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## Synthesis, Characterization of Telechelic Bromine Terminated Poly (Ethylene Oxide) and Its Inhibition Effect on Mild Steel Corrosion in Sulfuric Acid.

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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 1M sulfuric acid solution has been investigated at various inhibitor concentrations and temperatures by Potentiodynamic Polarization Study. The investigated results showed that the corrosion rate decreased significantly with an increase in the concentration of inhibitors. The shape of polarization profiles of the polymer at various concentrations indicated their mixed-type nature of inhibition.

**Keywords:** poly (ethylene oxide), PS-*b*-PEO-*b*-PS block copolymer , anionic polymerization, potentiodynamic polarization studies.

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## INTRODUCTION

Polymers have an edge over simple organic compounds as corrosion inhibitor for different media. 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 [1-4]. 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 [5]. 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 [6-16]. 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 [17-23]. 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 a temperature range of 298 K-328 K. 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 9000 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:

<i>C</i>	<i>Si</i>	<i>S</i>	<i>P</i>	<i>Mn</i>	<i>Fe</i>
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 1 M  $H_2SO_4$ .

The working electrode (WE) for the potentiodynamic studies was cut from mild steel rod and was soldered on one end with an insulated copper wire and it was then embedded in chemical epoxy resin (ARALDITE) leaving the exposed surface area of  $1\text{ cm}^2$  for the studies. The counter electrode was platinum and reference was saturated calomel electrode (SCE) coupled to luggin capillary. The potential of the metal electrode versus reference

electrode was measured with the help of Galvanostat. A steady state potential was achieved in 4-5 hours. Potentiodynamic polarization measurements were performed using electrochemical analyzer CHI 6021B under aerated conditions. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of  $0.001\text{Vs}^{-1}$  in the potential range from -1.2V to 0.2V relative to the corrosion potential ( $E_{\text{corr}}$ ).

## 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.<sup>24</sup> The procedure to prepare Br-PEO-Br from PEG of molecular weight 9000 ( $\text{PEG}_{9k}$ ) is presented here as reference procedure. Dried  $\text{PEG}_{9k}$  (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 ( $\text{PBr}_3$ ) (0.2 mL, 2.18 mmol) was added over a period of 30 min and the mixture was stirred at  $110\text{ }^\circ\text{C}$  for 5 h. The unreacted  $\text{PBr}_3$  was removed by applying vacuum of  $10^{-6}$  torr at  $60\text{ }^\circ\text{C}$  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 ( $\text{CDCl}_3$ ) 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  $\mu$ -styragel columns ( $10^5$ ,  $10^4$ ,  $10^3\text{ \AA}$ ) in series. HPLC grade THF was used as an eluent at a flow rate of  $1.0\text{ mL min}^{-1}$  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  $10\text{ }^\circ\text{C/min}$ . under nitrogen atmosphere. All the glass transition temperatures ( $T_g$ ) considered in this investigation are the middle points between the onset and offset points.

### Potentiodynamic Polarization Studies

In the present study, 1 M  $\text{H}_2\text{SO}_4$  was used for the polarization of mild steel at four temperatures namely 298K, 308K, 318K and 328K. Solutions of various concentrations of inhibitor were prepared in 1M  $\text{H}_2\text{SO}_4$  namely 1600ppm, 1200ppm, 800 ppm and 400 ppm which were then used for the polarization studies. Potential values were plotted against the logarithm of current densities and various parameters were calculated which are given in table 2. Figure 4 gives the cathodic and anodic polarization curves for these solutions at 298K. An increase in corrosion current values for 1 M  $\text{H}_2\text{SO}_4$  is observed with the increase in temperature thereby indicating that the extent of corrosion increases with the increase in

temperature.  $E_{\text{corr}}$  almost remains constant with increase in temperature. Anodic and cathodic Tafel slopes remain almost constant with temperature and  $b_c \approx b_a$ .

The inhibition efficiency was calculated using the following expression:

$$I\% = \left( \frac{i_o - i}{i_o} \right) \times 100$$

where,  $i_o$  is the corrosion current in the uninhibited solution and  $i$  is the corrosion current in the inhibited solution.

The corrosion current values are much lower in the presence of the inhibitor than in pure acid. 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. The values of  $b_c$  and  $b_a$  show irregular trend indicating the involvement of other species/anions present in the solution in the adsorption process.  $E_{\text{corr}}$  remains constant indicating that polyethylene oxide is a mixed type of inhibitor i.e. blocks both cathodic and anodic reactions to an equal extent.

## RESULTS AND DISCUSSION

Telechelic Br-PEO-Br was prepared by reacting PEG (Mn 9000) with  $\text{PBr}_3$  at 140 °C as reported by Lawrence et. al. The substitution of hydroxyl group of PEG by bromine from  $\text{PBr}_3$ , results the formation of Br-PEO-Br. To avoid incomplete substitution, little excess of  $\text{PBr}_3$  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  $^1\text{H}$  NMR spectrum [25, 26] of **Br-PEO-Br**, as depicted in Figure 1(b). The  $-\text{CH}_2$  protons of  $-\text{CH}_2-\text{CH}_2-\text{O}-$  repeating units present in **Br-PEO-Br** resonate at 3.65 ppm, and  $-\text{CH}_2-\text{Br}$  and  $-\text{OCH}_2$  protons of  $-\text{OCH}_2-\text{CH}_2-\text{Br}$  group resonate at 3.4 ppm and 3.7 ppm respectively. Though  $^1\text{H}$  NMR in  $\text{CDCl}_3$  confirms complete substitution of OH by Br, the molecular weight determination of PEG using the  $^1\text{H}$  NMR in  $\text{CDCl}_3$  was not accurate as reported by Jankova.<sup>27</sup> To know the molecular weight of PEG through NMR, similar to Jonkova,  $^1\text{H}$  NMR spectrum of PEG in  $\text{DMSO } d_6$  was used [28]. The molecular weight was determined by comparing the integration values of  $-\text{OH}$  and  $-\text{CH}_2-\text{CH}_2-\text{O}$  protons of PEG. The complete conversion of  $-\text{OH}$  to Br was also confirmed by FT-IR spectroscopy [29] using the peak at  $3600-3400 \text{ cm}^{-1}$  for  $-\text{OH}$  in PEG which is missing in **Br-PEO-Br** as shown in figure 2(b). In figure 2 (b) the absorption band at  $1110 \text{ cm}^{-1}$  is due to the stretching vibration of  $-\text{C}-\text{O}-\text{C}-$  of  $-\text{CH}_2-\text{CH}_2-\text{O}$  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**.

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  $-27\text{ }^{\circ}\text{C}$  and  $28\text{ }^{\circ}\text{C}$  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 [5]. 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 [27, 30-37]. To study the mild steel corrosion inhibitor telechelic Br-PEO-Br was synthesized as reported in the literature by using PEO having  $M_n$  9000. Then Br-PEO-Br was used to study as mild steel corrosion inhibitor.

## CONCLUSIONS

Br-PEO-Br is found to be an excellent inhibitor for mild steel corrosion in  $\text{H}_2\text{SO}_4$ . The inhibition efficiencies increase with increase in concentration but decrease with increase in temperature for Br-PEO-Br.  $E_{\text{corr}}$  remains constant indicating that Br-PEO-Br is mixed type of inhibitor in  $1\text{ M H}_2\text{SO}_4$  i.e., blocking both cathodic and anodic reactions to an equal extent. Adsorption of Br-PEO-Br may have the involvement of other species/anions present in the solution as indicated by the irregular trends of  $b_c$  and  $b_a$ .

**Table 1** Characterization of PEG and Br-PEO-Br.

Polymer	$\bar{M}_{n,th} \times 10^{-3}$	$\bar{M}_{n,NMR} \times 10^{-3}$	GPC results		
			$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w / \bar{M}_n$
PEG	9.00	8.590	8.685	10.335	1.19
Br-PEO-Br	9.125	8.763	8.820	10.054	1.14

**Table 2: Corrosion Parameters of mild steel in  $1\text{ M H}_2\text{SO}_4$  in the presence of Br-PEO-Br**

Temp. (K)	Conc. (ppm)	$i_{\text{corr}}$ (mA/cm <sup>2</sup> )	$-E_{\text{corr}}$ vs SCE (mV)	$b_a$ (mV/dec.)	$b_c$ (mV/dec.)	IE%
298	Blank	9.679	475	72.49	60.89	-
	400	0.101	458	73.12	81.50	98.95
	800	0.060	480	72.89	87.93	99.38
	1200	0.038	460	79.61	88.94	99.60
	1600	0.014	478	93.18	90.47	99.85
308	Blank	17.12	475	59.24	52.82	-
	400	0.428	466	60.25	71.82	97.50
	800	0.813	498	28.35	75.73	95.25
	1200	0.229	491	68.15	78.68	98.66
	1600	0.187	489	57.20	79.31	98.90
318	Blank	19.54	481	50.91	47.85	-
	400	1.799	461	59.76	68.26	90.79
	800	1.289	499	28.27	69.96	93.40
	1200	0.498	512	71.96	66.83	97.45
	1600	0.307	518	45.87	84.19	98.42
328	Blank	22.09	490	58.00	47.05	-
	400	6.547	478	89.43	53.97	70.36
	800	6.117	468	90.23	56.90	72.30
	1200	5.132	469	98.97	55.96	76.68
	1600	3.685	459	112.09	59.24	83.32

## Synthesis of Br-PEO-Br from PEG

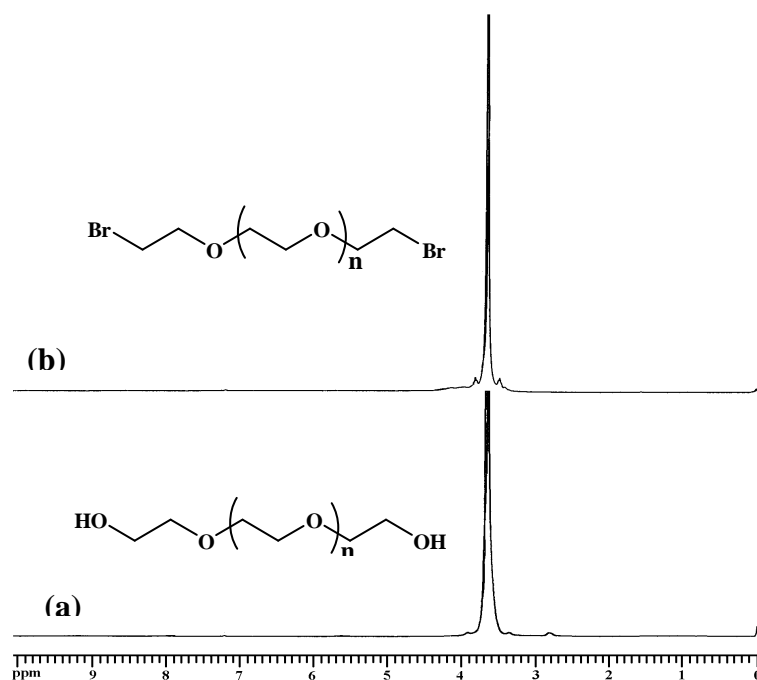
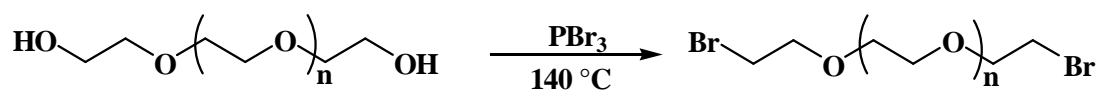
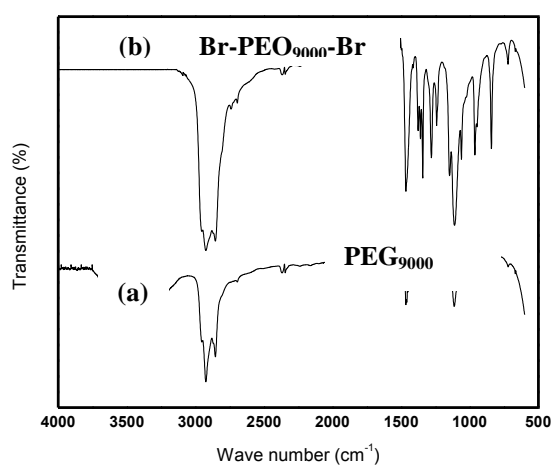

 FIGURE 1: <sup>1</sup>H NMR spectra of (a) PEG (b) Br-PEO-Br


FIGURE 2: FT-IR spectra of (a) PEG and (b) Br-PEO-Br

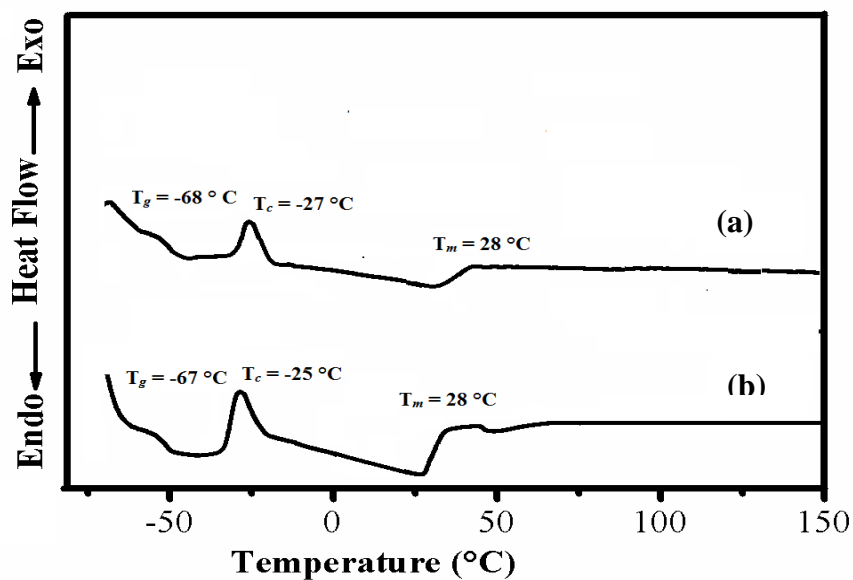


FIGURE 3: DSC curves of (a) PEG and (b) Br-PEO-Br

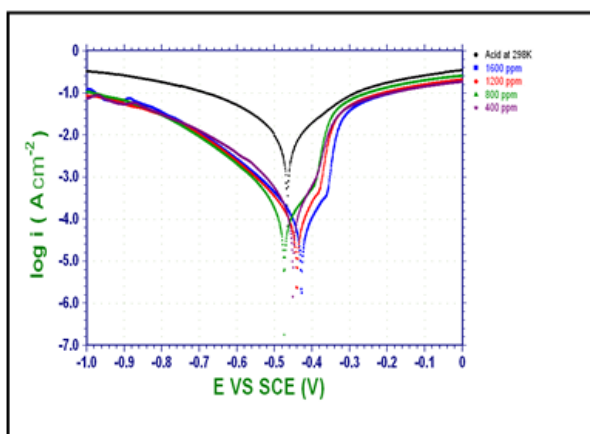


Figure 4: Tafel polarization curves of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> and in the presence of different concentrations of Br-PEO-Br at 298K

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