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The Inhibition of Corrosion of Mild Steel in 0.5 M Sulfuric acid Solution in the presence of Telechelic Bromine Terminated Poly (Ethylene Oxide)

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ABSTRACT

The telechelic bromine terminated poly (ethylene oxide) (Br-PEO-Br) was synthesized from poly (ethylene oxide) polymers and characterized by nuclear magnetic resonance spectroscopy, IR spectroscopy as well as GPC. The effect of Br-PEO-Br on the mild steel corrosion in 0.5 M sulfuric acid solution has been investigated at various inhibitor concentrations by weight loss method. The investigated results showed that the corrosion rate decreased significantly with an increase in the concentration of inhibitors.
Keywords: poly(ethylene oxide), anionic polymerization, Weight loss method.

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INTRODUCTION

It has been observed that a very small amount of certain water-soluble polymers, known to be effective as floculating agents, are extremely effective in inhibiting the corrosion of ferrous materials in contact with water. It has been found that such polymers, in an amount ranging from 5 x 10^{-6} to 2 wt% remove the products of corrosion formed prior to treatment and effectively prevent further corrosion.[1] Mild steel is an alloy, which is one of the commercial forms of iron and is very prone to corrosion particularly in acidic medium. Acidic solutions are extensively used for different purposes in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil well acidizing, etc. One way to protect the metal against corrosion is to add certain organic molecules, which adsorb on the surface and form a protective layer.[2-5] The unique advantage of the possibility of adding inhibitors is that this can be done without disruption of the industrial process. Specific chemical compounds are often used as inhibitors in these processes mainly to control the metal dissolution reaction and thereby increasing the service life of steel materials. Organic corrosion inhibitors are useful when their addition in small amounts prevents corrosion. At higher concentrations of organic compounds added additional testing for environmental impact is required. Compounds containing nitrogen, sulphur and oxygen are being used as inhibitors.[6] Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues. Therefore, it is expected that the polymers will be better corrosion inhibitors.[7-17] Larger corrosion inhibition efficiencies that are observed using conducting polymers are not only due to the presence of π-electrons but also can be attributed to the larger molecular size which ensures greater coverage of the metallic surface.[18] Khairo and El-Sayed[19,20] reported effect of some water-soluble polymers on corrosion of iron and cadmium. They found that the hydroxyl group of polyvinyl alcohol and polyethylene glycol could be bridge between the polymer and the surface of electrode and resulted in an inhibiting effect in the HCl solution.

However, by increasing the hydrocarbon chain length, solubility of the polymer decreases. Thus, the presence of hydrophilic functional groups which increase the solubility is required. The PEO was used as hydrophilic block in many polymers.[21-27] The objective of the present work is to synthesize telechelic-bromine terminated PEO (Br-PEO-Br) and to study its inhibition action on the mild steel corrosion in H_2SO_4 solution at 298 K temperature. The work is carried out to establish the effective concentration for good inhibition action for mild steel corrosion in H_2SO_4 solution.

MATERIALS AND METHODS

Poly(ethylene glycol) (PEG, Aldrich, USA) of molecular weight 20000 were dried by azeotropic distillation with toluene prior to use. Phosphorous tri-bromide (Spectrochem, India) was used as received.

The chemical compositions weight% of mild steel was as follows:

C	Si	S	P	Mn	Fe
0.15	0.31	0.025	0.025	1.02	Balance

All solutions were prepared from doubly distilled water and AR grade H_2SO_4 was used. The concentration range of inhibitor employed was 1600ppm, 1200ppm, 800ppm and 400ppm in 0.5 M H_2SO_4. Metal coupons of 1 cm × 1 cm × 1 cm were cleaned, washed with acetone, dried in a desiccator and weighed. The weight losses of the coupons were calculated in grams as the difference in weight of the coupons before and after the exposure which denotes as average corrosion rate.

EXPERIMENTAL

Synthesis of bromine terminated poly(ethylene oxide) (Br-PEO-Br)

Bromine terminated poly(ethylene oxide) (Br-PEO-Br) was prepared as shown in scheme 1 as reported in the literature.[28] The procedure to prepare Br-PEO-Br from PEG of molecular weight 20000 (PEG_{20k}) is presented here as reference procedure. Dried PEG_{20k} (2.22 mmol) was taken in a 250 mL two necked round bottom flask, which was kept under argon atmosphere after applying vacuum for two hours. Phosphorous tri-bromide (PBr_3) (0.2 mL, 2.18 mmol) was added over a period of 30 min and the mixture was stirred at 110 °C for 5 h. The unreacted PBr_3 was removed by applying vacuum of 10^{-6} torr at 60 °C and after cooling, chloroform (100 mL) was added to the reaction mixture, which was then filtered. Chloroform was evaporated in vacuum to get Br-PEO-Br as white waxy material.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets using Nicolet Impact 400 FTIR spectrophotometer. Fourier-transform nuclear magnetic resonance (FT-NMR) spectra were recorded using a Bruker DPX-300 NMR instrument using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane as an internal standard. Number average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights and molecular weight distribution (MWD) were determined by using a gel permeation chromatography (GPC; Waters, USA) instrument equipped with a 2414 differential refractometer (RI Detector) and three µ-styragel columns (10^5, 10^4, 10^3 Å) in series. HPLC grade THF was used as an eluent at a flow rate of 1.0 mL min^{-1} and molecular weight calibrations were carried out using polystyrene standards. Differential scanning calorimetric (DSC) studies were carried out using a DSC Q200 instrument (TA Instruments, USA) at a heating rate of 10 ^{o}C/min. under nitrogen atmosphere. All the glass transition temperatures (T_g) considered in this investigation are the middle points between the onset and offset points.

Weight loss method

In the present study, solutions of various concentrations of inhibitor were prepared in 0.5 M H_2SO_4 namely 1600 ppm, 1200 ppm, 800 ppm and 400 ppm which were then used for the weight loss studies. The weight losses of the coupons were calculated in grams as the difference in weight of the coupons before and after the exposure which denotes as average corrosion rate.

The inhibition efficiency was calculated by using the formula:

$$IE\% = (W_o-W_i / W_o) \times 100$$

Where W_o is the weight loss in the corrosive medium and W_i is the weight loss in the presence inhibitor into corrosive solution.

$$\text{RATE CONSTANT } k = 2.303/6 \log I_w/F_w$$

Where I_w= Weight of the coupon before dipping, F_w= Weight of the coupon after weight loss

$$\text{HALF LIFE } t_{1/2} = 0.693/k$$

Weight loss parameters which were calculated by using above formulae at 298 K are given in table 2. Table 3 shows the weight loss parameters for mild steel in *0.5M H_2SO_4* in presence of various concentration of Telechelic Bromine Terminated Poly(ethylene oxide) at 298 K. The corrosion rate constant values are lower in the presence of the inhibitor than in 0.5 M H_2SO_4 and these values decrease with increase in the inhibitor concentrations. The inhibition efficiency increases with the increase in concentration of the inhibitor. This shows that the inhibition is due to the adsorption of the additive on the mild steel surface.

Table 2: Weight loss parameters for mild steel in *0.5M H_2SO_4* at 298 K

Temp/K	Conc./mol	Weight Loss/g	I.E./%	Initial weight I_w/g	Final weight F_w/g	$k \times 10^4 \text{ hr}^{-1}$	$t_{1/2} \times 10^4 \text{ hr}$
298	0	0.0788		6.4629	6.3841	20.37	0.0340

Table 3: Weight loss parameters for mild steel in *0.5M H_2SO_4* in presence of various concentrations of Telechelic Bromine Terminated Poly(ethylene oxide) at 298 k

| Temp/K	Conc./ppm	Weight Loss/g	I.E./%	initial weight I_w/g	final weight F_w/g	$k \times 10^4 \text{ hr}^{-1}$	$t_{1/2} \times 10^4 \text{ hr}$
298	1600	0.0012	98.47	6.2152	6.2140	0.316	2.1930
	1200	0.0039	96.02	5.7845	5.7806	0.999	0.6936
	800	0.0053	93.27	6.7825	6.7772	1.666	0.5940
	400	0.0069	91.24	7.4518	7.4449	1.499	0.4623

RESULTS AND DISCUSSION

Telechelic Br-PEO-Br was prepared by reacting PEG (Mn 20000) with PBr$_3$ at 140 °C as reported by Lawrence et. al. The substitution of hydroxyl group of PEG by bromine from PBr$_3$, results the formation of Br-PEO-Br. To avoid incomplete substitution, little excess of PBr$_3$ was used, which was removed by applying vacuum of 10^{-6} torr at 60 °C.

The synthesis of Br-PEO-Br was confirmed by IR and NMR. The complete substitution of hydroxyl group by bromine can be confirmed by the absence of -OH signal in the ^{1}H NMR spectrum[29,30] of **Br-PEO-Br,** as depicted in Figure 1(b). The -CH$_2$ protons of -CH$_2$-CH$_2$-O- repeating units present in **Br-PEO-Br** resonate at 3.65 ppm, and -CH$_2$-Br and -OCH$_2$ protons of -OCH$_2$-CH$_2$-Br group resonate at 3.4 ppm and 3.7 ppm respectively.

Though ^{1}H NMR in CDCl$_3$ confirms complete substitution of OH by Br, the molecular weight determination of PEG using the ^{1}H NMR in CDCl$_3$ was not accurate as reported by Jankova.[31] To know the molecular weight of PEG through NMR, similar to Jonkova, ^{1}H NMR spectrum of PEG in DMSO d$_6$ was used.[32] The molecular weight was determined by comparing the integration values of –OH and –CH$_2$-CH$_2$-O protons of PEG. The complete conversion of –OH to Br was also confirmed by FT-IR spectroscopy[33] using the peak at 3600-3400 cm^{-1} for –OH in PEG which is missing in **Br-PEO-Br** as shown in figure 2(b). In figure 2 (b) the absorption band at 1110 cm^{-1} is due to the stretching vibration of -C-O-C- of -CH$_2$-CH$_2$-O repeating units. GPC analysis of **Br-PEO-Br** and PEG was carried out and the results are presented in Table 1. GPC analysis shows that there is no molecular weight reduction during the synthesis of **Br-PEO-Br** and absence of any side reaction during the synthesis of **Br-PEO-Br**.

Table 1: Characterization of PEG and Br-PEO-Br

Polymer	$\overline{M}_{n,th} \times 10^{-3}$	$\overline{M}_{nNMR} \times 10^{-3}$	GPC results		
			$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w / \overline{M}_n$
PEG	20.00	20.86	21.34	23.26	1.09
Br-PEO-Br	21.12	21.36	21.46	23.61	1.10

Synthesis of Br-PEO-Br from PEG
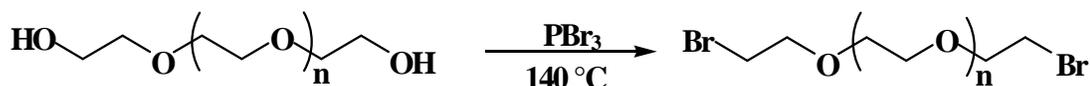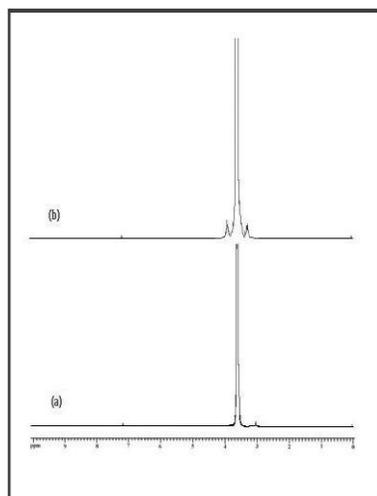
FIGURE 1: ^{1}H NMR spectra of
(a) PEG$_{20000}$ (b) Br-PEO$_{20000}$-Br
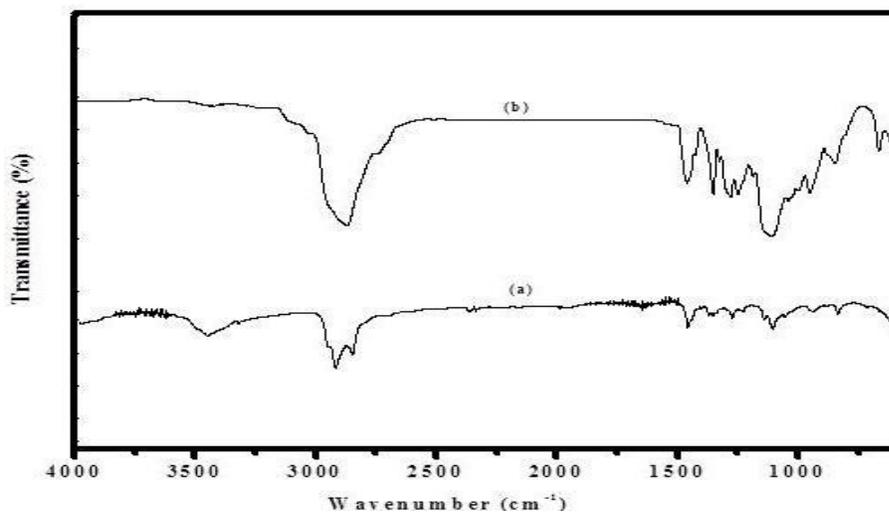
Figure 2: FT-IR spectra of (a) PEG$_{20000}$, (b) Br-PEO$_{20000}$-Br

For the thermal study DSC was carried out, here all the glass transition temperatures (T_g) in this investigation have been considered as the middle point between the onset and offset points. Figure 3 shows the DSC curve for PEO as well as Br-PEO-Br. The T_g of the PEO was observed at -67 °C and T_c, T_m were observed at -25 °C and 28 °C respectively same type of trend was observe for PEO segment present in Br-PEO-Br, -68 °C and T_c, T_m were observed at -27 °C and 28 °C respectively. The presence of similar T_g shows that there is no phase separation as well as presence of similar T_c shows that there is no effect on the crystallinity on PEO block due to addition of Br.

In the corrosion inhibitor study the organic moiety having heterocyclic atom like nitrogen, sulphur and oxygen are being used.[6] As compared to simple organic moiety a polymer shows better results due to its multiple adsorption sites. However, by increasing the hydrocarbon chain length, solubility of the polymer decreases. Thus, the presence of hydrophilic functional groups which increase the solubility is required. The PEO was used as hydrophilic block in many polymers.[31,34-41] To study the mild steel corrosion inhibitor telechelic Br-PEO-Br was synthesized as reported in the literature by using PEO having M_n 20000. Then Br-PEO-Br was used as inhibitor for mild steel corrosion in acidic medium.
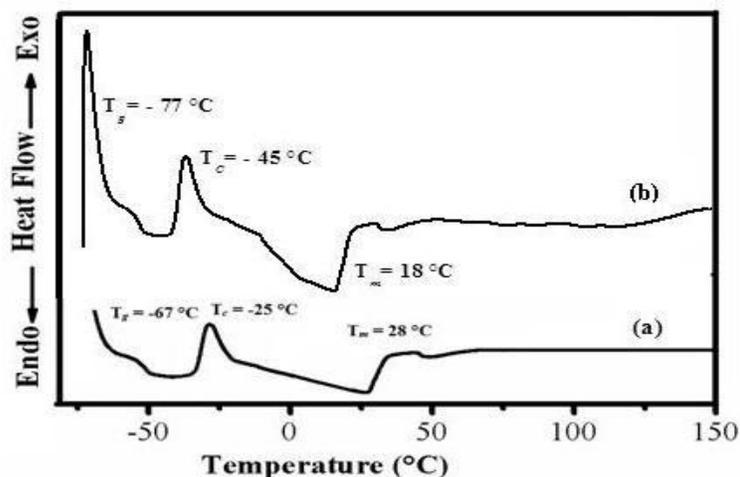

Figure 3: Dsc Curves OF (A) PEG$_{20000}$ and (b) Br-PEO$_{20000}$-Br

CONCLUSIONS

Br-PEO-Br is found to be an excellent inhibitor for mild steel corrosion in H_2SO_4. All the additives are effective corrosion inhibitors for mild steel in corrosive solution. The inhibition efficiency increases as concentration of inhibitor increases. The corrosion rate constant is maximum in corrosive solution as compared to those of the inhibitor solutions. Half life increases with concentration.

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