Electrochemical analysis of Poly (N-tert-amylacrylamide – co- Phenylacrylate)

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Abstract

In the present study, we reported the synthesis of poly (NTA-co-PA) and spectral characterization by ¹H- 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 of 87.0%.

Keywords: Phenylacrylate ; Corrosion inhibition ; Copolymers ; NMR spectroscopy

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. 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]. 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]

Experimental

Preparation of N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of tert-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%. The monomer was confirmed by both ¹H- NMR and ¹³C-NMR spectroscopy.

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 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%.

Electrochemical studies

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

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

The C_{dl} values were obtained from the relationship

$$IE\% = \frac{R_{\text{ct(i)}} - R_{\text{ct}}}{R_{\text{ct(i)}}} \times 100 \quad \text{----- (2)}$$

Results and discussion

The schematic representation shows the preparation of copolymers is given as scheme-1.

Scheme-1: Synthesis of poly(N-tert-amylacrylamide-co-Phenyl acrylate)

Figure 1. ¹H NMR spectra of poly(N-tert-amylacrylamide-co-Phenyl acrylate)

Spectral characterization

The ¹H-NMR spectra of copolymers, poly (NTA-co-PA) is shown in Figure- 1. The following peaks appear in the copolymer spectrum : at 1.1 -2.9 ppm for CH₂ group , at 2.7 ppm for backbone CH₂ , at 6.8-7.4 ppm due to PA aromatic protons and 7.7 for NH proton of NTA.

Potentiodynamic polarization of poly(N-tert-amylacrylamide-co-Phenyl acrylate)

Anti-corrosive behavior of the synthesized poly(NTA-co-PA) was characterized by electrochemical techniques such as potentiodynamic polarization and electrochemical impedance. The potentiodynamic polarization curves of the different molar ratio of polymers coated and uncoated metal in 0. 5M H₂SO₄ solution (Figure-2a). The Tafel plots of all the studied mole ratios of polymers 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 PA unit in the copolymer. The increase of inhibition efficiency (IE) due to blocked fraction of the electrode surface by adsorption. PA containing copolymer showed maximum inhibition efficiency of 87. 0%. Therefore, PA containing copolymer forms more stable and perfect film on the metal Surface.

Figure 2. Electrochemical Characterization of poly(N-tert-amylacrylamide-co-Phenyl acrylate) (a) Tafel plots (b) Nyquist plots

Table- 1. Potentiodynamic Polarization parameters of poly(NTA-PA)

Polymer samples	E_{corr} (mV)	β_a (V/dec)	β_c (V/dec)	I_{corr} (10^{-4} A cm $^{-2}$)	E_b (mV)	$R_p(\Omega)$	Rate(mpy)	IE(%)
blank	-481	0.20	0.04	1.620	-589	86.92	1.88	-
0.3-0.7	-582	0.17	0.17	0.324	-720	463.06	0.64	80
0.5-0.5	-580	0.17	0.16	0.211	-719	670.69	0.61	87
0.7-0.3	-582	0.18	0.17	0.301	-714	664.54	0.67	81

Electrochemical impedance of poly (NTA-co-PA)

The electrochemical impedance plots for in the presence and absence of various mole ratios of poly (NTA-co- PA) with mild steel shown in Figure-2b. 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 PA 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 [8,9]. From the Table -2, poly(NTA-co-PA) of equal mole ratio exhibit high Rct value (Table-2). This shows high corrosion protection efficiency. Hence, all the mole ratio of this polymer shows good inhibition against corrosion (83.0%). This behaviour due the uniform and adherent of copolymer on mild steel, which effectively prevent the penetration of corrosive ion [10].

Table-2: Electrochemical impedance parameters of poly(NTA-PA)

Polymer samples	$R_{ct} (\Omega)$	$C_{dl}(\mu F cm^{-2}) \times 10^{-5}$	IE (%)
blank	69.5	1.920	--
0.3-0.7	394.0	0.715	82
0.5-0.5	399.9	0.705	83
0.7-0.3	393.3	0.711	82

Conclusions

The poly (NTA-co-PA) was successfully synthesized by free radical polymerization using N-tert-amylacrylamide(NTA) and Phenyl acrylate(PA). The formation of copolymers was characterized by 1H -NMR spectroscopy. The synthesized copolymers exhibited IE (%) of 87.0 percentage and it behaves as good anti-corrosive material on metal surfaces.

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