. The basic measurement which is determined from corrosion is weight loss; the weight loss taking place over the period of exposure being expressed as corrosion rate.

$$\text{Inhibition Efficiency (\%)} = W_o - W / W_o \qquad \text{----------- (1)}$$

where, W_o and W are the weight loss in absence and presence of inhibitors.

$$\text{Corrosion Rate (mpy)} = 534 \times W / D \times A \times T \qquad \text{------------ (2)}$$

where, W is weight loss (mg); D is density of specimen (g/ cm^3);A is surface area of specimen (in^2); T is exposure time (h)

Potentiodynamic polarization

The potential of the working electrode was measured with respect to SCE and the platinum electrode was used as an auxiliary electrode. Potentiodynamic polarization curves were obtained by scanning the potential range from -200mv to +200 mv (+ Ecorr) at a scan rate of 10mV/s after 1h immersion time in 0. 5M H_2SO_4 with inhibitor solution. 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 inhibition efficiency of these systems was calculated by using the following equation.

$$IE\% \quad = \quad \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \qquad \text{------------(3)}$$

I_{corr} and $I_{corr(i)}$ are corrosion current density in the absence and presence of inhibitor respectively

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 25mV/sec was applied and the frequency was varied from 10 MHz to 10 KHz using electrochemical work station CHI 660 USA. Electrochemical data were obtained after 1h of immersion with the working electrode at the rest potential and tests have been performed in non-deaerated solutions under stirred conditions. 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

$$C_{dl} = \frac{1}{2\pi f_{max} \times R_{ct}} \qquad \text{---------- (4)}$$
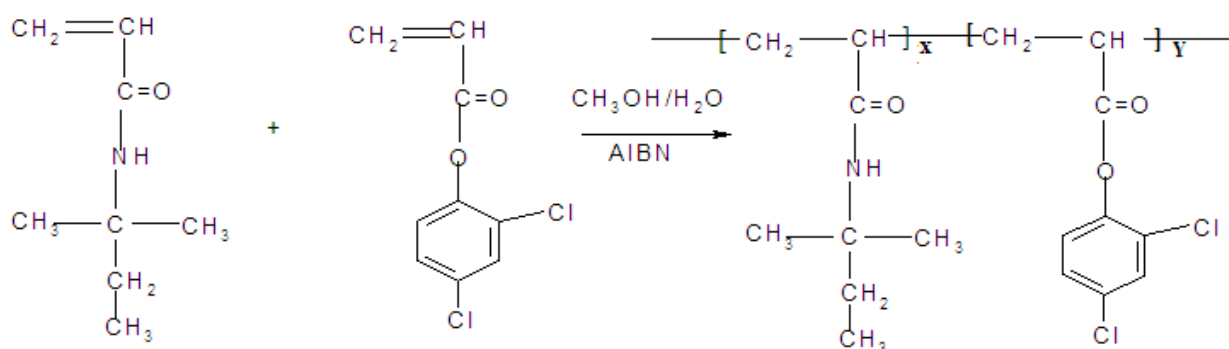
C_{dl} is double layer capacitance ; R_{ct} is Charge transfer resistance; f_{max} is frequency at Z" value maximum.

$$IE\% = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100 \qquad \text{---------- (5)}$$

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

Results and discussion

The schematic representation of copolymer preparation using NTA and 2,4-DCPA monomers at $60°C$ is given in scheme-1.

Scheme-1.Copolymerization of N-tert-amylacrylamide and 2,4-dichlorophenylacrylate

Spectral characterization: The ^{1}H-NMR spectrum of poly (NTA-co-DCPA) is shown in Figure 1 and the following peaks are appear in the copolymer spectrum: at 0.8 for CH_3 group ; at 1.34 –2.47 ppm for CH_2 group , at 3.21 ppm for backbone CH_2 , at 6.9 – 7.5 ppm due to DCPA aromatic protons.
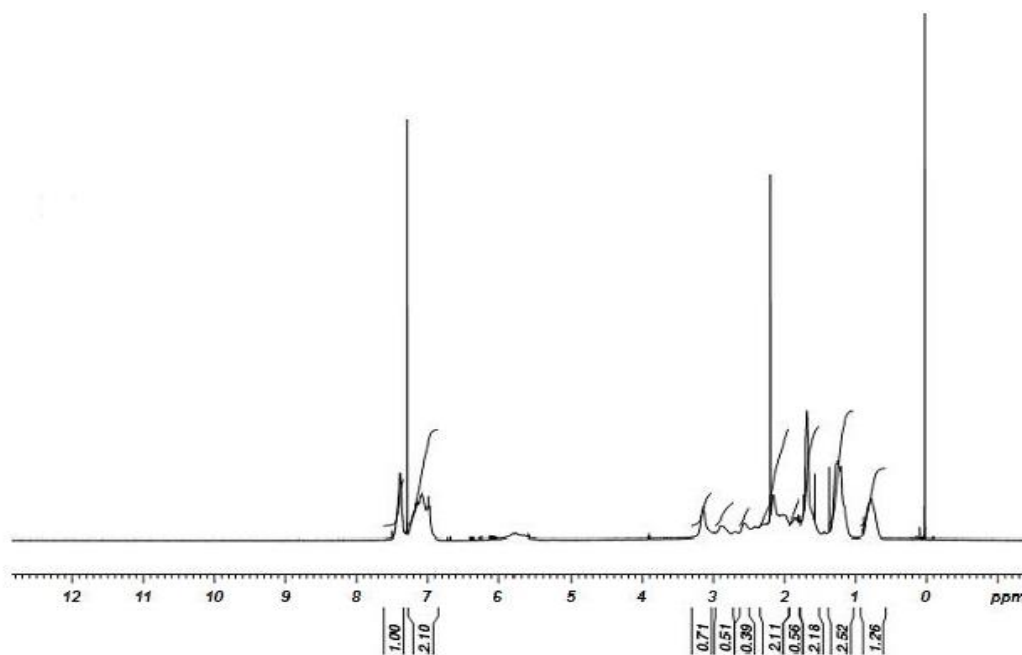
Figure -1. ¹H-NMR spectrul of poly(NTA-co-2,4DCPA)

Determination of copolymer composition

The copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymer. The phenyl peak area is used to determine the copolymer composition. Resonance signal at 6.9-7.5 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

$$X_{DCPA} - \frac{15A(aryl)}{3A(total) - 7A(aryl)} \qquad\qquad\qquad (6)$$

where X= mole fraction and A= peak area.

Thermal Studies of poly (NTA-co-2,4-DCPA)

Thermal behaviors of poly(NTA-co-DCPA) is shown in Figure -2 and the results are shown in Table- 2. It is observed that all the copolymers undergo triple stage decomposition. Initial weight loss is due to moisture content. The decomposition at stage-1 occurs in the region 200-390°C due to scission of ester/amide linkages and stage-2 at 390-480°C occurs due to possible decarboxylation and/or other reactions of side-chain units. The stage-3 weight loss indicates the main-chain degradation reactions and breakdown of the polymer backbone. T_g also found to increase with increasing feed content of DCPA. The increase in T_g may be due to reduction in segmental mobility. The T_g values of corresponding copolymers are lower than the NTA homopolymer.

Table- 2. TGA and DSC data for poly (NTA-co-2,4-DCPA)

Copolymers	Mole fraction of NTA, in feed	Mole fraction of DCPA, in feed	Mole fraction of DCPA, in copolymer	IDT (°C)	T_{50} (°C)	T_f (°C)	T_g (°C)
NTA-DCPA	0.70	0.30	0.3710	55	305	655	72.4
NTA-DCPA	0.50	0.50	0.5731	105	322	672	76.3
NTA-DCPA	0.30	0.70	0.7505	122	344	683	73.0
Poly-NTA	-	-	-	-	-		86.2

IDT: Initial Decomposition temperature; T_{50}: decomposition temperature at 50% weight loss

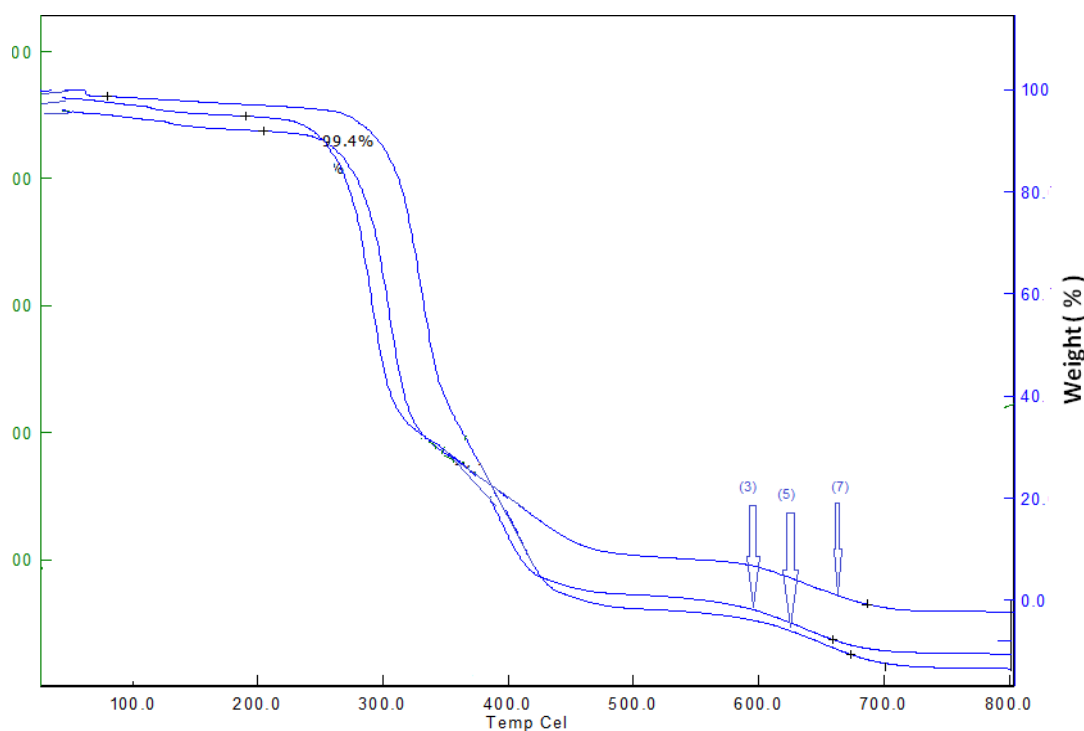T_f: final decomposition temperature; $T_{g:}$ glass transition temperature

Figure -2 : TGA curves of poly (NTA-co-2,4-DCPA) ; (3) Mole fraction NTA(0.3)

Electrochemical analysis

Potentiodynamic Polarization

Polarization curves of mild steel in 0. 5M H_2SO_4 with and without 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. 5M 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. It is observed from the Table-3 that Ecorr values are increased significantly for mild steel in the presence of copolymers. The Tafel plots of all the studied

mole ratios of poly(NTA-co-DCPA) have good corrosion inhibition behavior. As it 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 DCPA 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.
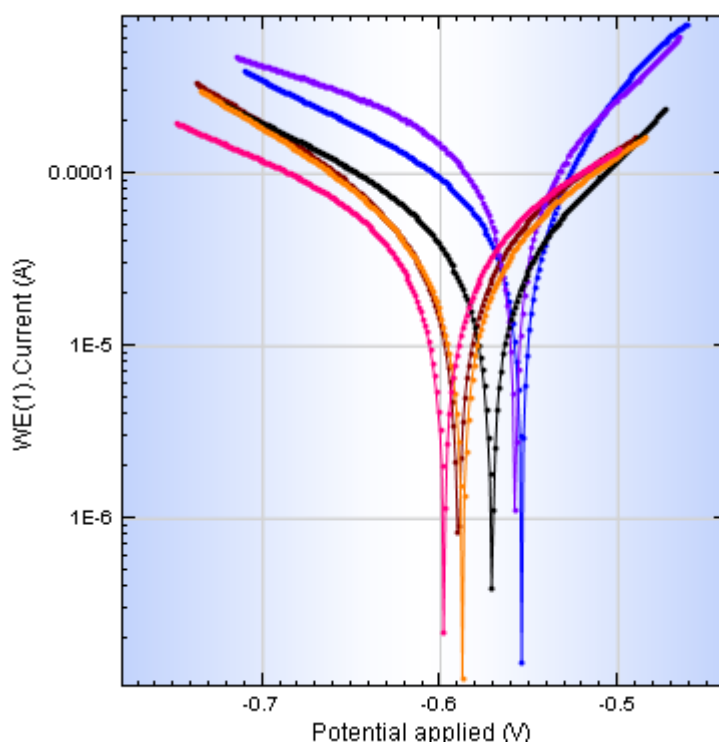

Figure-3. Tafel plots of   poly(N-tert-amylacrylamide-co-Phenyl acrylate)

Table- 3. Potentiodynamic Polarization parameters of poly(NTA-DCPA)

Polymer Sample	E_{corr} (mV)	βa (V/dec)	βc (V/dec)	Icorr (10^{-4} A cm^{-2}	Eb (mV)	Rp(Ω)	Rate(mpy)	IE(%)
blank	-481	0.20	0.04	1.620	-589	86.92	1.88	
0.2-0.8	-598	0.36	0.28	0.696	-736	847.99	0.94	57
0.3-0.7	-585	0.17	0.18	0.275	-721	846.87	0.57	83
0.5-0.5	-558	0.55	0.22	0.227	-581	259.84	3.08	86
0.7-0.3	-587	0.17	0.17	0.243	-723	846.87	0.52	85
0.8-0.2	-571	0.20	0.14	0.476	-714	766.11	0.55	71

Electrochemical impedance of poly (NTA-co-DCPA)

The electrochemical impedance plots for in the presence and absence of various mole ratios of poly (NTA-co-DCPA) with mild steel shown in Figure-4. The copolymer showed 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 DCPA composition decreases, the adhesiveness of the copolymer on mild steel decreases; this in turn decreases the corrosion resistance.

The decrease in the Cdl 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 [18,19]. From the Table -4, poly(NTA-co-DCPA) of equal mole ratio exhibit high Rct value (Table-4). This shows high corrosion protection efficiency. Hence, all the mole ratio of this polymer shows good inhibition against corrosion. This behavior due the uniform and adherent of copolymer on mild steel, which effectively prevent the penetration of corrosive ion.
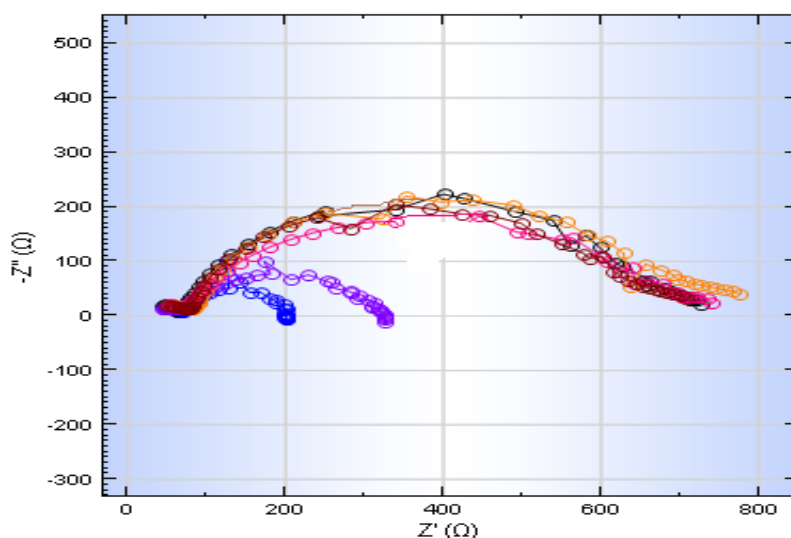

Figure-4 . Nyquist plots of **poly(N-tert-amylacrylamide-co-Phenyl acrylate)**

Table-4: Electrochemical impedance parameters of poly(NTA-DCPA)

Polymer Sample	R_{ct} (Ω)	C_{dl}(μ F cm^{-2}) x10^{-5}	IE(%)
blank	69.5	1.920	
0.2-0.3	162..9	0.774	57
0.3-0.7	420.1	0.321	83
0.5-0.5	487.9	0.636	86
0.7-0.3	484.1	0.687	85
0.8-0.2	447.3	0.697	84

Conclusions

The poly(NTA-2,4-DCPA) copolymers were synthesized by free-radical polymerization using AIBN initiator at 60°C. The formation of copolymers was characterized by ^{1}H-NMR spectroscopy. Both the EIS and PDP methods showed the corrosion efficiency of 86.0% .

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