

# Synthesis and Electrochemical Studies of N-Tert-Amylacrylamide and 7-Acryloyloxy- 4- Methyl Coumarin Copolymers

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## ABSTRACT

In the present study, we reported the synthesis of poly (NTA-co-ACU) and spectral characterization by <sup>1</sup>H-NMR spectroscopy. The synthesized copolymers were subjected to electrochemical analysis to study the corrosion inhibition properties. The Nyquist plots and Tafel plots of all the synthesized polymers showed good corrosion inhibition efficiency.

**Keywords :** Methacrylic, Coumarin Copolymers, Electrochemical Studies, N-Tert-Amylacrylamide

## I. 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 pickling agent of iron and steel, chemical cleaning of scale in metallurgy, acidizing in oil recovery and other petrochemical processes.

One of the means of 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 [2-9].

Contemporarily, numerous papers have been published on the inhibitive action of organic

heterocyclic compounds containing studies nitrogen, sulfur and oxygen on mild steel in acidic media [10-16].

Among the organic coating, recently, the methacrylic polymer coatings have found wide applications in several industries [17-19]. 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 [20].

Hence, in the present study experiments were carried out in order to exploit the adhesive behavior of methacrylates and the inhibiting behavior of Poly (ACU-Co-NTA) and dip coated on mild steel to increase the adhesion and corrosion resistance.

Synthesized poly (ACU-co-NTA) has been characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy. To evaluate the corrosion protection properties of these copolymers, the electrochemical experiments such as potentiodynamic polarization and electrochemical impedance studies were carried out with mild steel samples coated with different mole ratios of the copolymers in 0.05M H<sub>2</sub>SO<sub>4</sub>.

## II. EXPERIMENTAL

### 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. The white crystals have a mp.91° C (Lit.91-92° C) and the yield was -87%.

### Preparation of 7-acryloyloxy-4-methyl coumarin (ACU)

The 7-acryloyloxy-4-methylcoumarin (ACU) comonomer was prepared by esterification of 7-hydroxy-4-methyl coumarin and 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. Then, 7-hydroxy-4-methylcoumarin (0.2 mol) was added to the reaction mixture, which was then heated to room temp. 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-water where a white colored product was separated out. The product was filtered, washed thoroughly with cold water and recrystallized from methanol

### 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. 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, represent the experimental details of copolymerization and Table 2- 6 represent the preparation of series of copolymers.

**Table 1.** Copolymerization of N-tert-amylacrylamide and 7-acryloyloxy-4- methyl coumarin

S.No	Mole fraction of NTA ( M <sub>1</sub> )	Mole fraction of ACU ( M <sub>2</sub> )	Reaction Time ( min)	Weight of Copolymer (mg)	Copolymer Conversion %
2	0.3	0.7	360	160	3.2
4	0.5	0.5	360	140	2.8
6	0.7	0.3	360	135	2.7

### Preparation of specimens

The mild steel samples embedded in a polymer setting had an area of exposure of 1 cm<sup>2</sup>. These specimens were mechanically polished using different grades of emery paper. They were subsequently washed with double distilled water, degreased with methanol, and then dried at room temperature appropriate concentration of the acid was prepared using double distilled water

### Electrochemical studies

The inhibition efficiency of these systems was calculated by using the following equation.

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

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

The EIS study was carried out using electrochemical work station CHI 660 USA. 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

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

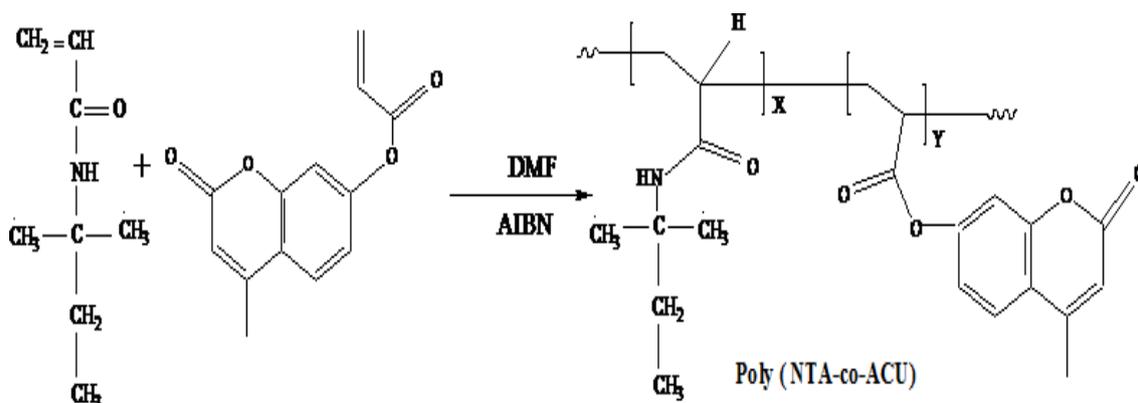
- Where,  $C_{dl}$  = double layer capacitance
- $R_{ct}$  = Charge transfer resistance
- $f_{max}$  = frequency at  $Z''$  value maximum.

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

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

- where,  $R_{ct}$  = Charge transfer resistance in the absence of inhibitor
- $R_{ct(i)}$  = Charge transfer resistance in the presence of inhibitor

### Synthesis of poly (ACU-NTA)



### III. RESULTS AND DISCUSSION

#### Spectral Characterization

##### <sup>1</sup>H-NMR spectrum of *N*-tert-amyl acrylamide (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) operating 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>, at 5.49 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 3)

6 163.90(CH<sub>2</sub> = C(H)-CO-NH..);

6 132.93(CH<sub>2</sub> =C(H)-CO-NH...);

6 123.87(CH<sub>2</sub>=C(H)-CO-NH..) ;

6 52.82(-CO-NH-C(CH<sub>3</sub>)-CH<sub>2</sub>);

6 31.87(-CO-NH-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>);

6 26.19(-CO-NH-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)

6 8.26(-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>).

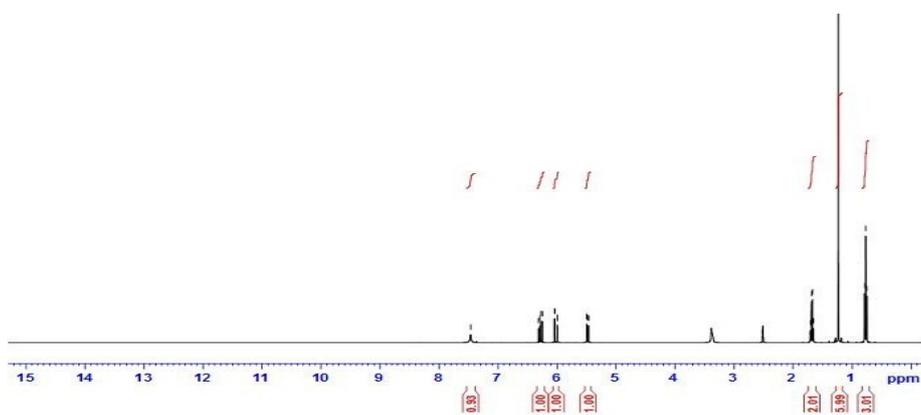


Figure 1. <sup>1</sup>H-NMR spectrum of N-tert-amylacrylamide (NTA)

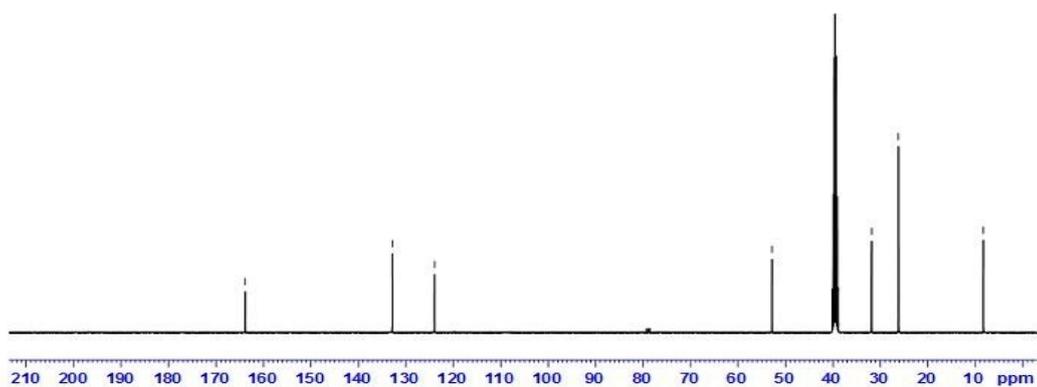


Figure 2. <sup>13</sup>C-NMR spectrum of N-tert-amylacrylamide

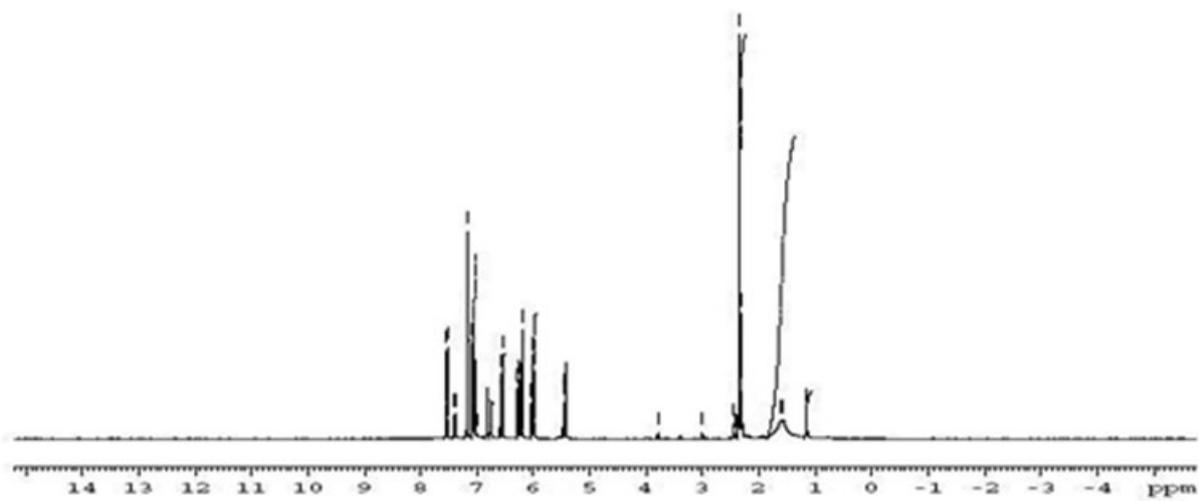
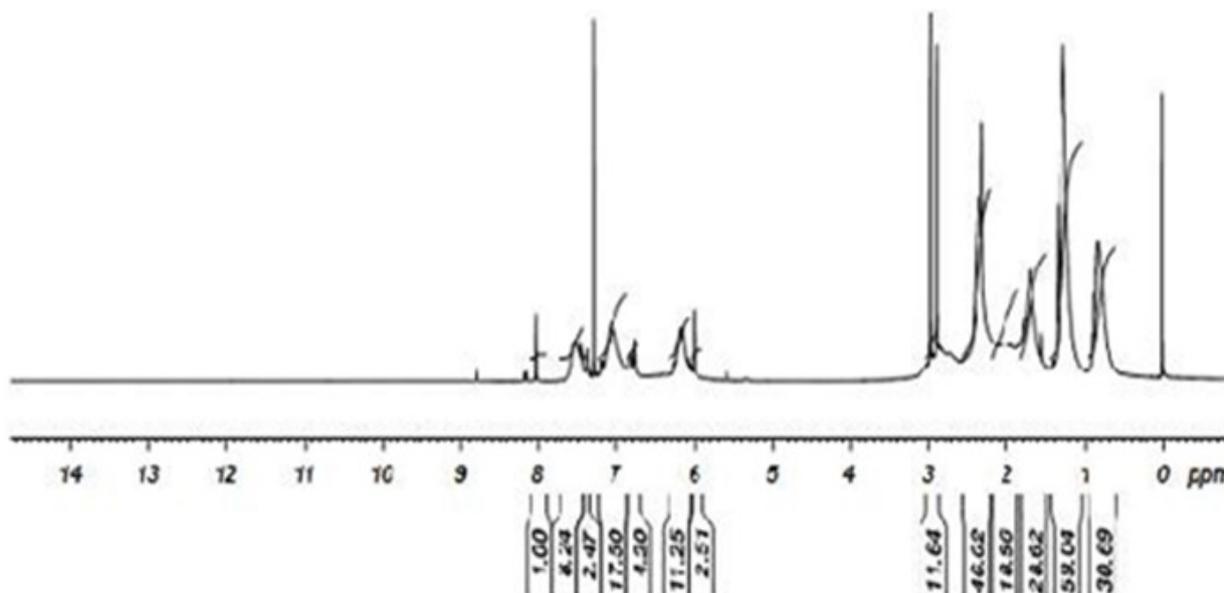


Figure 3. : <sup>1</sup>H-NMR spectrum of 7-acryloyloxy-4-methyl coumarin (ACU)



**Figure4.**  $^1\text{H-NMR}$  spectra of poly (NTA-co-ACU) 0.5:0.5

### Characterization of Copolymer

The  $^1\text{H-NMR}$  spectrum of copolymers, poly (NTA-co-ACU) is shown in Figure 4 and the following peaks appear in the copolymer spectra : at 1.14 -2.96 ppm for  $\text{CH}_2$ ,  $\text{CH}_3$  of ACU group , at 3.08ppm for backbone  $\text{CH}_2$  , at 6.8-7.8 ppm due to ACU aromatic protons and 8.1 ppm for NH proton.

### 3.2 Solubility Test

The solubility of synthesized copolymer derivatives were tested in various solvents in room temperature.

All the studied copolymers derivatives were easily soluble in various organic solvents, namely acetone, dichloromethane, toluene, benzene, 1,4-dioxane, chloroform, chlorobenzene and dimethyl formamide and insoluble in water , methanol and ethanol. The solubility test clearly shows that there is wide possibility for using different solvents for the copolymers in order to be used in coating applications.

### Electrochemical Characterization of poly(ACU-co-NTA)

Anti-corrosive behavior of the synthesized poly(ACU-co-NTA) was characterized by electrochemical techniques such as potentiodynamic polarization and electrochemical impedance. The potentiodynamic polarization curves of the different molar ratio of poly(ACU-NTA) coated and uncoated metal in 0.05M  $\text{H}_2\text{SO}_4$  solution. The Tafel plots of all the studied mole ratios of poly(ACU-co-NTA) have good corrosion protection behavior. It can be noticed that the polymer causes a decrease in the corrosion rate i.e. shifts both anodic and cathodic curves to lower values of current densities as compared to the blank. Moreover these results indicate the polymer acts as mixed type of corrosion protection. IE% values are increases with the increasing molar ratios of ACU unit in the copolymer. The increase of inhibition efficiency(IE) due to blocked fraction of the electrode surface by adsorption. ACU containing copolymer showed maximum inhibition efficiency of 97. 0%. Therefore ACU containing copolymer form more stable and perfect film on the metal Surface.

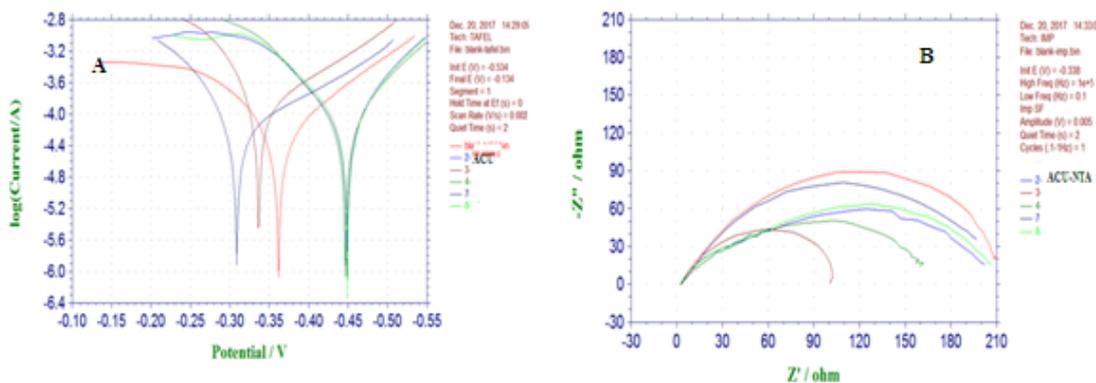


Figure 5. Electrochemical analysis of poly(ACU-co-NTA) (a)Tafel (b) Nyquist plots

### III. COCLUSION

The Poly(ACU-co-NTA) was successfully synthesized by free radical polymerization using 7-acryloyloxy-4-methyl coumarin (ACU) and N-tert-amylacrylamide(NTA). The formation of copolymers were characterized by <sup>1</sup>H-NMR spectroscopy. The synthesized copolymers exhibited IE(%) to 97.0 percentage and it behaves as good anti-corrosive material on metal surfaces.

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