

Synthesis, Characterization of Water Soluble PS-*b*-PEO-*b*-PS Tri-block Copolymers and its Corrosion Inhibition Behaviour on Mild Steel in Acidic Solution

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Abstract- The high molecular weight poly (ethylene oxide) was used to synthesize telechelic bromine terminated poly (ethylene oxide) polymers. The low molecular weight polystyrene anion was generated by living anionic polymerization by controlling monomer/initiator ratio. The living polystyrene anion was reacted with telechelic bromine terminated poly (ethylene oxide) polymers to obtain water soluble polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene tri-block copolymers. The effect of polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene (PS-*b*-PEO-*b*-PS) block copolymer 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 increase in the concentration of inhibitors. The shape of polarization profiles of the polymer at various concentrations indicated their mixed-type nature of inhibition.

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

I. INTRODUCTION

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. Iron and its alloys could corrode during these acidic applications particularly with the use of hydrochloric acid and sulphuric acid, which effects in dreadful waste of both resources and money. 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 The most efficient inhibitors are organic compounds having pi bonds in their structures. 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.^{10,17-22} Depending on the ratio of hydrophilic and hydrophilic block solution behaviour of the block copolymers may change. For instance if the block copolymers consist of bulkier hydrophilic block and smaller hydrophobic block then it can directly dissolve in water to studied the solution behaviour.²³ Since the concept was established by Szwarc in 1956.²⁴ The living anionic polymerization method has become a very useful technique to synthesize well-defined polymeric materials with controlled molecular weight and narrow polydispersity index.²⁵ This technique is very helpful to design the degree of polymerization in requisite block by simply controlling the monomer/initiator ratio for the synthesis of block copolymers by sequential living anionic polymerization.²⁶⁻²⁸ But due to due to the low nucleophilic reactivity of poly(ethylene oxide) oxyanion which cannot initiate the polymerization of styrene,^{28,29} it was difficult to synthesize amphiphilic polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene (PS-*b*-PEO-*b*-PS) triblock copolymers through living anionic polymerization.²⁸ The synthesis of PS-*b*-PEO-*b*-PS tri-block copolymers was carried out by our research group by using telechelic bromine-terminated PEO oligomer (Br-PEO-Br).³⁰ However, the low contents of PEO block results poor water solubility of. In this report, telechelic bromine-terminated PEO polymers was used to synthesize water soluble PS-*b*-PEO-*b*-PS tri-block copolymers through living anionic polymerization by controlling monomer/initiator ratio. The water soluble PS-*b*-PEO-*b*-PS tri-block copolymers were used to study its inhibition action on the mild steel corrosion in H₂SO₄ 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 H₂SO₄ solution.

II. MATERIALS AND METHODS

Poly(ethylene glycol) (PEG, Aldrich, USA) of molecular weight 20000, were dried by azeotropic distillation with toluene prior to use. A trace of residual toluene was removed under vacuum just prior to use. Styrene (Aldrich, USA) was washed with 10 % (w/v) of aqueous NaOH solution followed by washing with distilled water to remove the inhibitor and stirred over CaH₂ overnight. Then, the styrene was distilled under reduce pressure and the middle portion was stored under argon atmosphere until use. Tetrahydrofuran (THF, Spectrochem, India) was first distilled and then the middle portion was refluxed over Na-benzophenone complex until the purple colour persists. Phosphorous tribromide (Spectrochem, India) and *sec*-butyllithium (*sec*-BuLi, Aldrich, USA) were 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 H₂SO₄ was used. The concentration range of inhibitor employed was 1600ppm, 1200ppm, 800ppm and 400ppm in 1 M H₂SO₄.

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 cm² 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 0.001Vs⁻¹ in the potential range from -1.2V to 0.2V relative to the corrosion potential (E_{corr}).

III. EXPERIMENTAL

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

Bromine terminated poly(ethylene oxide) (Br-PEO-Br) was prepared as reported in the literature.³¹ The procedure to prepare Br-PEO-Br from PEG of molecular weight 20000 (PEG) is presented here as reference procedure. Dried PEG (25 g, 1.25 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 tribromide (PBr₃) (0.1 mL, 1.25 mmol) was added over a period of 30 min and the mixture was stirred at 110 °C for 5 h. The unreacted PBr₃ 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.

Synthesis of PS-*b*-PEO-*b*-PS tri-block copolymers using Br-PEO-Br

To synthesize PS-*b*-PEO-*b*-PS tri-block copolymers, first, Br-PEO-Br was prepared as reported in the literature.³¹ Then, in a reaction flask, living polystyryl anion (PSLi) was generated as reported in the literature.³² In a separate reaction flask, fitted with the 3-way stopcock which consists of argon containing balloon, required quantity of Br-PEO-Br was taken and vacuum of 10⁻⁶ mm/Hg was applied at 80 °C for 6 h to remove any traces of moisture. Then, a known quantity of freshly freeze-pump-thawed THF was vacuum-transferred into the flask containing Br-PEO-Br. The resulting THF solution of Br-PEO-Br (20 % w/v) was transferred into the living PSLi (polystyrene anion: Br-PEO-Br = 2.4:1 molar ratio) under argon atmosphere at -78 °C using flamed dried cannula. Within few seconds, the persisting orange red colour of living PSLi was disappeared and turns into colourless solution. The solution was stirred for another 3 h at -78 °C and then warmed to room temperature. At the end, the reaction mixture was poured into ten fold excess of hexane and the resulting white precipitate was filtered, dried, washed with cyclohexane to remove homo polystyrene.

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 (CDCl₃) as the solvent and tetramethylsilane as an internal standard. Number average (\bar{M}_n) and weight-average (\bar{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 (10⁵, 10⁴, 10³ 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 °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 H₂SO₄ 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 H₂SO₄ 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 3. Figure 4 gives the cathodic and anodic polarization curves for these solutions at 298K. An increase in corrosion current values for 1 M H₂SO₄ is observed with the increase in temperature thereby indicating that the extent of corrosion increases with the increase in temperature. E_{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_{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.

IV. RESULTS AND DISCUSSION

Living anionic polymerization is playing a major role for the synthesis of well-defined block copolymers by simply controlling the initiator/monomer ratio. Depending on the nature and ratio of other block, the block copolymers having hydrophilic block like PEO shows solubility in water. The PS-*b*-PEO-*b*-PS tri-block copolymers may act as efficient mild steel corrosion inhibitor due to presence of pi bond to its structure as well as hetero elements like oxygen. It is an amphiphilic block copolymers. To increase the solubility in water the telechelic bromine-terminated PEO polymer was used to synthesize PS-*b*-PEO-*b*-PS tri-block copolymers through living anionic polymerization. The degree of polymerization of polystyrene (PS) was controlled by styrene/*sec*-BuLi ratio.

Synthesis of PS-*b*-PEO-*b*-PS tri-block copolymers from Br-PEO-Br

The well-known reaction between alkyl bromide and PSLi was effectively used³³⁻³⁸ by reacting bromide terminated PEO with PSLi to obtain PS-*b*-PEO-*b*-PS tri-block as shown in Scheme 2. For the synthesis of PS-*b*-PEO-*b*-PS tri-block copolymers, bromine terminated PEO, **Br-PEO-Br**, was prepared from PEG (M_n , 20000) using the known procedure.³¹ The complete substitution of hydroxyl group by bromine can be confirmed by the absence of OH signal in the ¹H NMR spectrum^{30,39} of **Br-PEO-Br**, as depicted in Figure 1(b). The -CH₂ protons of -CH₂-CH₂-O- repeating units present in **Br-PEO-Br** resonate at 3.65 ppm, and -CH₂-Br and -OCH₂ protons of -OCH₂-CH₂-Br group resonate at 3.4 ppm and 3.7 ppm respectively. Though ¹H NMR in CDCl₃ confirms complete substitution of OH by Br, the molecular weight determination of PEG using the ¹H NMR in CDCl₃ was not accurate as reported by Jankova.²⁸ To know the molecular weight of PEG through NMR, similar to Jonkova,⁴⁰ ¹H NMR spectrum of PEG in DMSO d₆ was used.⁴⁰ The molecular weight was determined by

comparing the integration values of -OH and -CH₂-CH₂-O protons of PEG. The complete conversion of -OH to Br was also confirmed by FT-IR spectroscopy⁴¹ 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 -CH₂-CH₂-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**.

After successful synthesis of **Br-PEO-Br**, as shown in Scheme 1, it was reacted with PSLi to get PS-*b*-PEO-*b*-PS tri-block copolymers and the results are presented in Table 2. For the polymerization, the molar concentration of **Br-PEO-Br** was calculated by using the molecular weight of **Br-PEO-Br** obtained through ¹H NMR in DMSO d₆. The stoichiometry of 1: PSLi is very crucial factor to obtain PS-*b*-PEO-*b*-PS tri-block copolymer otherwise it may give mixture of di-block and tri-block copolymers. To ensure the formation of tri-block copolymers, the mole ratio between **Br-PEO-Br** and living PSLi was maintained at 1: 2.4 and the excess polystyrene was removed by washing the product with cyclohexane. To confirm the formation of the tri-block copolymers, GPC was carried out and the results are presented in Table 2. The theoretical molecular weight matches with the experimental molecular weight and MWD of all the tri-block copolymers are narrow. These results show that the formation of tri-block copolymers is through living polymerization.

Spectral studies of PS-*b*-PEO-*b*-PS tri-block copolymers

After successful synthesis, the structure of the PS-*b*-PEO-*b*-PS tri-block copolymers was confirmed using ¹H NMR spectroscopy and ¹H NMR spectrum of P2 shown in Figure 1(c). The -CH₂ protons of CH₂-CH₂-O repeating units of PEO appear at 3.65 ppm, but the peaks at 3.4 ppm and 3.7 ppm are absent due to the removal of Br during the synthesis of tri-block copolymers. The terminal -CH₃ protons of *sec*-BuLi appear at 0.56 ppm. The -CH and -CH₂ protons of polystyrene block generally appear at 1.90 ppm and 1.42 ppm respectively, but in the present case, they merge with the -CH₂ and -CH protons of

sec-BuLi at 1.22-1.92 ppm. The \overline{M}_n values of the tri-block copolymers were calculated also using ¹H NMR spectra by comparing the integration values of -OCH₂-CH₂ protons of PEO and phenyl protons present in the polystyrene block of the tri-

block copolymers. It is interesting to note that the \overline{M}_n values calculated through ¹H NMR spectra match with the \overline{M}_n determined through GPC as summarized in Table 2. These results, again, confirm the formation of PS-*b*-PEO-*b*-PS tri-block copolymers. The PS-*b*-PEO-*b*-PS tri-block copolymer, P2. To confirm the structure further, FT-IR spectra of PS-*b*-PEO-*b*-PS tri-block copolymer were obtained. **Figure 2 (c)** depicts the FT-IR spectrum of PS-*b*-PEO-*b*-PS triblock copolymer P2 (c.f **Table 2**). In the FT-IR spectrum of PS-*b*-PEO-*b*-PS triblock copolymer, -C-H asymmetric and symmetric stretching vibrations of -CH₂ groups present in PSt and PEO are observed at 2853-3058 cm⁻¹.

The absorption band at 1110 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 present in PEO block. In addition to these absorption peaks, new peaks were observed at $3060-3095\text{ cm}^{-1}$, 1601 cm^{-1} , $1454-1492\text{ cm}^{-1}$, and $757-698\text{ cm}^{-1}$ which are due to the $-\text{C}=\text{C}-\text{H}$ stretching of phenyl ring, $-\text{C}=\text{C}-$ stretching of phenyl ring, benzene ring stretching and $-\text{C}=\text{C}-\text{H}$ out plane bending of phenyl ring of PSt blocks respectively. These new peaks were not present in the FT-IR spectrum of Br-PEO-Br. The presence of all peaks which corresponds to PEO block and new peaks of PSt blocks further support the formation of PS-*b*-PEO-*b*-PS triblock copolymer.

Thermal studies of PS-*b*-PEO-*b*-PS tri-block copolymers

PS-*b*-PEO-*b*-PS triblock (P2) copolymer and Br-PEO-Br were further characterized by DSC and the results are presented in **Figure 3**. PEO segment present in Br-PEO-Br shows T_g at $-77\text{ }^\circ\text{C}$ and melting point (T_m) and crystallization temperature (T_c) of Br-PEO-Br were observed at $18\text{ }^\circ\text{C}$ and $-45\text{ }^\circ\text{C}$ respectively. The glass transition temperatures of the PEO and the PS segments present in the PS-*b*-PEO-*b*-PS tri-block copolymers were observed at $-70\text{ }^\circ\text{C}$ and $72\text{ }^\circ\text{C}$ respectively. The presence of two

the solution as indicated by the irregular trends of b_c and b_a .

glass transition temperatures in the PS-*b*-PEO-*b*-PS tri-block copolymers shows the presence of phase separation in the tri-block copolymers.

V. CONCLUSIONS

PS-*b*-PEO-*b*-PS tri-block copolymers are synthesized by living anionic polymerization. The PS-*b*-PEO-*b*-PS tri-block copolymers found to be water soluble having low content of polystyrene block. These PS-*b*-PEO-*b*-PS tri block copolymers are found to be an excellent inhibitor for mild steel in H_2SO_4 . The inhibition efficiencies increase with increase in concentration but decrease with increase in temperature for PS-*b*-PEO-*b*-PS. E_{corr} remains constant indicating that PS-*b*-PEO-*b*-PS is a mixed type of inhibitor in $1\text{ M H}_2\text{SO}_4$ i.e., blocking both cathodic and anodic reactions almost to an equal extent. Adsorption of PS-*b*-PEO-*b*-PS 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 For $M_n = 20,000$

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	20.00	20.86	21.34	23.26	1.09
Br-PEO-Br	21.12	21.36	21.46	23.61	1.10

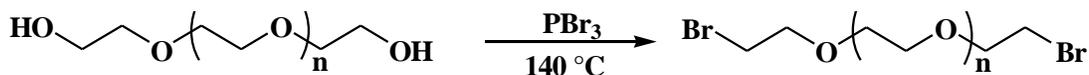
Table 2: Synthesis of PS-*b*-PEO-*b*-PS tri-block copolymers by using 1 at $-78\text{ }^\circ\text{C}$

Code	Styrene (mmol)	sec-BuLi (mmol)	^a sec-BuLi : Styrene	Br-PEO-Br (mmol)	^b $\bar{M}_{n,th} \times 10^{-3}$	^c $\bar{M}_{n,NMR} \times 10^{-3}$	GPC Results		
							$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	\bar{M}_w / \bar{M}_n
P1	9.27	10.87	1:0.852	5.435	20.41	20.89	21.07	23.18	1.10
P2	12.13	4.25	1:2.854	2.125	20.83	21.25	21.89	23.20	1.06
P3	13.45	2.77	1:4.855	1.385	21.24	21.67	22.13	23.45	1.06
P4	28.79	1.53	1:18.816	0.765	24.16	24.78	25.37	27.14	1.07
P5	65.87	1.69	1:38.976	0.845	28.33	28.96	29.89	32.28	1.08

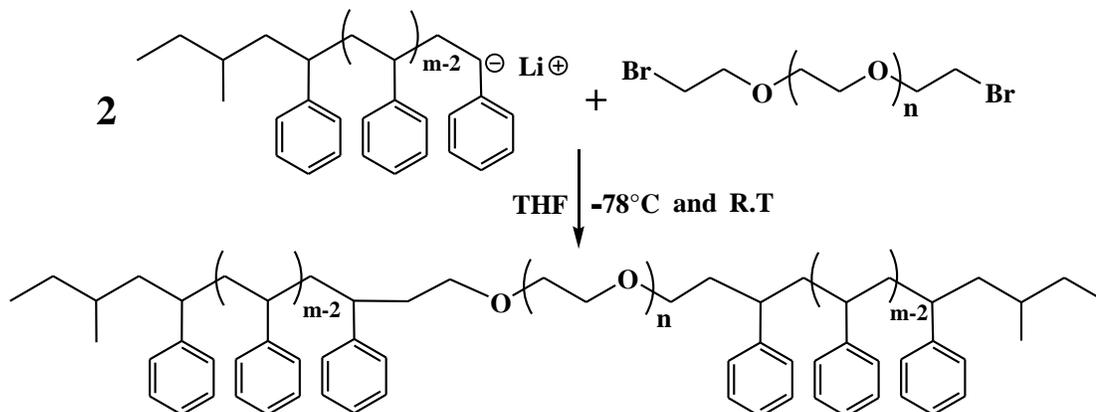
Table 3: Corrosion Parameters of mild steel in 1 M H₂SO₄ in the presence of PS-*b*-PEO-*b*-PS triblock copolymer

Temp.(K)	Conc. (ppm)	I _{corr} (mA/cm ²)	-E _{corr} vs SCE (mV)	b _a (mV/dec.)	b _c (mV/dec.)	IE%
298 K	Blank	9.679	465	70.59	60.89	-
	400	1.682	447	127.19	75.19	82.62
	800	0.962	460	268.13	77.79	90.06
	1200	0.362	457	241.14	82.16	96.26
	1600	0.124	441	283.45	89.13	98.72
308 K	Blank	17.12	475	59.24	52.82	-
	400	3.371	441	83.47	65.45	80.31
	800	2.280	425	87.52	81.79	86.68
	1200	1.349	432	123.12	85.48	92.12
	1600	0.656	425	163.67	88.19	96.17
318 K	Blank	19.54	481	50.91	48.05	-
	400	7.296	427	74.97	59.09	62.66
	800	6.049	451	72.11	65.52	69.04
	1200	3.836	428	83.32	61.78	80.37
	1600	1.155	473	165.31	59.14	94.09
328 K	Blank	22.09	490	58.00	47.05	-
	400	8.889	429	79.19	53.13	59.76
	800	8.137	485	43.21	49.51	63.16
	1200	7.405	424	81.54	54.32	66.48
	1600	6.746	438	78.09	59.25	69.46

Scheme 1: Synthesis of Br-PEO-Br from PEG



Scheme 2: Synthesis of PS-*b*-PEO-*b*-PS triblock copolymers by living anionic polymerization



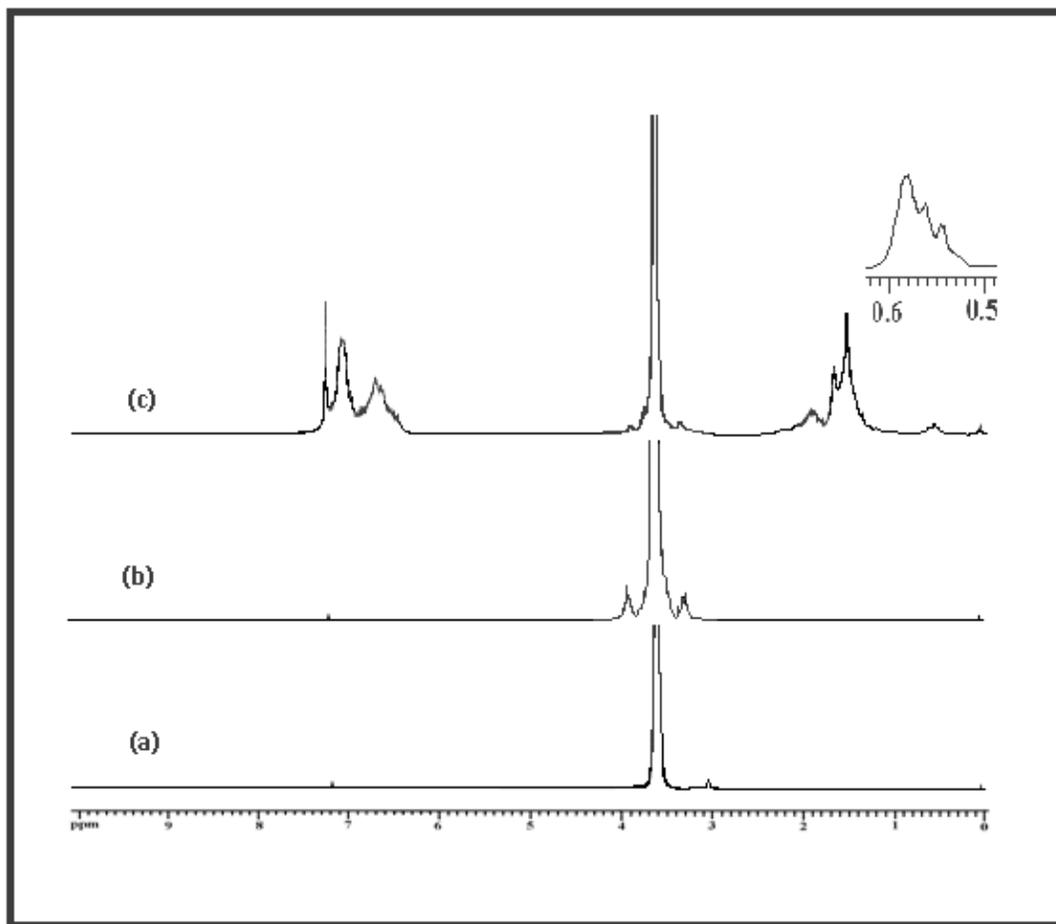


Figure 1: ^1H NMR spectra of (a) PEG (b) Br-PEO-Br and (c) PS-*b*-PEO-*b*-PS tri-block copolymers, P2

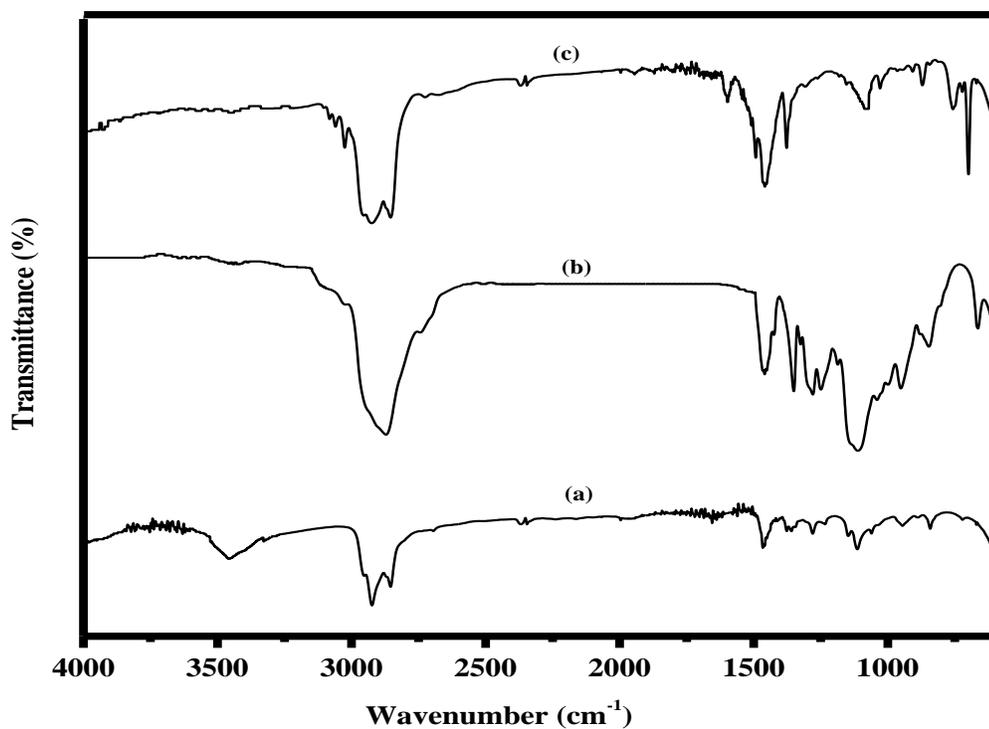


Figure 2: FT-IR spectra of (a) PEG, (b) Br-PEO-Br and (c) PS-*b*-PEO-*b*-PS tri-block copolymer, P2

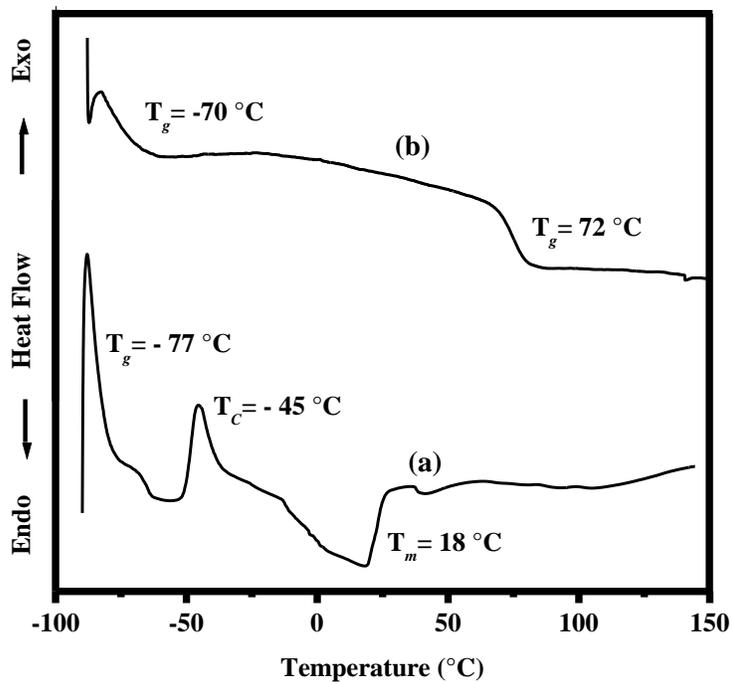


Figure 3: DSC curves of Br-PEO-Br and (b) PS-*b*-PEO-*b*-PS tri-block copolymer, P2

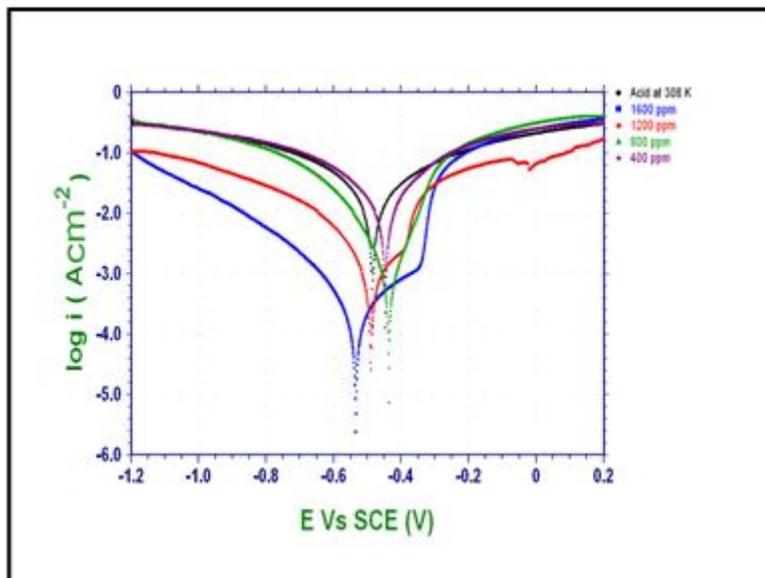


Figure 4: Tafel polarization curves of mild steel in 1M H₂SO₄ and in the presence of different concentrations of PS-*b*-PEO-*b*-PS tri-block copolymer, P2 at 298K.

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