Synthesis of Poly(methylmethacrylate-co-N-vinyl-2-pyrrolidone) Polymer†

CHUNYANG ZHU¹, YUANPENG WU¹, AMBRISH SINGH^{1,2}, YUANHUA LIN^{1,*}, WANYING LIU³ and KUANHAI DENG⁴

¹State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Southwest Petroleum University), Chengdu 610500, Sichuan, P.R. China

²Department of Chemistry, School of Civil Engineering, LFTS, Lovely Professional University, Phagwara-144 402, India

³School of Material Science and Engineering (Southwest Petroleum University), Chengdu 610500, Sichuan, P.R. China

⁴CNPC Key Lab for Tubular Goods Engineering (Southwest Petroleum University), Chengdu 610500, Sichuan, P.R. China

*Corresponding author: Tel: +86 13908085550; E-mail: yhlin28@163.com

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The synthesis of polymer poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone) [P(MMA-co-VP)] from 2-(methoxycarbonyl)-1-propene monomer and N-vinyl-2-pyrrolidone monomer in the presence of potassium peroxodisulfate was done at 75 °C. The polymerization was refluxed for 6 h under continuous stirring. Nitrogen gas was used to remove the oxygen present in the reflux container during the whole reaction. The polymer was further analyzed using FTIR spectroscopy, X-ray diffraction and nuclear magnetic resonance spectroscopy methods. P(MMA-co-VP) polymer also finds its application as an effective corrosion inhibitor in the presence of CO₂ for J55 steel in oil and petroleum industry.

Keywords: Poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone), NMR, XRD.

INTRODUCTION

In China, oil and gas field with CO₂ content is mainly distributed in Songliao basin, Bohai gulf basin, Subei-Nanhuanghai basin, Sichuan basin and Jilin basin. In Songliao region, the CO₂ content of some gas field is as high as 99.02 %. Gas fields in Bohai gulf basin and Jilin basin also contain high CO₂. Puguang gas field is the highest CO₂ content gas field in Sichuan area, with a proportion of 7.94-9.07 %. In order to enhance oil recovery in Jilin oilfield; liquid CO₂ is injected into the formation followed by the hot water. Hence the liquid CO₂ and hot water will be miscible to drive the oil out of the formation, which is called miscible displacement to improve oil recovery. However, the CO₂ dissolved in water will lead to severe carbon dioxide corrosion.

Inhibitors are chemicals that are used to mitigate the surface of metals used in oil and gas industries to mitigate corrosion. The inhibitor is adsorbed on the surface of the metal forming a compact protective thin layer¹⁻³. Several chemical compounds have been tested for corrosion inhibition of metals and alloy. However, the compounds having N, S and O heteroatoms, incorporated in an aromatic system, have been found to possess excellent anti corrosion potential. Because of increasing ecological awareness and strict environmental regulations, as well as the inevitable drive toward sustainable and environ-

mentally benign processes, attention has been focused toward the development of nontoxic alternatives to inorganic and organic inhibitors applied so far⁴⁻⁶.

The use of polymers as corrosion inhibitors has drawn considerable attention due to their inherent stability and cost effectiveness⁷. They form complexes with metal ions, which occupy a large surface area thereby blanketing the surface and protecting the metal. Both natural and synthetic polymers have been used as corrosion inhibitors⁸. The insolubility of most of the polymers is the major limitation in corrosion inhibition application. Recently, some attempts have been made to increase the solubility of polymers. The main approaches for preparing soluble polymers are functionalization and copolymerization of polymers⁹. It is well known that compounds with high molecular weight and bulky structure cover more area on the metal surface that leads to high inhibition efficiency.

EXPERIMENTAL

Synthesis of polymer: 2-(Methoxycarbonyl)-1-propene (MMA) monomer and N-vinyl-2-pyrrolidone (NVP) monomer were used at 1:1 ratio in 30 mL water. Potassium peroxodisulfate (KPS) (0.0380 g) dissolved in 10 mL water that was used as an initiator. It was added slowly with stirring at a constant temperature of 75 °C. The reaction mixture was refluxed for

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4 h with continuous stirring until a white emulsion was obtained. The poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone) [P(MMA-co-VP)] was filtered, washed and dried. The appropriate solutions of different concentrations were prepared in 3.5 % NaCl for corrosion study. The structures of copolymers are given in Fig. 1.

Fig. 1. Synthesis of P(MMA-co-VP) polymer

FTIR was carried out by using Fourier transform infrared spectrometer model NICOLET 6700 connected with OMNIC software. The dried and powdered polymer was mixed with KBr and grinded in agar-mortar and then mounted onto a metal case that was used for the study. The dried polymer was analyzed by using X-ray diffractometer, X Pert PRO incorporated with Higscore software. ^{13}C and ^1H NMR was carried out using Bruker at 400 MHz. Topspin software was used to study the structure of molecules, the interaction of various molecules, the kinetics or dynamics of molecules and the composition of mixtures of synthetic solutions.

RESULTS AND DISCUSSION

FTIR: The peaks observed in FTIR are 921.34 cm^{-1} -OH group/ olefin's single substitution; 991.92 cm^{-1} C-O bending; 1086.04 cm^{-1} C-O stretching; 1172.31 cm^{-1} C-H bending; 1254.66 cm^{-1} C=C (Aromatic)/ C-O stretching; 1372.30 cm^{-1} C=C stretching; 1458.57 cm^{-1} C-H bending; 1537.00 cm^{-1} N-H stretching; 1623.27 cm^{-1} C=C stretching; 1744.83 cm^{-1} C-O stretching; 1858.55 cm^{-1} CO (antisymmetric stretching vibration); 2850.67 cm^{-1} -CH stretching vibration; 2925.17 cm^{-1} CH stretching/ OH group.

X-Ray diffraction (XRD): X-Ray diffraction was used to determine the degree of crystallinity of the polymer as a function of annealing time. Fig. 2 yielded peaks at lower values, which are considered to be more accurate. Although the peaks were broadened but, the peaks at lower 2θ degrees showed the crystalline effect. These lower values of 2θ degrees were attributed to the absence of a recrystallization result of the polymer in the method.

Nuclear magnetic resonance (NMR) spectroscopy: ^{13}C NMR peaks obtained are as follows: $^4\text{CH}_2$ 43.80 ppm; $^3\text{CH}_2$

Fig. 2. XRD analysis of P(MMA-co-VP) polymer

18.40 ppm; CH_3 (methylmethacrylate) 16.20 ppm; CH (vinyl) 44.16 ppm; OCH_3 (methylmethacrylate) 51.62 ppm; CH_2 (methylmethacrylate and vinyl) 53.59 ppm. ^1H NMR peaks were as follows: CH_3 (methylmethacrylate) 0.742 to 1.454 ppm; $^4\text{CH}_2$ 2.948 ppm; $^2\text{CH}_2$ 1.812 ppm; $^3\text{CH}_2$ 1.756 ppm; OCH_3 3.557 ppm.

Application of polymer: 3.5 % NaCl solution was saturated with CO_2 at a pressure of 5 MPa for 0.5 h in 4 necks round bottom bottle that was thoroughly covered with silicone resin to avoid leakage of CO_2 gas. Corrosion tests were performed on a J55 steel of the following percentage composition (weight %): C 0.24; Si 0.22; Mn 1.1; P 0.103; S 0.004; Cr 0.5; Ni 0.28; Mo 0.021; Cu 0.019; Fe balance, which were metallographically abraded according to ASTM A262, with fine grade Emery papers from 600 to 1200 grade to get a mirror finish. The specimens were washed thoroughly with double distilled water and finally degreased with acetone and dried at room temperature.

The electrochemical studies were made using an Autolab three electrode cell assembly at room temperature. The J55 steel was the working electrode, platinum electrode was used as an auxiliary electrode and standard calomel electrode (SCE) was used as the reference electrode. Electrochemical impedance spectroscopy and Tafel Polarization measurements were performed using Autolab Potentiostat Galvanostat model GSTAT302N with EIS software FRC and GPES for EIS measurements and data fitting. Prior to the electrochemical measurement, a stabilization period was allowed to attain a stable value of E_{corr} .

The impedance parameters such as solution resistance (R_s), charge transfer resistance (R_{ct}), n , L and inhibition efficiency (η %) are listed in Table-1. The values of η % are calculated using the following equation:

$$\eta (\%) = \frac{R_{\text{ct},i} - R_{\text{ct},0}}{R_{\text{ct},i}} \times 100 \quad (15)$$

where, $R_{\text{ct},i}$ and $R_{\text{ct},0}$ are charge transfer resistances in presence and absence of P(MMA-co-VP), respectively. It is clear from Fig. 3a that by increasing the inhibitor concentration the inhibition efficiency increases. This situation was due to an increase in the surface coverage by the inhibitor, which led to an increase in the inhibition efficiency. It is apparent from Nyquist plots that the impedance response of J55 steel in inhibited 3.5 % NaCl solution saturated with CO_2 has significantly changed

TABLE-1
ELECTROCHEMICAL IMPEDANCE PARAMETERS AT AN AMPLITUDE OF 10 mV FOR J55 STEEL
IN 3.5 % NaCl SOLUTION SATURATED WITH CO₂ IN ABSENCE AND PRESENCE OF P(MMA-co-VP)

Solution	R _s (Ω cm ²)	R _{ct} (Ω cm ²)	N	Y ₀ (Ω ⁻¹ s ⁿ /cm ²)	τ (s)	C _{dl} (μF cm ²)	L (H cm ²)	Chi (Square)	η (%)	Surf. coverage (θ)
3.5 % NaCl	2.5	145	0.848	246	496.2	79.8	-	0.0006	-	-
In h 250 ppm	2.2	550	0.851	116	154.1	45.8	98	0.0008	73	0.74
In h 500 ppm	1.7	1389	0.856	78	55.7	36.7	104	0.0013	89	0.89
In h 1000 ppm	1.2	3348	0.872	43	19.6	25.1	80	0.0007	95	0.95

Fig. 3. Electrochemical study of (a) Nyquist (b) Tafel polarization plot

after the addition of P(MMA-co-VP) in solution and that the impedance of inhibited substrate increases with increasing concentration of P(MMA-co-VP). The Nyquist plots showed that on increasing P(MMA-co-VP) concentration, charge transfer resistance increases. From Table-1, it is clear that the greatest effect was observed at 1000 ppm of P(MMA-co-VP) that gives R_{ct} value of 3348 Ω cm² in 3.5 % NaCl solution saturated with CO₂, respectively.

The extrapolation of Tafel straight line allows the calculation of the corrosion current density (I_{corr}). The values of I_{corr}, the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c, b_a) and inhibition efficiency (η %) are given in Table-2. The (η %) is calculated using the following equation:

$$\eta (\%) = \left(\frac{I_{\text{corr}}^0 - i_{\text{corr}}}{I_{\text{corr}}^0} \right) \times 100 \quad (25)$$

where, I_{corr}⁰ and I_{corr}ⁱ are the corrosion current density values without and with inhibitor, respectively. From Fig. 5b, clearly the potential shift affects both the anode and the cathode. In literatures, it has been reported that (i) if the displacement in E_{corr} is > 85 mV with respect to E_{corr}, the inhibitor can be seen as a cathodic or anodic type and (ii) if displacement in E_{corr} is < 85, the inhibitor can be seen as mixed type. In the present study, shift in E_{corr} values is in the range of 58 mV, suggesting that P(MMA-co-VP) acted as mixed type of inhibitor. The value of I_{corr} decreases with increasing P(MMA-co-VP) concentration from 9.1 to 0.4 A cm⁻²; this indicated that P(MMA-co-VP) adsorbed on the metal surface and hence inhibition occurs.

The polymer proved to be an effective corrosion inhibitor for J55 steel in 3.5 % NaCl solution saturated with CO₂. The maximum inhibition efficiency obtained using electrochemical impedance spectroscopy was 95 % at 1000 ppm of polymer. It was 96 % inhibition efficiency in case of Tafel Polarization curves at 1000 ppm. Based on these facts one can conclude that this polymer can be used as a corrosion inhibitor in the oil and petroleum industries.

Conclusion

2-(Methoxycarbonyl)-1-propene (MMA) monomer and N-vinyl-2-pyrrolidone (NVP) monomer were used in presence of potassium peroxodisulfate to synthesize poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone) polymer [P(MMA-co-VP)]. Characterization of P(MMA-co-VP) was performed using FTIR, XRD and NMR. P(MMA-co-VP) is a good inhibitor for J55 steel corrosion in 3.5 % NaCl solution saturated with CO₂.

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TABLE-2
POLARIZATION PARAMETERS FOR J55 STEEL IN 3.5 % NaCl SOLUTION SATURATED WITH CO₂ AT A SCAN
RATE OF 1 mV/s IN THE ABSENCE AND PRESENCE OF DIFFERENT CONCENTRATIONS OF P(MMA-co-VP)

Conc. (ppm)	Tafel data					
	E _{corr} (V vs. SCE)	I _{corr} (A cm ⁻²)	B _a (V d ⁻¹)	-b _c (V d ⁻¹)	H (%)	Surface coverage (θ)
3.5 % NaCl	-0.596	9.1	0.06	1.03	-	-
P(MMA-co-VP) 250 ppm	-0.632	1.8	0.08	0.79	79	0.79
P(MMA-co-VP) 500 ppm	-0.650	1.1	0.06	0.44	86	0.86
P(MMA-co-VP) 1000 ppm	-0.654	0.4	0.04	0.23	96	0.96

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