

**"SYNTHESIS AND APPLICATION OF
CYCLOPOLYMERS CONTAINING CHELATING
MOTIFS OF
 β -AMINOETHYLIMINODIACETIC ACID"**

**BY
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Dedicated to

My

Parents, Brothers,

and Sister

Mentors whose love and supports know no bounds

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LIST OF ABBREVIATIONS

AIBN	: Azosobutyronitrile
AMPH	: 2,2'-azobis(2-methylpropionamidine) dihydrochloride
APS	: Ammonium Persulfate
CAPE	: Cross-linked Anionic Polyelectrolyte
CB	: Concentrated Brine
CPZA	: Cross-linked Polyzwitterionic Acid
CSC	: Critical Salt Concentration
DTS	: Dispersion Technology Software
EDX	: Energy-Dispersive X-ray
FTIR	: Fourier Transformation Infrared Spectroscopy
IEC	: Ion Exchange Capacity
LCST	: Lower Critical Solution Temperature
MA	: Maleic Acid
MB	: Methylene Blue
PA	: Polyampholyte
PRH	: Pararosaniline Hydrochloride
PSI	: Percent Scaling Inhibition
PTA	: Polytetraanion
PZ	: Polyzwitterion
PZDA	: Polyzwitterion/Dianion
PZTA	: Polyzwitterion/Trianion
RO	: Reverse Osmosis
RU	: Repeating Unit
SEM	: Scanning Electron Microscopy
TGA	: Thermogravimetric Analysis

pHPZC : point of zero charge
WCDA : Waste Catalyst-Derived Adsorbent

ABSTRACT

Full Name : [Mohammed K.R Aldahdooh]
Thesis Title : ["Synthesis and application of cyclopolymers containing chelating motifs of B-aminoethyliminodiacetic acid "]
Major Field : [Chemistry]
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A new quaternary diallyl amine salt monomer (**I**) containing the chelating motif of β -aminoethyliminodiacetic acid (EAIDA) was synthesized $[(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)_2\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}^+(\text{CH}_2\text{CO}_2\text{H})_2\text{Cl}^-](\text{I})$.

Monomer (**I**) upon free radical cyclopolymerization using azo initiators gave a unique pH-responsive poly(bis-zwitterion), whereby each repeating unit is embedded with the chelating motifs of N-(2-aminoethyl)iminodiacetic acid (AEIDA) in its bis-zwitterionic form (**II**) in high yield. Solution properties and full characterization of this new polybiszwitterionic PBZ (**II**), alongside some of its prospective application, were extensively studied. Electrically neutral polybiszwitterionic (**II**) was found to be water-insoluble. However, salts like NaCl imparted water-solubility. The polymer was insoluble inside a pH window of 1.5-3.92 owing to the equilibration of pH-responsive (**II**) to charge-imbalanced polymer chain with a point of zero charge at pH 3.82. Such impressive solution properties make polymer(**II**) smart adaptive. The ‘apparent’ pKas of the two acidic NH^+ centers were determined to be 5.89 and 10.57. Polybiszwitterionic PBZ (**II**) was found to be an effective antiscalant and mild steel corrosion inhibitor. As antiscalant, a concentration of 2.5 ppm prevented the formation scale $\text{CaSO}_4(\text{s})$ for more than 30 min

from its supersaturated solution. while a concentration of 20 ppm with the help of potassium iodide KI imparted 99% of mild steel corrosion in 1M HCl for 6h at 60°C. Moreover, monomer **(I)** underwent separate copolymerization with Maleic acid using APS initiator to afford a new copolymer **(III)** and with SO₂ to generate pure alternate copolymers **(IV)** using AIBN as initiator. Applications and solution properties were extensively investigated. Both copolymers were water-insoluble but adding salts such NaCl imparted solubility. In addition, the point of zero charge was found to be at pH 2.5 for both copolymers. The copolymer **(III)** and **(IV)** were soluble outside pH windows 1.49-3.35 and 0.81-4.46 respectively. The copolymer **(III)** was found to be a powerful antiscalant at 5 ppm avoided the formation of CaSO₄ for 30h from its supersaturated solution. Besides, it was an impressive corrosion inhibitor with 98.5% inhibition ability at 20 ppm concentration with help of 200ppm KI for 24h in 1M HCl at 60°C.

ملخص الرسالة

الاسم الكامل: محمد كامل رمضان الدحود

عنوان الرسالة: "البلمرة الحلقية المتماثلة والمشاركة المتناوبة: إصطناع فئة جديدة من المبلمرات الأيونية ثنائية الشحنات المتعاكسة وتطبيقاتها"

التخصص: الكيمياء

تاريخ الدرجة العلمية: نوفمبر 2020

تم تحضير مونمر (I) جديد من املاح ثنائي اليل امين يحتوي على مجموعة تسمى بيتا اميدو ثنائي حمض الكربوكسيل. بعد ذلك تم تصنيع مبلمر جديد (II) بناتج ممتاز من هذا المونمر باستخدام تقنية بلمرة الجذور الحرة باستخدام حفاز يحمل مجموعة الازو في تركيبه ، حسب بروتوكول بتلر للبلمرة. دراسة الخواص الفيزيائية لهذا المبلمر أثبت ان له خواص المبلمرات الذكية القابلة للتكيف حسب طبيعة الظروف المحيطة. حيث وجد مبلمر (II) غير ذائب بالماء النقي ،لانه متعادل كهربيا من حيث تساوي عدد المجموعات التي تحمل شحنات متعاكسة ،ولكن عند اضافة املاح مثل ملح كلوريد الصوديوم للماء اصبح المبلمر ذائب بشكل كامل. من ناحية اخرى عند دراسة ذوبانية مبلمر (II) تحت درجات حموضة مختلفة وجد أن المبلمر يكون ذائب خارج المدى 3.92- 1.5. بحيث تكون الهيمنة للشحنات الموجبة عند درجة حموضة اقل من pH 1.5 ،بينما تكون الشحنات السالبة مهيمنة على سلاسل المبلمر عندما تكون درجة الحموضة اعلى من pH 3.92 ، وكذلك اثبت أن المبلمر يكون تماما متعادل كهربيا عند درجة حموضة 3.92 pH. هذه الخواص تجعل من مبلمر (II) متكيف و ذكي، لانه من الممكن التحكم بسلوك المبلمر عن طريق التحكم في بيئته المحيطة. من حيث التطبيقات ،وجد ان مبلمر (II) له كفاءة عالية في منع تكون الكلس اثناء تنقية المياه نتيجة لزيادة تركيز الاملاح في مراحل التنقية، حيث اعطى كفاءة في منع ترسب الكلس من محلوله المشبع تصل 100% عند تركيز 2.5ppm لمدة نصف ساعة. ايضا مبلمر (II) منع تآكل الحديد في وسط حمضي بكفاءة مبهرة تصل الى 99% عند تركيز 20ppm بوجود كمية قليلة من KI لمدة ست ساعات عند درجة حرارة 60.

بعد ذلك تم تصنيع اثنين من المبلمرات المتناوبة عن طريق تفاعل المونمر الجديد (I) بشكل منفصل مع حمض الماليك لينتج مبلمر (III) و مع الكبريت ثنائي الاكسجين لينتج مبلمر (IV) باستخدام حفازات مختلفة. كل من المبلمرات الجديدة المتناوبة (III) و (IV) لم تذوب في الماء النقي ولكن عند اضافة املاح اعطت ذوبانية لهذه المبلمرات الجديدة في الماء. عند دراسة ذوبانية مبلمر (III) تحت درجات حموضة مختلفة وجد ان المبلمر يكون ذائب خارج المدي 1.5-3.35، بينما مبلمر (IV) يكون ذائب خارج المدي 0.81-4.46. ووجد ايضا عند درجة حموضة 2.4 pH يكون كل من المبلمرين متعادل كهربيا بشكل كامل، حيث عدد الشحنات السالبة يساوي تماما الشحنات الموجبة.

من حيث التطبيقات كلاهما كان ممتاز في منع تكون الكلس اثناء عملية معالجة الماء وتنقيته من الاملاح وبكفاءة مرتفعة. حيث ان مبلمر (III) اعطى كفاءة في منع ترسب الكلس من محلوله المشبع تصل ل 100% لمدة 30 ساعة عند تركيز (5 ppm)، بينما مبلمر (IV) اعطى كفاءة تصل ل 99% لمدة 370 دقيقة عند تركيز 20 ppm. ايضا تم اختبارهم في تثبيط تآكل الحديد في الوسط الحمضي، كلاهما كان له تأثير قوي وفعال وبكفاءة مذهلة. مبلمر (III) منع تآكل الحديد في وسط حمضي بكفاءة مبهرة تصل الى 98% عند تركيز 20 ppm بوجود كمية قليلة من KI لمدة 24 ساعة عند درجة حرارة 60، بينما مبلمر (IV) منع تآكل الحديد في وسط حمضي بكفاءة رائعة تصل الى 92% عند تركيز 50 ppm لمدة 24 ساعة عند درجة حرارة 60.

CHAPTER 1

INTRODUCTION

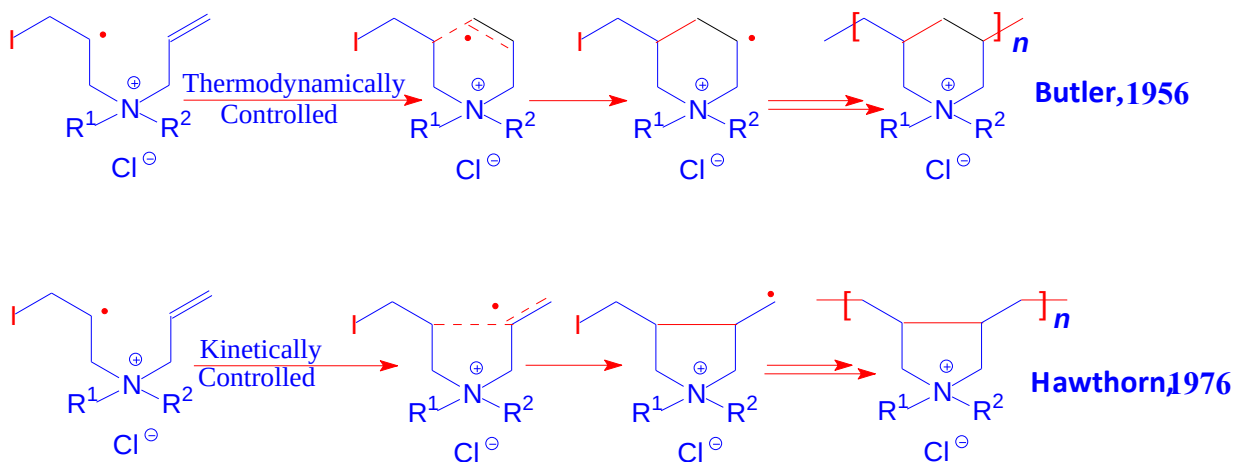
Polymers, naturally exists or synthesized in laboratories, have many applications in all aspects of live. Specially, ionic water-soluble polymers which are considered one of the most important types of polymers with impressive applications in biotechnology, drug delivery, water treatment, etc.

Generally, polymers with ionic charges can be classified into polyampholytes and polyelectrolytes based on the distribution of charges in the polymer's backbone. Polycations or polyanions are referred as polyelectrolytes, containing the same charges incorporated in the polymer chain [1,2]. As a result, due to the coulombic repulsion between similar charges, these polymers have a large hydrodynamic volume and a less favored extended structure in deionized water. However, polyelectrolytes adopt a more preferred globular structure with smaller hydrodynamic volume after adding low molecular weight electrolyte e.g. NaCl, such phenomena known as the polyelectrolyte effect[3].

On the other hand, polyampholytes, occasionally given the name polybetaines, are polymers composed of oppositely charged anionic and cationic sites, more commonly known as zwitterionic polymers, imbedded in the same polymer chain [1,2]. Surprisingly, there is a special type of charged polymers, called stimuli-responsive polymers, where the stoichiometric balance between negative and positive charges in a polymer backbone can be manipulated, affected, or shifted towards the cationic or anionic character.

Such polymers can smartly change their structure charges weight balance to be turned

between polyelectrolyte and antipolyelectrolyte as their environment changes; therefore, sometimes they are regarded as smart “adaptive” responsive polymers with dual-behavior[4]. Because solution properties as well as the behavior of such polymers are different under various environmental conditions, these polymers have received tremendous attention academically and industrially owing to their potential suitability to different research applications. Depending on the importance of ionic polymers, scientists have tried to synthesize different polymers directly or by post-polymerization reactions on polymers to modify their structure. Modern polymerization methods generally have facilitated the preparation of charged polymers. However, among the most popular methods to synthesize ionic polymers, particularly stimuli-responsive polymers, Butler’s cyclopolymerization method is extensively utilized. This kind of polymerization was introduced by Butler in 1957[5]. It was found to be that diallyl amine salt derivatives go free radical alternative intra- inter cyclopolymerization to generate polymer with cyclic repeating units structure containing a nitrogen heteroatom. In the beginning, Butler thought that the thermodynamically six-membered (endo cyclized radical formation) piperidine was formed in the polymer backbone. However, later Hawthorn et al. proved that the polymerization process was kinetically controlled and took place through the formation of a five-member ring (exocyclic radical formation) as better orbital overlap in transition state [6], as shown in (Scheme.1.1).



Scheme 1.1 Cyclopolymerization of diallyl amine salt derivatives

Cyclopolymers prepared by Butler protocol of polymerization have gained a lot of attention industrially and academically. Since the discovery of this kind of polymerization different types of ionic polymers containing ionic groups such as carboxylate ($-\text{CO}_2^-$), phosphonate ($-\text{PO}_3^{2-}$), or sulfonate ($-\text{SO}_3^-$) have been synthesized. Structure manipulation of diallyl amine monomers affords the platform to generate pH-responsive polymer with the ability to change weight charge balance upon different pH environments, as shown (Figure 1.1). Such polymers have remarkable solution properties and industrial significances.

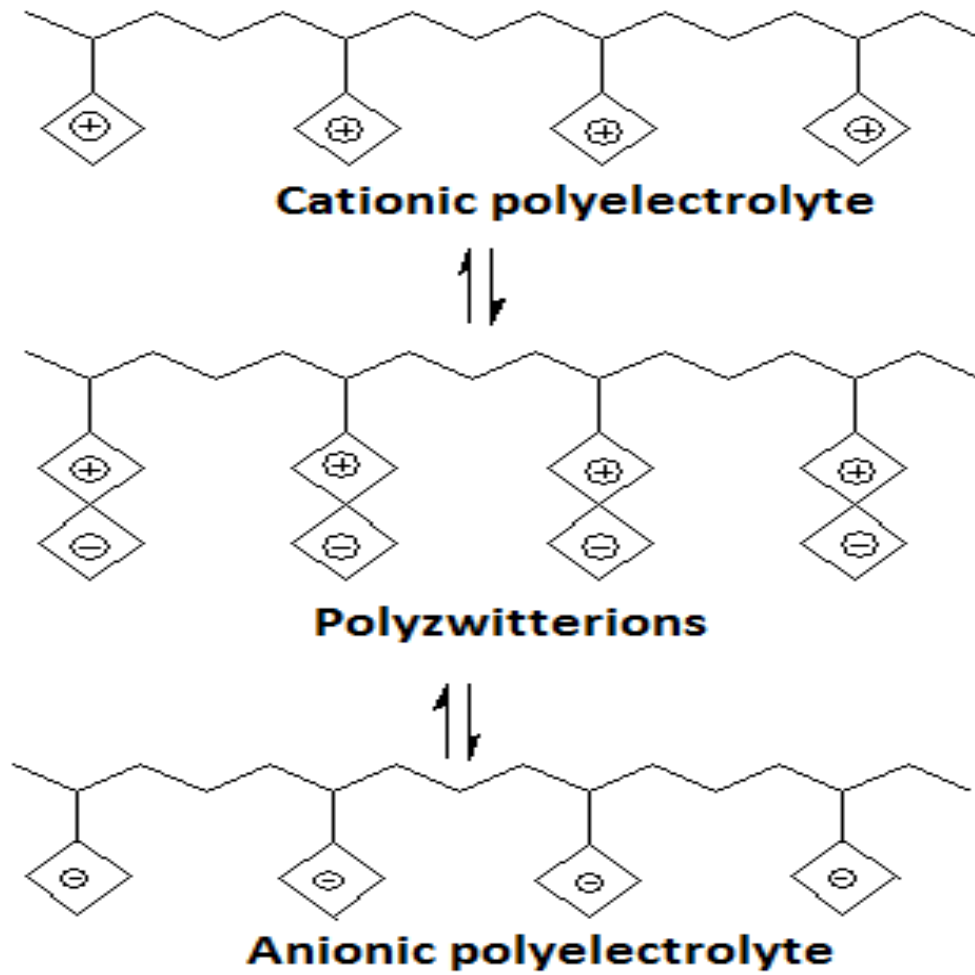
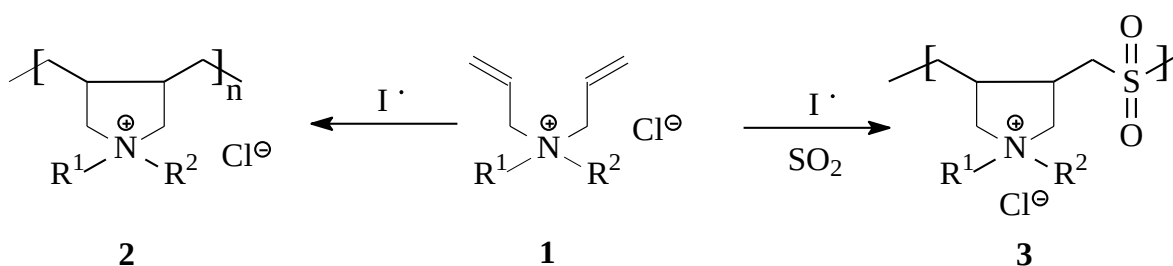


Figure1.1 Interconversion of the pH-responsive polymers

1.1 Ionic Polymers by Cyclopolymerization

As a result of the ability to change the attached groups on the nitrogen atom in diallyl amine, Butler's cyclopolymerization protocol [7-13] is considered a powerful tool in polymerizing diallyl ammonium salts **1** into a plethora of cyclopolymers **2** which have five-member ring "pyrrolidine" incorporated in a polymer chain to afford the eighth most important structural type of polymers in literature [14,15] (Scheme 1.2).

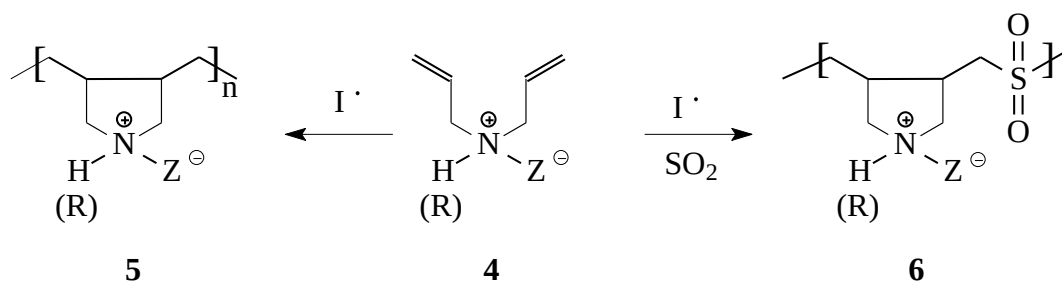
Polycationic (diallyldimethylammonium chloride) has been reported in numerous patents and publications (> 1000): personal care formulation and water purification stay the important areas of its application [7]. The synthetically significant water-soluble cationic polyelectrolytes can be directly prepared by the cyclopolymerization of diallyldimethylammonium chloride **2** or, alternatively, via copolymerization with sulfur dioxide **3** [16-18].



Scheme 1.2 Butler's cyclopolymerization protocol.

Using Butler's protocol Cyclopolymerization of diallylammonium monomers **4**, the polyzwitterions **5** can be prepared to generate polymer with both positive and negative sites in the same repeating unite (M^+). Similarly, the cyclopolymerization of diallylammonium monomers **4** and sulfur dioxide afforded zwitterionic copolymers **6** (Scheme 1.3)

[8-11, 14-26].



Scheme 1.3 Cyclopolymerization of diallylammonium monomers **4**, and sulfur dioxide.

Considering the definition of a polyampholyte, polymers with both cationic M^+ and anionic M^- sites are present in the same chain regardless of the groups of charges [20]. Such polymers have low hydrodynamic volume owing to the presence of (equal neutral) opposite charges in the polymer chain. Accordingly, upon adding low molecular weight electrolytes such as NaCl, the polyzwitterions and polyampholytes exhibit ‘anti-polyelectrolyte behavior [23-29]. Where the effective interaction between opposite charges sites in the polymer chain is reduced by alternative interaction with charges coming from NaCl. Therefore, the solubility and viscosity values of polyampholyte increased as the concentration of NaCl increased due to the effective partial neutralization of the opposite charges of the polymers, and the polymers adopted new extended confirmations with higher hydrodynamic volume.

On the contrary, a typical polyelectrolyte exhibits the opposite behavior (i.e., increasing the concentrations of NaCl, the viscosity decreases), (Figure 1.2).

polyampholytes and polyzwitterions polymers prepared from acrylamide and acrylate simulating in their composition biopolymers such as DNA and proteins found wide popularity commercially and have been used in many industrial applications including textiles, colloids, and charge dispersion agents[21].

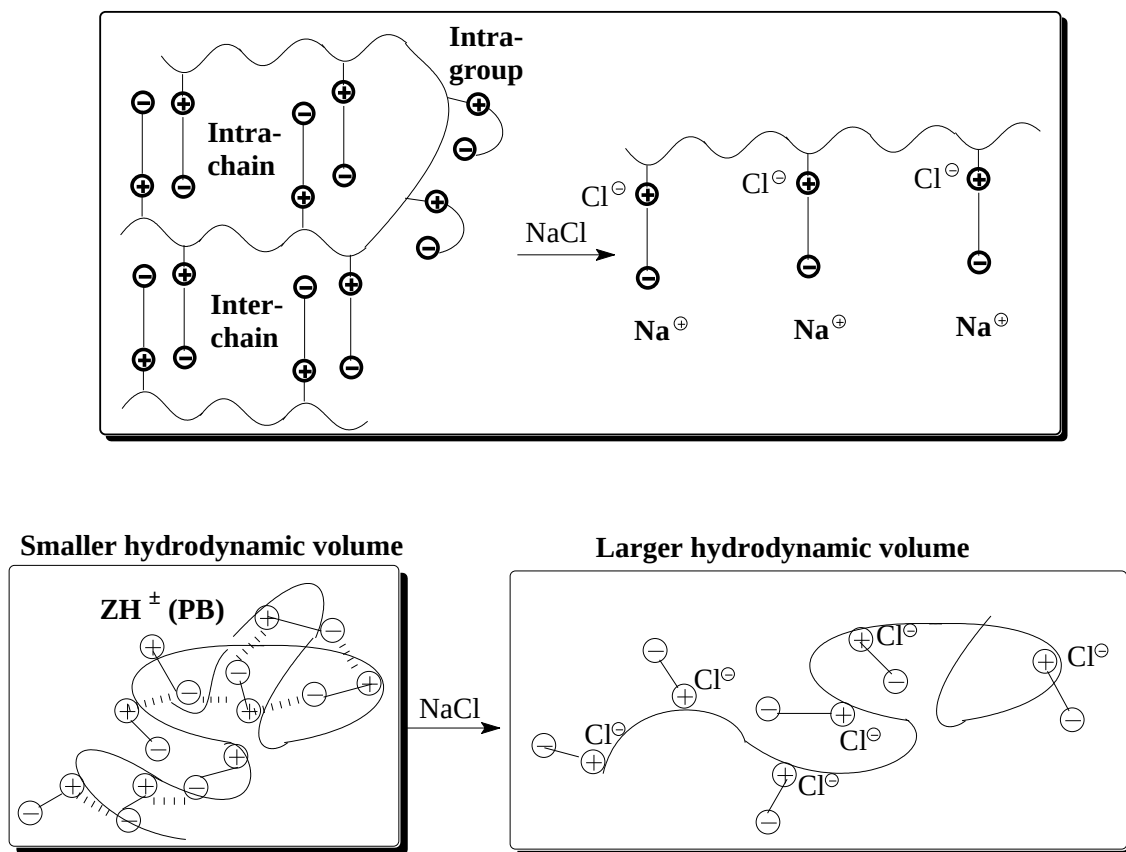
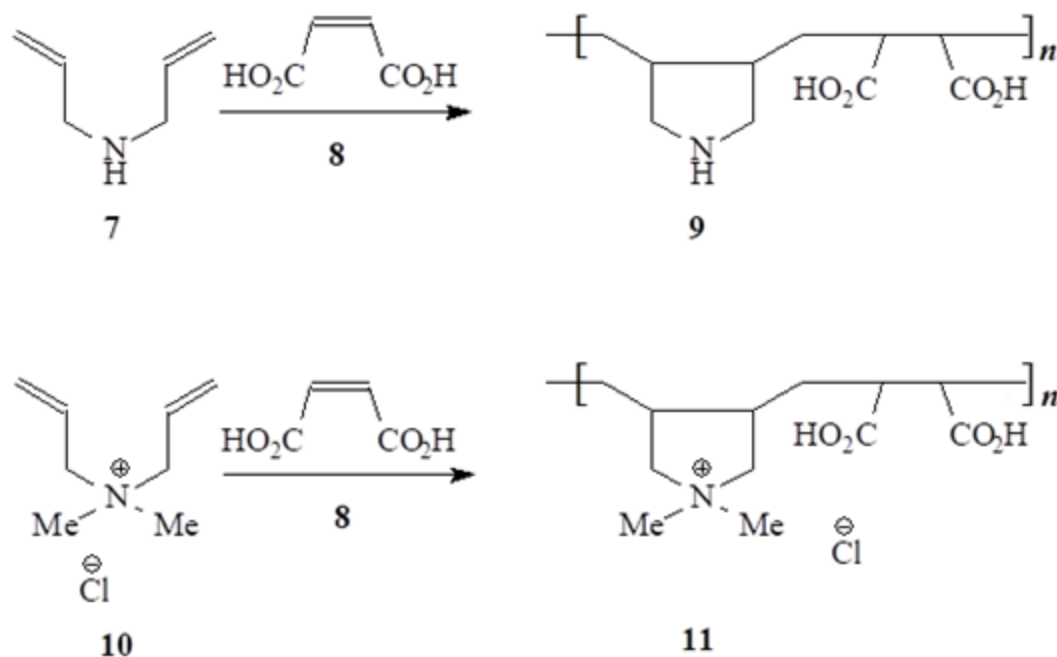


Figure 1.2 Antipolyelectrolyte behavior of polyzwitterions. Dashed lines (||||) indicate intrachain attraction.

Sometimes, interactions between the zwitterionic charges are so strong, and therefore a high critical salt concentration (CSC) of NaCl is required in order to disrupt or weaken the inter and intrachain interactions and then impart water solubility [16,30]. In the absence of an electrolyte (e.g. NaCl), the polyzwitterions (PZs) adopt globular coil conformations, due to the strong intragroup, inter and intra-chain electrostatic attractions, through the ionically cross-linked network and are usually insoluble in salt-free water [8,9,26,28,31,32]. As mentioned, the PZs show ‘anti-polyelectrolyte behavior’. The observed increase in viscosity values upon adding NaCl was referred to the effective disruption and partially neutralization of the opposite charges of the polymers in a collapsed coil conformation [26,33,34]. The cationic and anionic charge sites in a polymer chain are shield (neutralize) or interacted with Na^+ and Cl^- ions to a various extent; accordingly, a net charge is left on the polymer chain leading to the expansion of a polymer chain (Figure 1.2).

polyampholytes **9** was produced upon free-radical copolymerization of diallyl amine **7** with maleic acid (MA) **8**. This polymer **9** dissolves completely or to a large extent in water (Scheme 1.4) [35].



Scheme 1.4 Alternate copolymerization of substituted diallylamines derivatives with maleic acid 8.

Generally, it is well known that polyampholytes have poor solubility in water owing to the strong affinity attraction between the oppositely charged moieties of the polymer. On the contrary to the typical behavior, the polyampholytes prepared from diallyl amines, allyl, and MA **8** showed high solubility in water either over the whole range or over a major part of the pH scale. For instance, dimethyldiallylammonium chloride **10** polymerized with MA **8** to give the water-soluble copolymer **11** as shown in (scheme1.4) [36].

1.2 Literature Review

1.2.1 Polymers containing iminodiacetic acid(IDA) motif

Iminodiacetic acid (IDA), nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), β -ethylaminoiminodiacetic acid (EAIDA) (also known as *N*-(2-aminoethyliminodiacetic acid), and diethylenetriaminepentaacetic acid (DTPA) are important chelating ligands (Figure 1.3).

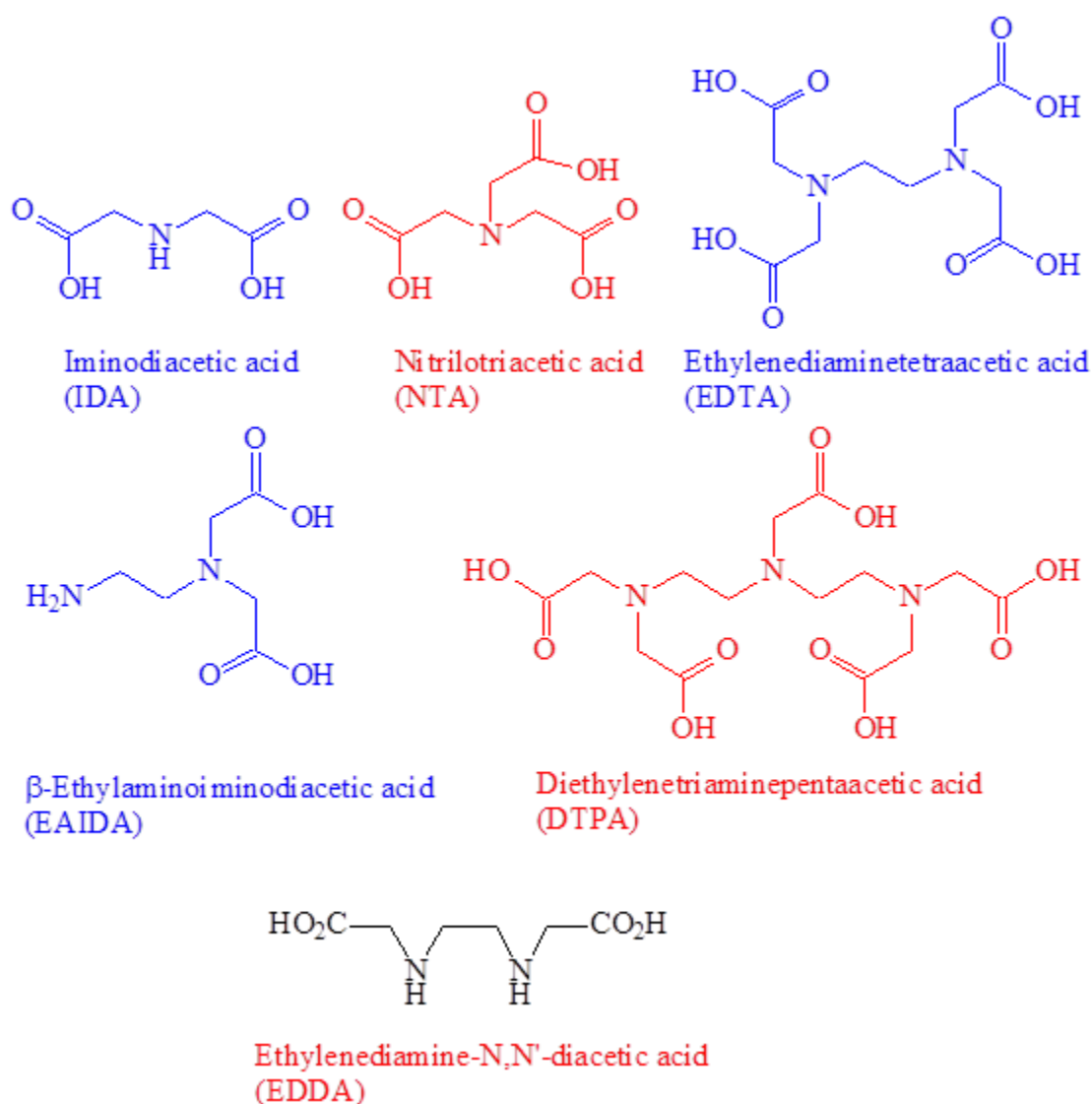


Figure 1.3 Structures of IDA, NTA ,EDTA, EAIDA, DTPA ,and EDDA.

Adsorption technology a promising method for the removal of heavy metals from contaminated waters[37,38]. A review paper summarizes excellent chelating properties of adsorbents functionalized with aminopolycarboxylic acid of IDA, NTA, EDTA, and DTPA[39]. The adsorbents are highly efficient in removing toxic metal ions from wastewaters. It is well known that wastewater containing toxic metal ions have a negative impact on the environment and human health[40]. To mitigate contaminated water as well as water scarcity a strategy of recycling is of paramount importance keeping in view of the alarming statistics of rapid population growth, increased urbanization, and more stringent health-based regulations[41,42]. Concerted efforts have led to the development of promising techniques such as adsorption[43], precipitation[44], dialysis[45], ion exchange[46], reverse osmosis[47] and extraction[48] for the removal of metal contaminants from wastewater.

However, among all these developed systems, the adsorption process is one of the most widely used processes which involves the use of various solid adsorbents like activated carbon[49], organic ion-exchange polymers[49], and numerous chemically anchored organic functionalities on silica gel[49,50], clays[51], and mesoporous silica[52,53].

The use of the adsorption process in purification technology is extremely important; but this process is still inconvenient for highly contaminated aqueous sample purification due to its limited density of surface-active sites, the slow kinetics of sorption in heterogeneous systems, etc[54]. For greater efficacy, an adsorbent must strongly bind metal ions on its surface. Chelating motifs in aminopolycarboxylic acids (APCAs) form stable structures and thereby sequester metal ions. APCAs are also used to prevent the formation of metal precipitates by removing metal ions from systems. IDA, NTA, EDTA, and DTPA are used to construct APCAs which are known as chelating or ion-exchange resins[39].

styrene divinylbenzene chelating resins with an iminodiacetic acid functional group has been synthesized and used for the removal of toxic metal ions (Figure 1.4)[56].

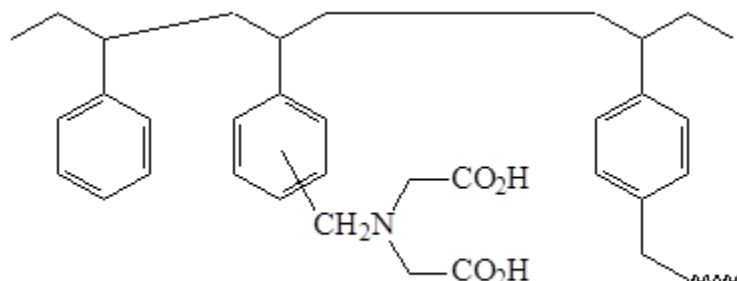


Figure 1.4 IDA-Functionalized polystyrene-divinylbenzene copolymer.

A review summarizes the results of recent studies on ethylenediaminediacetic acid (EDDA)-type metal complexes[57]. Some of the EDDA-type is represented by ethylenediamine-*N,N'*-diacetate and ethylenediamine-*N,N*-di-acetate (Figure 1.3). The IDA anion can act as a tridentate ligand to form a metal complex with two, fused, five-membered chelate rings (Figure 1.5). It can also act as a bidentate ligand through its two carboxylate groups. The functional motifs can be inserted in a polymer to create an ion-exchange resin such as chelex 100 (a styrene-divinylbenzene co-polymer containing iminodiacetic acid groups)[58] by replacing its H by a carbon atom of a polymer.

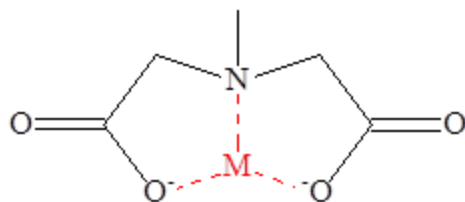


Figure 1.5 Chelating ligand of amino acetate

A hydrophilic acrylate monomer was prepared by reacting glycidyl methacrylate and iminodiacetic acid. The chelating resin was prepared by inversion suspension polymerization (Figure 1.6)[59]. The chelating resins were useful not only in recovering metal ions but also in removing phenol pollutants from wastewater.

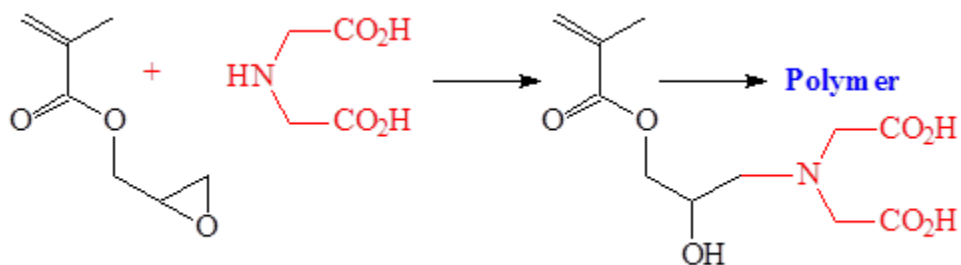


Figure 1.6 Methacrylate polymer containing IDA ligands.

1.2.2 Chemicals to Control Scale Formation in Desalination Plants

The antiscalants are extensively used to control scale formation of CaCO_3 , CaSO_4 , Mg(OH)_2 , etc. in desalination plants, Reverse Osmosis, cooling towers, etc[60,61]. The mechanistic pathway for the mitigation of scale formation has been reported[62]. Various additives are used to mitigate the scale formation[63]. In addition to a plethora of small molecules, polymer-based materials are also used as antiscalants: the effectiveness of poly(maleic acid) (PMA) and polyphosphonate (PPN) based additives in scale control has been reported.[64] The anionic antiscalants sequester the harmful cations thereby preventing scale formation. The commonly used poly(acrylic acid) and poly(acrylamide) antiscalants have the disadvantage of not being biodegradable[65]. The demand for biodegradable water-soluble polymer encouraged the use of biodegradable sodium polyaspartate to exploit its chelating ability[66-70]. Dispersants for polymeric silica, a cause for problems in desalination plants, based on phosphonate, carboxylate, and sulfonates has been reported[71]. Chelating properties of some important chelating motifs are exploited to remove toxic metal ions from wastewater [72-74]. Formation of soluble Ca(II) complex, the chelating motifs help keep the Ca(II) in solution thereby mitigating the scale formation on the membrane surface in desalination plants.

1.2.3 Mild steel corrosion inhibitor

Metal corrosion problems have a negative and costly impact on the economy. Globally, an estimated annual cost due to the corrosion is 2.5 trillion US dollars in 2016[75]. There are several different methods used to control corrosion that could reduce the annual cost by 15%-35% [76]. Organic corrosion inhibitors containing lone pair donating O, N, S atoms are widely used to mitigate corrosion attack on metals, particularly mild steel, during industrial acid cleaning, acid pickling, and oil well acidizing [77,78]. The inhibitors are adsorbed to cover the metal surface physically or chemically thereby restraining corrosive attack. Polymers, as compared to monomers, having large surface area and multiple anchoring functional motifs have received enormous attention as corrosion inhibitors since they can more efficiently block the metal surface by forming metal (Fe^{2+})-polymer complex [79-82,83]. EDTA [84,85], IDA [86], *N*-(phosphonoalkyl)IDA [87] have been used to mitigate mild steel corrosion in HCl media with some success.

1.3 Present State of the Problem

The impressive chelating ability of aminopolycarboxylic acids (APCAs) motifs made them a matter of great interest to research industrially and academically. These multidentate ligands (Fig1.3) especially AEIDA have a countless number of biological and industrial applications. Introducing one of these ligands into a linear or cross-linked polymer backbone is considered one of the most important methods used to effectively take the most of such ligands. For example, cross-linked polymers containing such multidentate ligands were proved to be effective adsorbents to remove toxic metals from wastewater [58-59]. Making new smart pH-responsive polymers containing amine and carboxylate motifs in the same repeating unit would offer the opportunity to investigate cationic polyelectrolyte-to-polyzwitterionic-to-anionic polyelectrolyte transitions in ionic polymers. The frequently utilized poly(acrylic acid) and poly(acrylamide) as anti-scalants polymers in water desalination plants suffer from the problem that; they are non-degradable polymers [88]. Therefore, the demand for the synthesis of new water-soluble bio-degradable effective antiscalants and corrosion inhibitors is big.

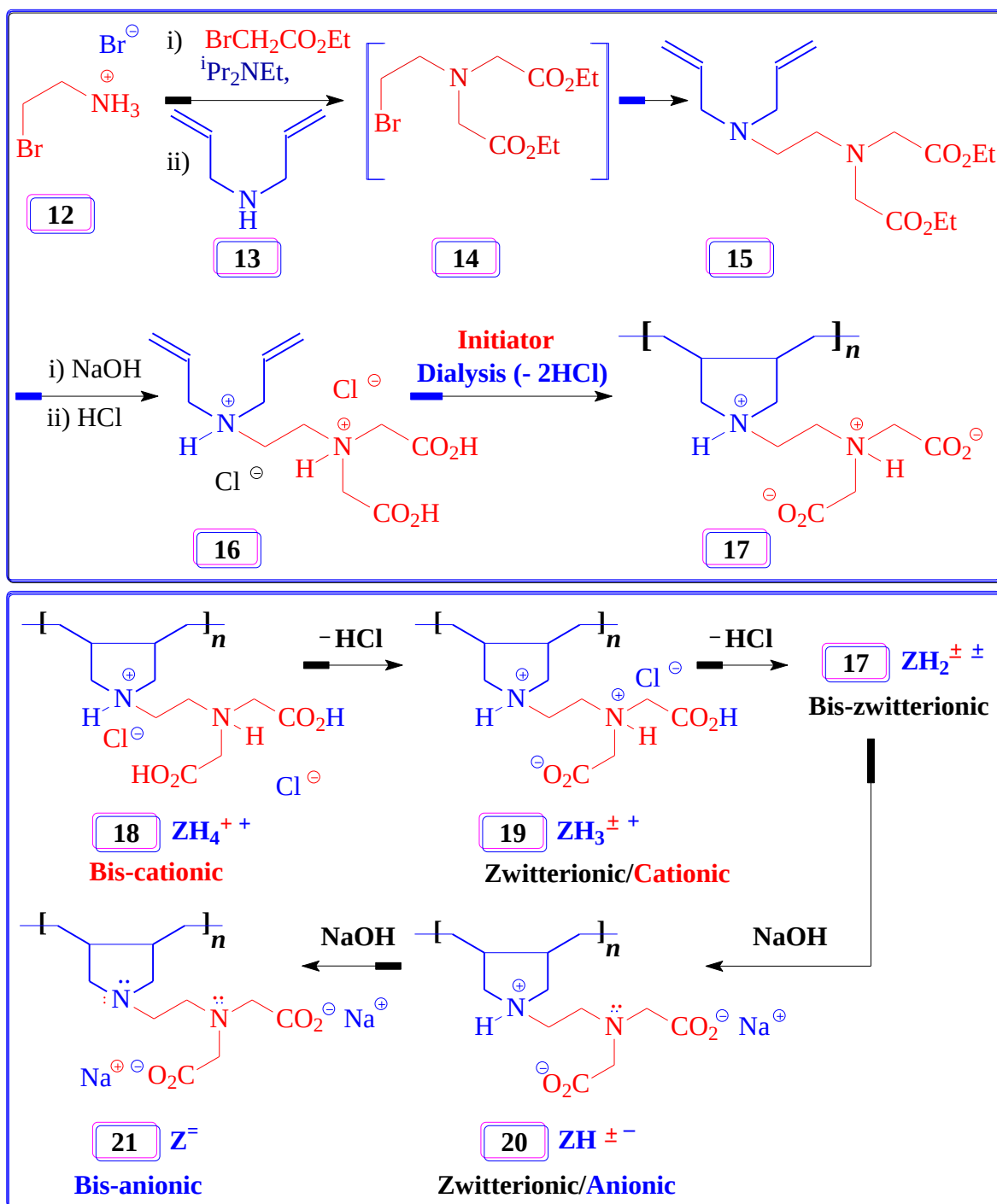
In this work, homo and copolymers containing a high charge density of N-(2-aminoethyl)iminodiacetic acid (AEIDA) group will be synthesized. Solution properties for such new ionic polymers containing tetradentate ligand in its bis-zwitterionic form will be investigated. Moreover, it is predicted that these polymers will be powerful antiscalants to mitigate the scale formation on the membrane surface in desalination plants as well as mild steel corrosion inhibitors in acidic medium.

1.4 Objectives

This research aims to synthesize a new series of stimuli-responsive ionic polymers via cyclooligomerization of newly synthesized diallyl ammonium monomer and separately copolymerization with maleic acid and Sulphur dioxide. This research is divided into two-folds : (i) preparation of interesting newly ionic cyclopolymers, and (ii) investigation their applications in different fields. The proposed work is thus of both academic and industrial interests. The presence of multiple cationic and anionic sites in linear polymers is anticipated to sequester metal ions to prevent scale formation, and effectively inhibit mild steel corrosion. In addition, cross-linked polymer might form efficient resin to remove charged organic dyes and pollutants alongside toxic metal ions from wastewater.

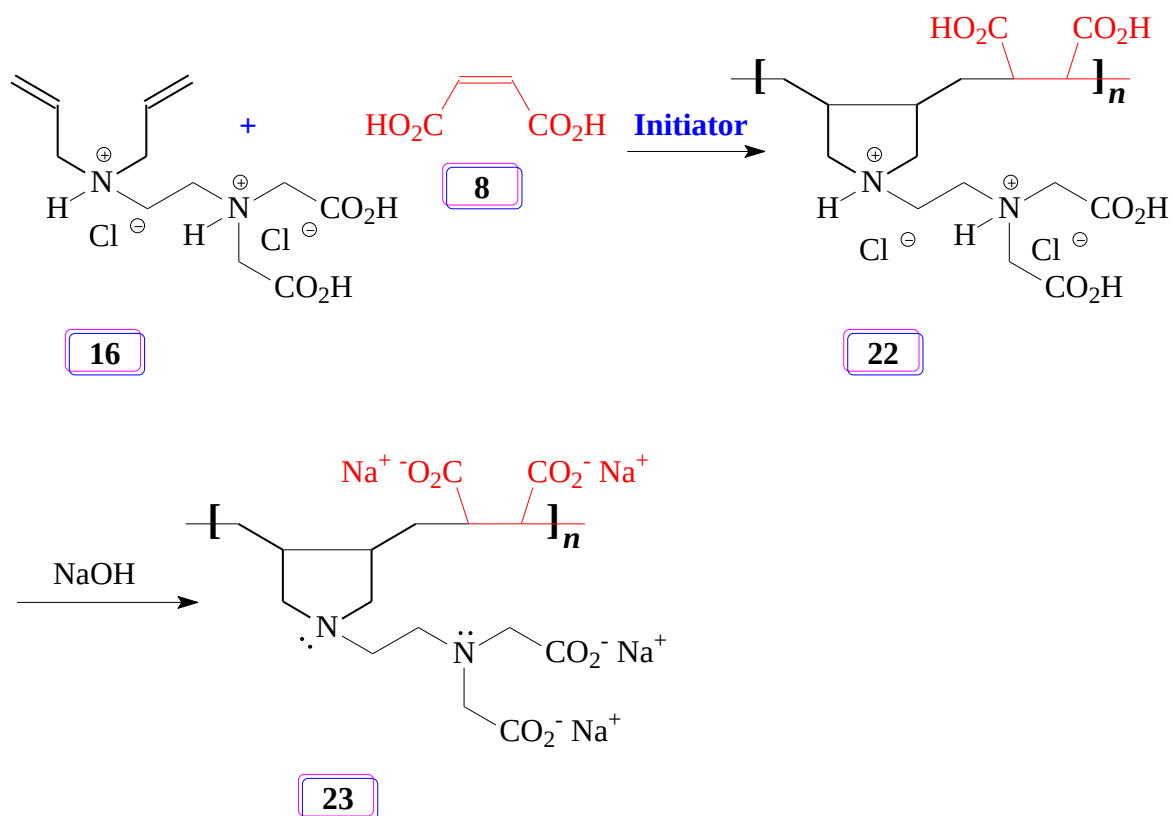
More specifically, the proposed study has the following objectives:

- i) Synthesis and cyclopolymerization of monomer **16** to give polymer **17** (Scheme 1.5)



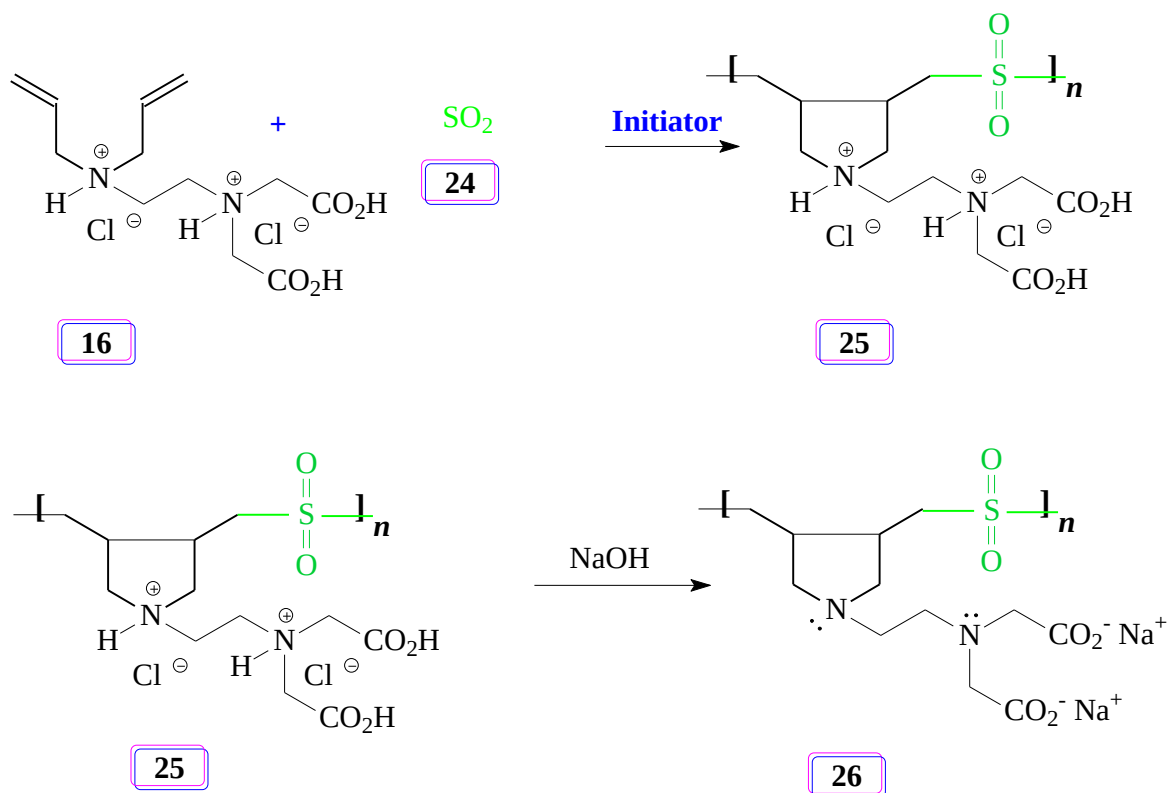
Scheme 1.5 Synthesis and cyclopolymerization of a diallylamine salt containing *N*-(2-aminoethyl)iminodiacetic (AEIDA) motifs.

ii) Alternate Copolymerization of monomer **16** and maleic acid **8** to generate **22** copolymer (Scheme 1.6).



Scheme 1.6 Alternative copolymerization of maleic acid and diallylamine salt containing β -aminoethyl iminodiacetic acid motifs.

- iii) Alternate Copolymerization of monomer **16** and sulphardioxide SO_2 **24** to generate copolymer **25** (Scheme 1.7).

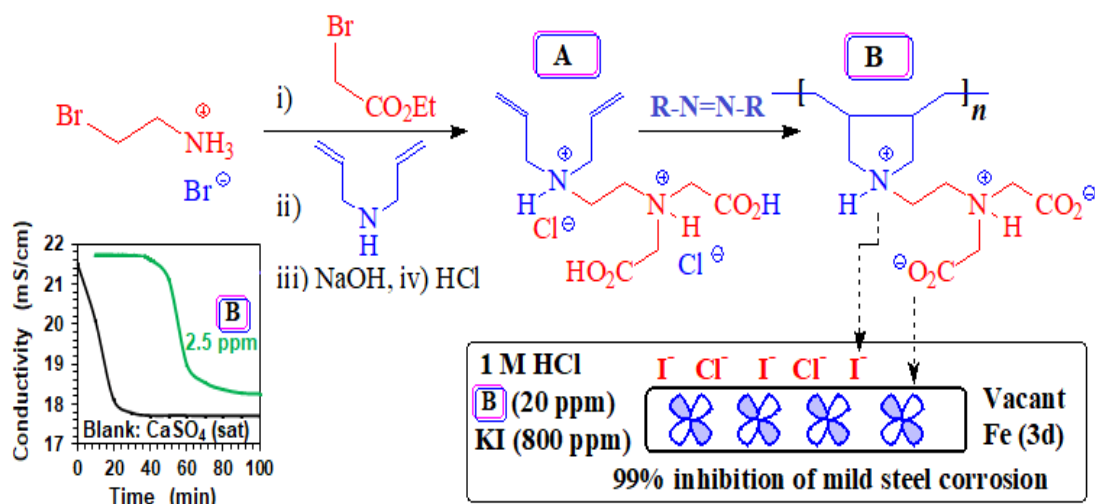


Scheme 1.7 Alternate cyclopolymerization of a diallylamine salt containing N-(2-aminoethyl)iminodiacetic (AEIDA) motifs with SO_2 .

- iv) Physical characterization and solutions properties of polymers **17,22**, and **25** (viscosity, solubility TGA, etc.).
- v) Study on the antiscalant behavior of polymers **17,22**, and **25**.
- vi) Study on the mild steel corrosion inhibition behavior of polymers **17,22** and **25**.

CHAPTER 2

SYNTHESIS AND APPLICATION OF A POLY(BIS-ZWITTERION) CONTAINING CHELATING MOTIFS OF N-(2-AMINOETHYL)IMINODIACETIC ACID



Bis-zwitterionic **B** is an excellent antiscalant (2.5 ppm) and inhibitor (99%) of mild steel corrosion in 1M HCl

Graphical Abstract

2.1 Abstract

A bis-cationic (+ +) diallyl monomer [(H₂C=CHCH₂)₂NH⁺(CH₂)₂NH⁺(CH₂CO₂H)₂•2Cl⁻] (I) was prepared by a one-pot, two-step reaction of 2-bromoethylamine hydrobromide, ethyl bromoacetate and diallylamine to generate [(H₂C=CHCH₂)₂N(CH₂)₂N(CH₂CO₂Et)₂] followed by ester hydrolysis. I underwent cyclopolymerization to afford a unique poly(bis-zwitterion) (PBZ) (± ±) II, containing repeating unit embedded with chelating motifs of N-(2-aminoethyl)iminodiacetic acid in bis-zwitterionic form NH⁺(CH₂)₂NH⁺(CH₂CO₂⁻)₂. Electroneutral II was found to be water-insoluble, while salts like NaCl imparted water-solubility. The polymer was soluble outside a pH window of 1.5-3.5 owing to the equilibration of pH-responsive II to charge-imbalanced polymer chain. The ‘apparent’ pK_as of the two NH⁺ centers were determined to be 5.89 and 10.57. At 2.5 ppm concentration, antiscalant PBZ II imparted 100% inhibition of CaSO₄ scale formation for 30 min from its supersaturated solution, while at 20 ppm concentration aided by KI, it demonstrated an outstanding synergistic 99% inhibition of mild steel corrosion in 1 M HCl.

Keywords:

pH-responsive polymers

Diallylamine salts

Antiscalant.

Mild steel corrosion

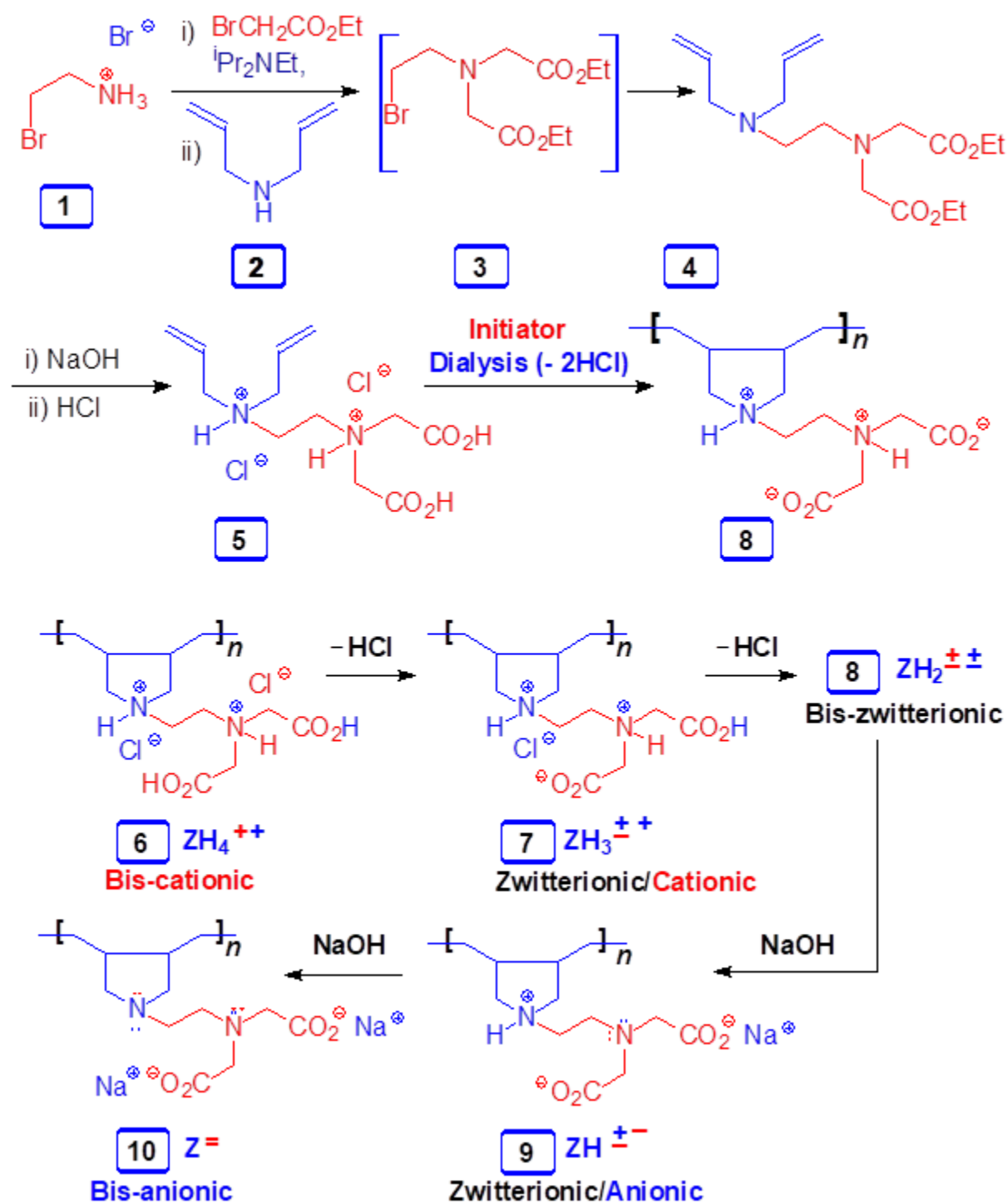
N-(2-aminoethyl)iminodiacetic acid

Cyclopolymerization

2.2 Introduction

The industrially important Butler's cyclopolymerization protocol involves cyclopolymerization of a plethora of diallylamine salts [89,90], having unquenched nitrogen valency as well as their quaternary derivatives [91,92], to generate the eighth most important architecture of synthetic polymers whose backbones are embedded with five-membered pyrrolidine ring [93,94]. It is worth mentioning that annual production of millions of pounds of poly(dimethyldiallylammonium chloride), documented in over 1000 patents and publications, is intended for water purification, paper industry and personal care formulations [95]. Structural variations in the substituents of diallylamine derivatives have been exploited to generate pH-responsive ionic polymers [95-97]. Polyampholytes and polyzwitterions, which seem to mimic biopolymers, have also offered many new applications in biotechnology, medicine, oil industry, and hydrometallurgy [95,96].

Iminodiacetic acid $[\text{NH}(\text{CH}_2\text{CO}_2\text{H})_2]$ (IDA), ethylenediaminetetraacetic acid (EDTA) and *N*-(2-aminoethyl)iminodiacetic acid $[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}(\text{CH}_2\text{CO}_2\text{H})_2]$ (AEIDA) are important chelating ligands [98]. The current chapter describes the synthesis of a pH-responsive poly(bis-zwitterion) (PBZ) $(\pm \pm)$ **8** via Butler's cyclopolymerization protocol [91,92,95], whereby each repeating unit has the bis-zwitterionic motifs of AEIDA in the form: $\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}^+(\text{CH}_2\text{CO}_2^-)_2$ (Scheme 2.1). PBZ **8**, to our knowledge, would be the first example of a cyclopolymer, whereby each repeating unit has the bis-zwitterionic dipoles, and where the integrity of all four original functionalities of AEIDA (i.e. two unquenched nitrogen valency and two CO_2H groups) has been kept intact.



Scheme 2.1 Synthesis and cyclopolymerization of a diallylamine salt containing *N*-(2-aminoethyl)iminodiacetic (AEIDA) motifs.

The high density of chelating ligands in PBZ **8** is expected to impart interesting solution properties, excellent antiscalant and corrosion inhibition activities in addition to metal ion-removal capacity from contaminated wastewaters. Our expectation is based on the precedent literature which is traversed through in the subsequent paragraphs.

The excellent chelating properties of adsorbents functionalized with aminocarboxylic acid of IDA and EDTA make them highly efficient in removing toxic metal ions from waste waters [99]. An article describes the studies on ethylenediamine-*N,N'*-diacetate- and ethylenediamine-*N,N*-diacetate-metal complexes [100]. Chelation therapy using EDTA involves removal of toxic metals from human [101]. Styrene/divinylbenzene chelating ion-exchange resin, sold under the commercial name chelex 100 having IDA functional motifs – $\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$] attached to some of the phenyl rings, has been shown to be efficient in removing toxic metal ions [102,103]. An IDA functionalized methacrylate monomer led to a resin which was useful in trapping metal ions as well as phenol contaminants from industrial effluents [104]. The IDA anion, being a tridentate ligand, can form metal complexes having fused five-membered chelate rings. A recent article describes the use of an iron oxide core coated with different pH-responsive polyampholytes containing $-\text{NH}^+-\text{C}-\text{CO}_2^-$ motifs to pH-dependent catch-and-release of either cationic or anionic dyes [105].

The antiscalants are extensively used to mitigate CaCO_3 , CaSO_4 , $\text{Mg}(\text{OH})_2$ scales in desalination and reverse osmosis(RO) plants, cooling towers, etc. [106,107]. By the formation of soluble $\text{Ca}(\text{II})$ -complex, the chelating motifs of antiscalants like EDTA help keep the $\text{Ca}(\text{II})$ in solution, thereby mitigating the scale formation on the membrane surface in desalination plants [60].

While biodegradation of EDTA is difficult, the IDA is easily biodegradable [61,62]. In addition to a plethora of small molecules, polymer-based materials are also used as antiscalants. The commonly used poly(acrylic acid) and poly(acrylamide) antiscalants have the disadvantage of not being biodegradable [63].

Corrosion of metals is a costly problem. Annually, the global cost due to corrosion in 2016 is estimated to be 2.5 trillion US dollars [75]. Using available corrosion control practices, the cost of corrosion could be reduced by 15-35% [76]. Organic corrosion inhibitors containing lone pair donating O, N, S are widely used to mitigate corrosion attack on mild steel and iron during industrial acid cleaning, acid pickling, and oil well acidizing [77,78]. The inhibitors are adsorbed to cover the metal surface physically or chemically thereby restraining corrosive attack. Polymers, as compared to monomers, having multiple anchoring functional motifs have received particular attention as corrosion inhibitors since they can more efficiently block the metal surface by forming metal (Fe^{2+})-polymer complex [79-83]. EDTA [84,85], IDA [86], *N*-(phosphonoalkyl)IDA [87] have been used to mitigate mild steel corrosion in HCl media with some success.

The above discussion attempted to shed some light on the importance of aminoacetate chelating motifs. Herein we describe the synthesis, solution properties, antiscalant behavior, and corrosion inhibition activity of the newly synthesized PBZ **8** with the anticipation of an exciting outcome.

2.3 Experimental

2.3.1 Materials

Diallylamine, tertiary butyl hydroperoxide (TBHP) from Fluka Chemie AG were used. 2-Bromoethylamine hydrobromide salt **1** and diisopropylethylamine from Tokyo Chemical Industry, ammonium persulfate (APS), ethyl bromoacetate, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPD) from Sigma-Aldrich were purchased. HPLC grade organic solvents and Millipore water (double distilled, 18.2 M Ω ·cm) were used. Dialyses were performed in spectra/Por membranes of MWCO of 6000–8000 from Spectrum Laboratories.

2.3.2 Characterization Methods

A Perkin Elmer Elemental Analyzer Series 11/2400 (Waltham, Massachusetts) was utilized to find atomic compositions. An FTIR spectrometer (Nicolet 6700, Thermo Electron Corporation) was utilized to record IR spectra. Thermogravimetric analyses (TGA) were performed under a flow of N₂ using an SDT analyzer (Q600: TA Instruments). pH measurements were performed by a Sartorius pH meter. Quattro ESEM-FEG integrated with energy dispersive x-ray spectrometer (EDX, Oxford Instruments) from ThermoFisherTM Scientific was utilized to examine the surface morphology of the samples. ¹H and ¹³C NMR spectra were recorded in CDCl₃ (TMS) and in D₂O on a Bruker Avance^{III} 400 MHz spectrometer. The ¹H and ¹³C chemical shifts in D₂O were referenced with sodium 3-trimethylsilylpropionate-2,2,3,3-d₄ (TSP-deuterated, δ 0 ppm) and dioxane (δ 67.4 ppm).

Conductance measurements were carried out using an Orion Versastar Conductometer (Thermo Scientific). Viscosity measurements were performed in an Ubbelohde viscometer (Viscometer Constant = 0.005 cSt/s) in the presence of N₂ atmosphere at 30.0±0.1°C as controlled by a water bath CT72/P, SI Analytics, Germany. Double distilled water, purged with N₂ at 90 °C for 15 min to make it CO₂-free, was used for viscosity measurements; the presence of CO₂ in the air may otherwise affect the viscosity values especially in the alkaline solutions. Viscosity values are average of at least three values at each concentration to obtain an average error in time of <0.2%.

Size Exclusion chromatography (SEC) was performed on an Agilent 1200 series high performance liquid chromatograph equipped with a micro vacuum degasser, a binary pump, an auto-sampler, a column thermostat, Refractive index detector, and three columns in series (PL aquagel-OH 40, PL aquagel-OH 30, and PL aquagel-OH 20). A 0.5 M NaCl containing 0.05 M NaNO₃ was used as eluant at a flow rate of 0.8 mL/min at 30 °C. A sample solution of 2 mg/mL was prepared in 0.5 M NaCl containing 0.05 M NaNO₃ and filtered using 0.45 µm syringe filters. The resulting solution (50 µL) was injected into the GPC columns and chromatographic data was analyzed using Cirrus GPC data analysis tool. The equipment was calibrated using nine polyethylene oxide (PEO) standards.

2.3.3 Polymer Synthesis

2.3.3.1 Synthesis of Diethyl β -diallylaminoethyliminodiacetate (**4**)

2-Bromoethylamine hydrobromide salt **1** (20.5 g, 100 mmol) was added portion wise (*ca.* 20 min) to a mixture of ethyl bromoacetate (41.8 g, 250 mmol) and diisopropylethylamine (45.2 g, 350 mmol) in acetonitrile (120 mL) at 0 °C [108] and stirred at 23 °C under N₂ for 20 h. Without isolating the generated diethyl β -bromoethyliminodiacetate (**3**), the above reaction mixture was treated with diallylamine (**2**) 40 mL, 30.5 g, 314 mmol) and stirred 1 h each at 23, 35 and 65 °C. After concentrating, the residue in a solution of water (100 mL) and K₂CO₃ (60 g) was extracted with ether (3×100 mL). The organic layer, after drying (Na₂SO₄), concentrating, was distilled to obtain compound **4** (25.8 g, 82.5%) as a colorless liquid (bp_{0.5} mbar Hg 122 °C). (Found: C, 61.3; H, 8.9; N, 8.9%. C₁₆H₂₈N₂O₄ requires C, 61.51; H, 9.03; N, 8.97%); $\nu_{\max}$ (KBr): 3076, 2980, 2932, 2808, 1734, 1642, 1447, 1419, 1373, 1260, 1189, 1031, 996, 920, 865, 807, 729, and 585 cm⁻¹. δ_{H} (CDCl₃) 1.24 (6H, t, *J* 7.2 Hz), 2.57 (2H, t, *J* 7.0 Hz), 2.83 (2H, t, *J* 7.0 Hz), 3.07 (4H, d, *J* 6.4 Hz), 3.56 (4H, s), 4.14 (4H, q, *J* 7.2 Hz), 5.11 (4H, m), 5.82 (2H, m); δ_{C} (CDCl₃) 14.13 (2C), 51.42 (1C), 51.48 (1C), 55.35 (2C), 56.99 (2C), 60.30 (2C), 117.48 (2C, CH=CH₂), 135.32 (2C, CH=CH₂), 171.19 (2C), (CDCl₃ middle C: 77.00): 67.40 ppm). The ¹³C assignments were confirmed by a DEPT 135 NMR spectrum.

2.3.3.2 Synthesis of monomer β -diallylaminoethyliminodiacetic acid dihydrochloride (**5**)

Under N₂, a heterogeneous mixture of **4** (22 g, 70.4 mmol), water (55 mL) and NaOH (6.2 g, 155 mmol) was vigorously stirred at 40 °C for 2.5 h during which the mixture became homogeneous, and the hydrolysis was complete as indicated by ¹H NMR. The mixture was cooled (0 °C) and neutralized by gradual addition of concentrated HCl (37%, 30.6 g, 310 mmol). The neutralized mixture was freeze-dried, and the resultant solid was triturated with 20:80 mixture of hot acetone/MeOH (100 mL), filtered, and the NaCl residue was washed with hot acetone/MeOH (20:80) mixture (200 mL). The filtrate after rotovaporation gave a faint yellow solid which was washed with acetone to give monomer **5** as a white crystalline solid (20.1 g, 87%). Mp 178-181 °C; (Found: C 43.3; H 6.9; N 8.3%. C₁₂H₂₂Cl₂N₂O₄ requires C 43.78; H 6.74; N 8.51%); $\nu_{\max}$ (KBr): 3445 (broad), 3097, 3019, 2997, 2960, 2923, 1757 (strong), 1735, 1637, 1458, 1412, 1252, 1200, 1056, 989, 951, 900, 854, 804, 712, 669, 650, and 546 cm⁻¹; δ_{H} (D₂O) 3.29 (4H, m), 3.64 (4H, d, *J* 7.2 Hz), 3.78 (4H, s), 5.40 (4H, m), 5.72 (2H, m); (HOD signal at δ 4.65 ppm); [With TSP, the HOD appeared at δ 4.84]. δ_{C} (D₂O) 49.20 (1C), 50.79 (1C), 56.52 (2C), 56.79 (2C), 126.42 (2C, $\underline{\text{C}}\text{H}=\text{CH}_2$), 128.56 (2C, $\text{CH}=\underline{\text{C}}\text{H}_2$), 171.15 (2C), (dioxane: 67.80 ppm). The ¹³C assignments were confirmed by a DEPT 135 NMR spectrum.

An ¹H NMR titration using a mixture of monomer **5** (168 mg) and ethanol (23.1 mg, 0.501 mmol) in D₂O revealed the molecular weight (MW) of the monomer as 336.8 g mol⁻¹. The MW, determined by area integration of several ¹H signals of **5** and ethanol, compared very well with the theoretical value of 329.2 g mol⁻¹. The experiment thus revealed the formation of the dihydrochloride salt **5**.

2.3.3.3 Synthesis of poly(bis-zwitterion) (PBZ) **8**

The polymerization was carried out as described in [Table 2.1](#). For instance, as in entry 1, a solution of bis-cationic **5** (6.58 g, 20 mmol) and AMPD (200 mg) in water (3.5 mL) (i.e. monomer/water wt ratio of 65:35) in an RB flask was heated under N₂ at 75 °C for 18 h and then at 85 °C for 6 h. The crude polymer was dialyzed against deionized water for 24 h with frequent change of water. The polymer slowly separated as a milky thick liquid during the dialysis. The whole mixture after freeze-drying afforded PBZ **8** as a creamy white solid (3.75 g, 73%). Note the crude reaction revealed the formation of 88% PBZ **8**; as such low molar mass fraction of the polymer escaped the dialysis bag. (Found: C 56.0; H 7.8; N 10.7%. C₁₂H₂₀N₂O₄ requires C 56.24; H 7.87; N 10.93%); ν_{max} (KBr): 3437 (broad), 2924, 2858, 1724, 1632, 1455, 1394, 1214, 1081, 981, 706, and 560 cm⁻¹.

Table 2.1 polymerization of monomer **5** to give PBZ **8**.

Entry	5 (mmol)	Water (wt%)	Initiator (mg/mmol 5)	Temp. (°C)	Time (h)	Yield ^a (%)	Intrinsic Viscosity ^b (dL g ⁻¹)	$\bar{M}_w$ (g mol ⁻¹)	PDI ^c
1	20	35	AMPD (10)	75-85	24	73 (88)	0.0707	16,500	2.2
2	10	35	AMPD (20)	75	14	69 (80)	0.0663	16,000	2.2
3	10	35	APS (140) ^d	100	0.5	35 (67)	0.0446	9,100	2.3
4	10	35	TBHP (25)	75-95	48	26 (64)	0.0574	—	—

^aIsolated yield precede the NMR yield in parentheses.

^bViscosity of 1-0.25 % in 1.0 M NaCl at 30 °C.

^cPolydispersity Index

^dInitiator was added onto the heated reaction mixture at 100 °C in four equal portions in every 2 min interval.

2.3.4 Measurement of critical salt concentration (CSC)

Water-solubility of PBZ **8** was determined in the presence of several salts at 23 °C. An 1% wt/wt of the polymer in the presence of sufficient concentration of a salt was titrated with deionized water to reach the first cloud point. The experiments were triplicated; the minimum CSC required to impart solubility was thus determined and found to accuracies of 1-2%.

2.3.5 Basicity constants (K)

The determination of basicity or protonation constant (*K*) of various basic centers has been detailed elsewhere [93,109]. A certain mmol of PBZ **8** and monomer **5** were dissolved in CO₂-free water (200 mL) and its pH value was recorded after each addition of 0.1 - 0.15 mL of titrant NaOH.

2.3.6 Antiscalant behavior of the synthesized polymer

Conductivity measurements were carried out as described [109]. The stock solutions of CaCl_2 and Na_2SO_4 were prepared using their anhydrous salts. A stock solution of PBZ **8** (1,000 ppm) was prepared by dissolving it water (2 mL) in the presence of a minimum amount of NaHCO_3 and thereafter diluting it in a volumetric flask. Two separate solutions at 40 ± 1 °C of $12,600 \text{ mg L}^{-1}$ (i.e. 12,600 ppm) SO_4^{2-} (60 mL) (containing 2x ppm PBZ **8**) and $5,200 \text{ mg L}^{-1} \text{ Ca}^{2+}$ (60 mL) were mixed and stirred (300 rpm) using a stir-bar in the absence (blank) and presence of various concentrations of PBZ **8** in the range 2.5-20 mg L^{-1} . The dilution now makes the resultant concentration of Ca^{2+} , SO_4^{2-} and antiscalant **8** as 2600, 6300 and x ppm, respectively. The conductivity of the solution was measured at 1 min after addition, and thereafter at every 10 min interval. The above solution is supersaturated with respect to CaSO_4 . A sudden and large decrease in conductivity, after a certain time called induction time, signals the formation of CaSO_4 (s) scale thereby decreasing the concentrations of the corresponding ions. The turbidity and crystal formation can be seen visually.

2.3.7 Corrosion inhibition of mild steel in 1 M HCl by the synthesized polymer8

Gravimetric weight-loss measurements were performed as described [110] using mild steel coupons of dimension of $2.5 \times 2.0 \times 0.1 \text{ cm}^3$ and elemental analysis (wt%) of 0.082 % (C), 0.032 % (Si), 0.062 % (Ni), 0.207 % (Mn), 0.016 % (Cr), 0.045 % (Al), 0.029 % (Cu), 0.042 % (W), 0.048 % (Sn), 0.017 % (Zn), ≈ 99.3 % (Fe) in 1 M HCl ((250 mL) in the absence (blank) and presence of (1, 3, 5, 10, 20, 50, 100, 150 and 200 ppm) of PBZ **8** at 60 °C for 6 h. Each test was triplicated and for the coupons of similar masses, the percent inhibition ($\% \eta$) was calculated using Equation (1):

$$\% \eta = \frac{W_{lb} - W_{li}}{W_{lb}} \times 100 \quad (1)$$

where W_{lb} and W_{li} represent weight-loss in the absence (blank) and presence of inhibitor, respectively. The average percent inhibition efficiency is found to have a standard deviation of 0.4–1.1%. In cases where the coupons are not of similar masses, the weight losses were calculated by a relative weight-loss method [110].

2.4 Results and discussion

2.4.1. Synthesis and characterization of monomer and polymer

A one-pot, two-step synthesis of diester **4** has been achieved in excellent yield of 82.5% *via* reaction of 2-Bromoethylamine hydrobromide salt **1** with ethyl bromoacetate, followed by alkylation of diallylamine **2** with the intermediate bromo aminoester **3** (Scheme 2.1). The ester functionalities in **4** was readily hydrolyzed to afford monomer **5** in 87% yield. Both ¹H NMR titration using known concentration of ethanol as well as elemental analysis established the monomer as a dihydrochloride salt. Bis-cationic monomer **5** underwent cyclopolymerization initiated by three different initiators, and the results are given in Table 2.1. Azo-initiator AMPD gave the best result yielding PBZ **8** in 88% as revealed by ¹H NMR spectrum of the crude mixture. However, the isolated yield was 73% after dialysis. Note that during dialysis, the initial formed poly(bis-cation) (PBC) **6** upon depletion of two equivalents of HCl afforded PBZ **8** *via* poly(zwitterion-cation) (PZC) **7** as evinced by elemental analyses (Scheme 2.1). The complete depletion of HCl cannot be assured as the SEM (the micrograph not shown) and EDX analysis revealed the presence of a minute amount of chloride, while the C/Cl atom ratio for monohydrochloride **7** is 12:1, EDX analysis revealed the ratio to be 12:0.006.

The pH at point of zero charge (pHPZC) was determined by a pH-drift method. The pHs of a series of a 0.1 M NaNO₃ (10 mL) were adjusted at certain values; then PBZ **8** (50 mg) was added and the mixtures were stirred for 6 h and the final pHs were recorded. The ΔpH (difference between initial and final pH) versus initial pH plot gave pHPZC value 3.85 which is the value at which ΔpH becomes zero (Fig. 2.1a). The PBZ **8** will have excess positive charge below pH 3.85, while it will have negative charge above 3.85.

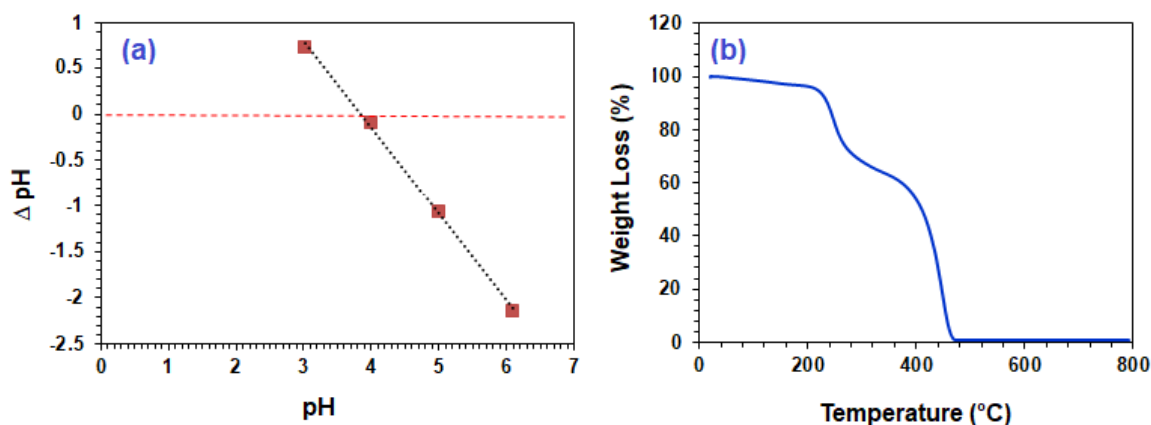


Figure 2.1(a) pH versus ΔpH plot to determine pH of point of zero charge for PBZ **8**; (b) TGA curves of PBZ **8**.

The TGA curve revealed that PBZ **8** is stable up to 200 °C with a 4% loss accounted for the removal of moisture (Fig. 2.1b). The two major losses of 31 and 61%, occurred in the temperature ranges 200 – 325 °C and 325 – 515 °C, respectively, were presumably attributed to the loss of pyrrolidine backbone and the pendant zwitterionic motifs. While monomer **5** has IR bands at 1757 and 1735 cm⁻¹ attributed to the C=O stretch of monomeric and dimeric CO₂H, respectively, the bands at 1394 and 1632 cm⁻¹ were assigned to the symmetric and anti-symmetric stretching [111] of COO⁻ in the zwitterionic form of PBZ **8**. The presence of a minor band at 1724 cm⁻¹ could be accounted for the presence of CO₂H arising out of the equilibration: $\text{--NH}^+\text{CH}_2\text{CO}_2^- \rightleftharpoons \text{--NCH}_2\text{CO}_2\text{H}$.

The ¹H and ¹³C NMR spectra are displayed in respective Figs. 2.2 and 2.3. Upon polymerization, the signals for alkene protons [Fig. 2.2(a)] and alkene carbons [Fig. 2.3(a)] in monomer **5** have disappeared in the respective spectra Fig. 2.2(b) and Fig. 2.3(b) of PBZ **8**. No residual alkene signals can be found either in the ¹H or ¹³C spectrum as a result of the chain termination *via* abstraction of allylic proton [112] in monomer **5** and/or coupling [113]. The presence of two signals for each carbon marked ‘a’ and ‘b’ confirms the presence of *cis*- and *trans*-substituents on the ring in an approximate ratio of 3:1 [114,115].

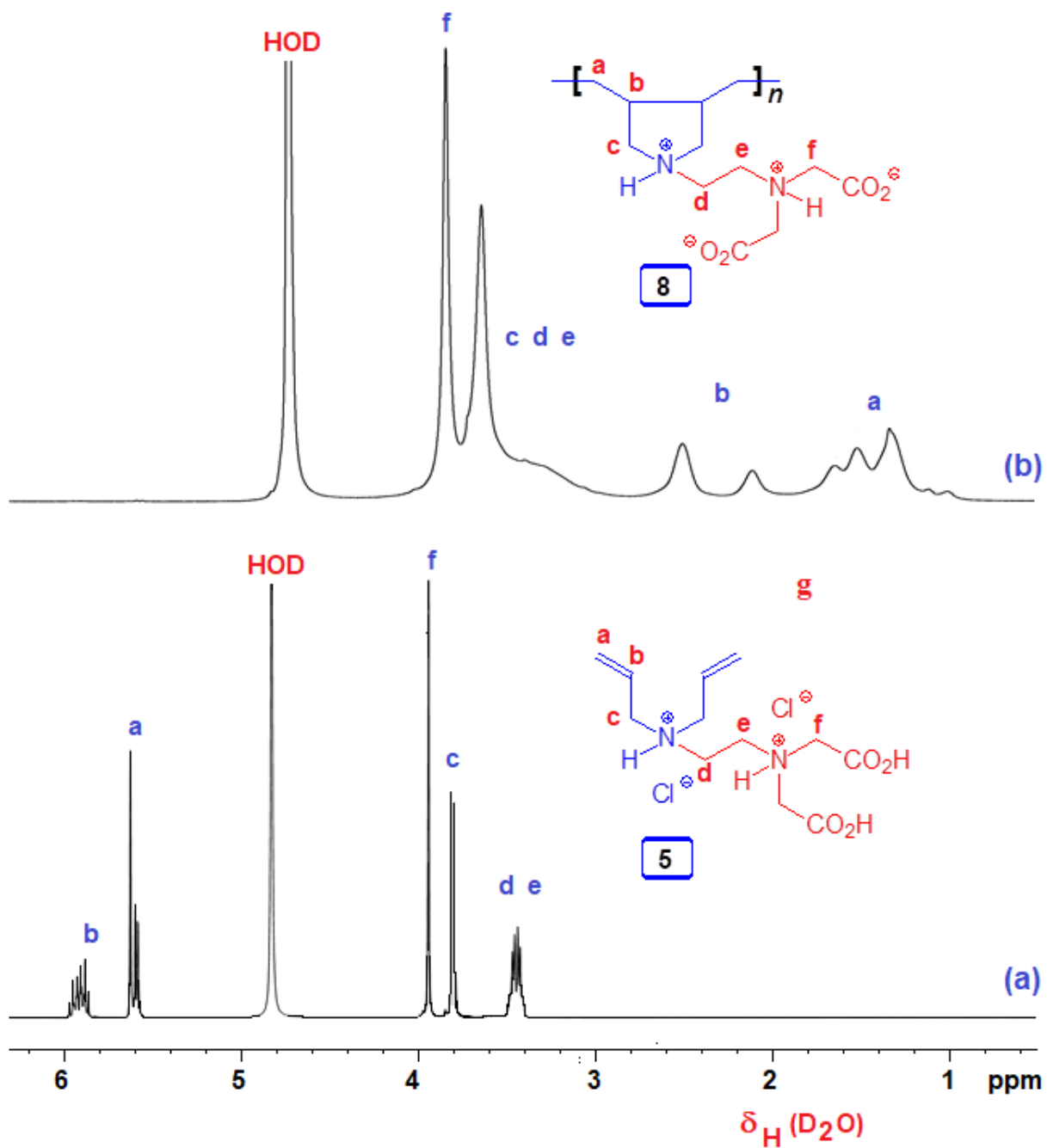


Figure 2.2 ^1H NMR (400 MHz) spectra of (a) monomer 5 and (b) PBZ 8 in D_2O at 23 $^\circ\text{C}$.

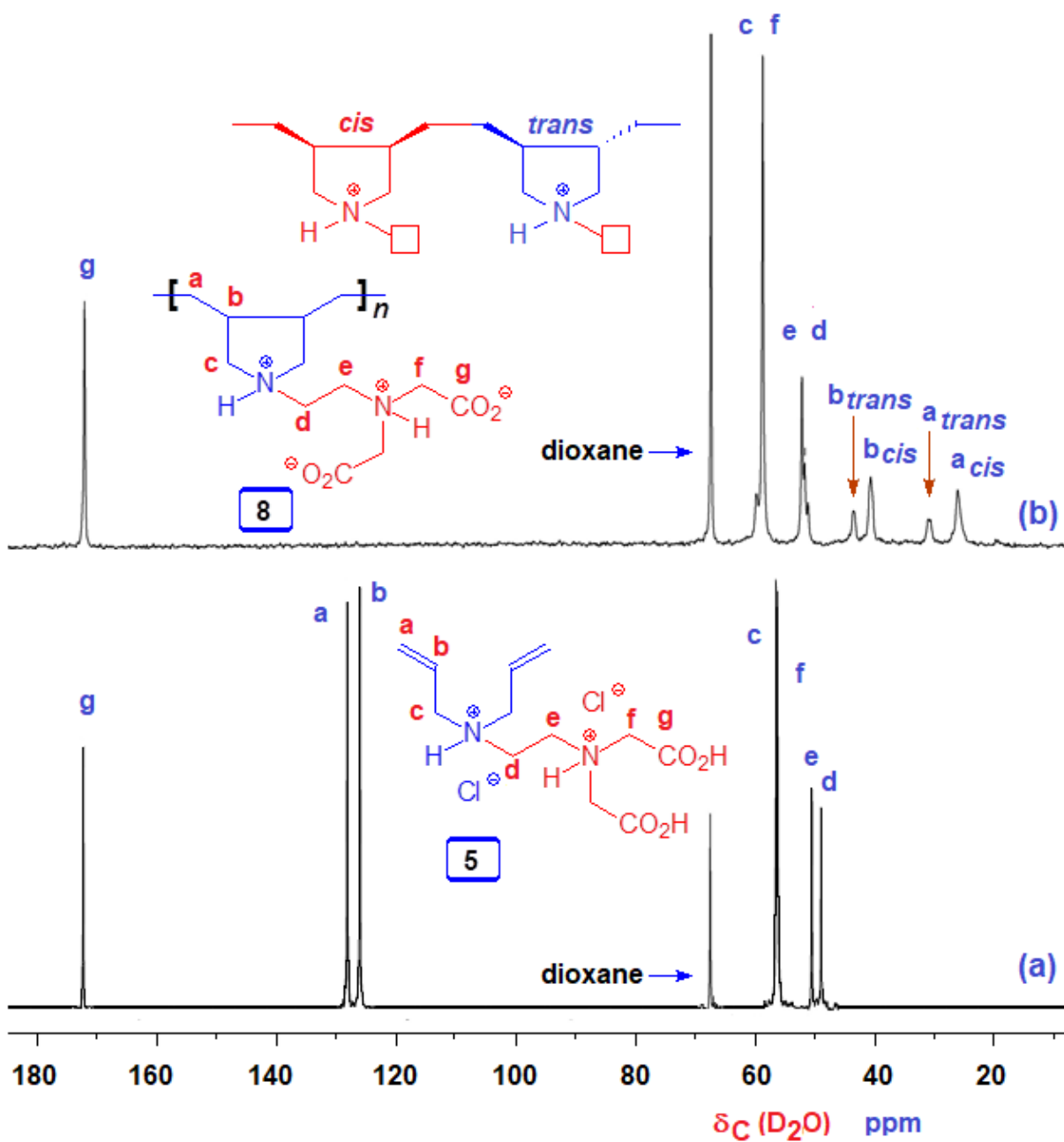


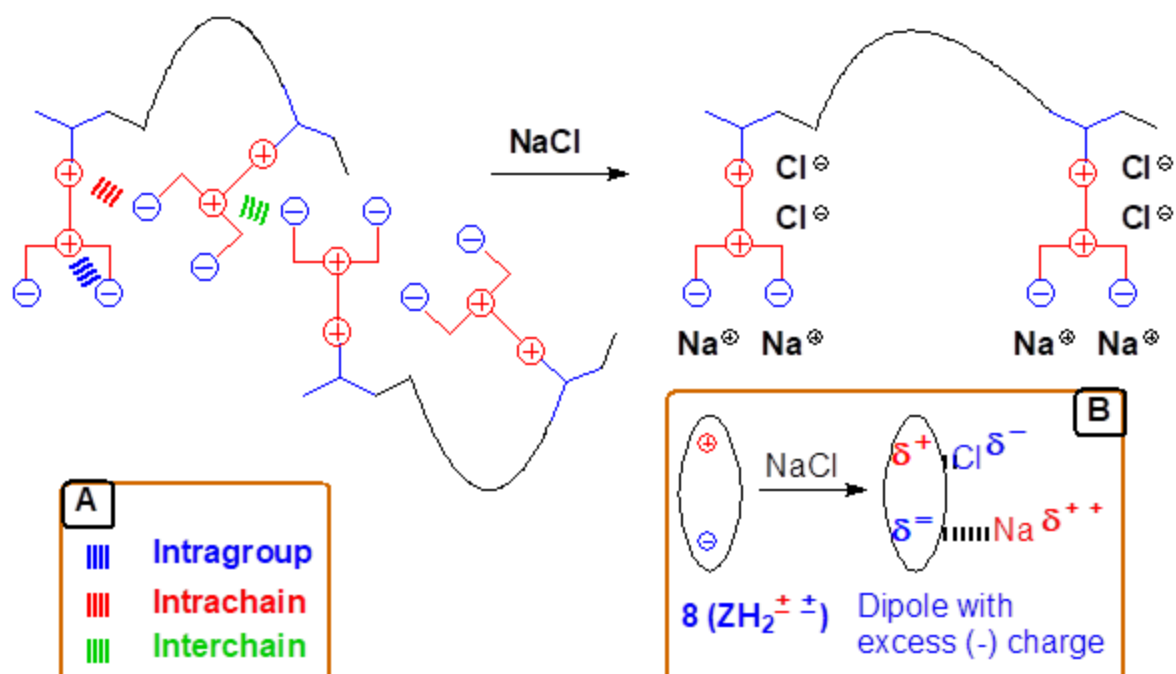
Figure 2.3 ^{13}C NMR (100.57 MHz) spectra of (a) monomer 5 and (b) PBZ 8 in D_2O at 23 °C.

Polymers containing amine and carboxyl functionalities tend to stick to the GPC columns strongly [116]. Attempts to obtain the molar mass of water-insoluble PBZ **8** at higher pH values (to make water-soluble species of PZA **9**) by GPC gave erratic results. However, PBZ **8** becomes water-soluble in 0.5 M NaCl; the presence of salt allows the screening of the positive charges in order to minimize ionic interactions and allow the polymer chains to form random coils. The $\bar{M}_w$ and PID values of the synthesized polymers are given in Table 2.1. The polymer from entry thus have $\bar{M}_n$, $\bar{M}_w$ and PID values of 7,500, 16,500 g mol⁻¹ and 2.2, respectively. The polymer has low viscosity value thereby suggesting its low molar mass. Taking approximate K and ' α ' value as 1.12×10⁻⁴ dL g⁻¹ and 0.73, the molar mass $\bar{M}_v$ for entry 1 (Table 2.1) sample was calculated to be $\approx$ 7,000 g mol⁻¹ using Mark-Howink equation ($[\eta] = KM^a$) [117].

2.4.2. Solubility behavior

PBZ **8** was found to be water-insoluble [118,119], however it became water-soluble in the presence of various salts. The polyelectrolytes are in most cases water-insoluble because of strong intragroup, intra- and inter-chain interactions of the zwitterionic dipoles (Scheme 2.2, Box A) [97]. The neutralization of ionic charges leads the polymer chain to adopt globular conformation, thereby decreasing its hydrophilicity. However, these zwitterionic interactions could be disrupted in the presence of salt like NaCl, whereby Cl^- ions bind strongly to neutralize the positive nitrogen centers (Scheme 2.2). The corresponding neutralization of negative CO_2^- by Na^+ is not as effective because of its large hydration shell which impedes its approach close enough to the CO_2^- . Unequal neutralization of the dipole leaves a residual negative charge in the dipolar motifs (Scheme 2.2, Box B), which leads to repulsion and increased hydrodynamic volume, hydrophilicity, water-solubility, and viscosity of the bis-zwitterion.

CSC required to promote water-solubility of 1 wt% PBZ **8** by NaCl, NaBr, NaI, HCl, and CaCl_2 were determined to be 0.342, 0.194, 0.0803, 0.0173, 0.509 M, respectively (Table 2.2).



Scheme 2.2 Intragroup, intra- and interchain zwitterionic interactions in PBZ 8 and their disruptions in the presence of NaCl.

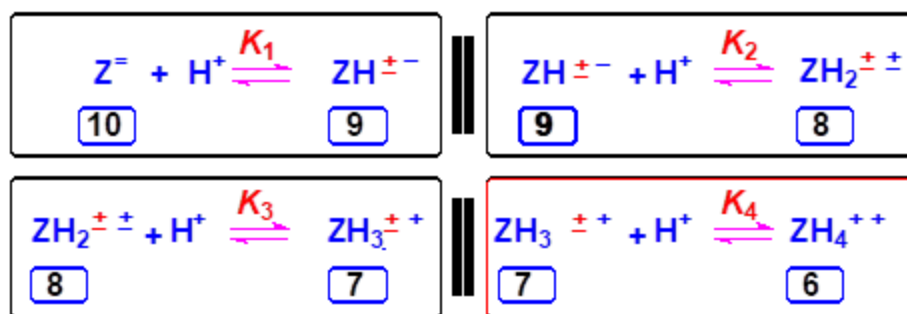
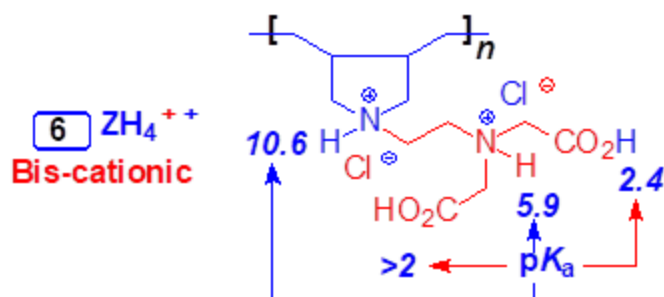
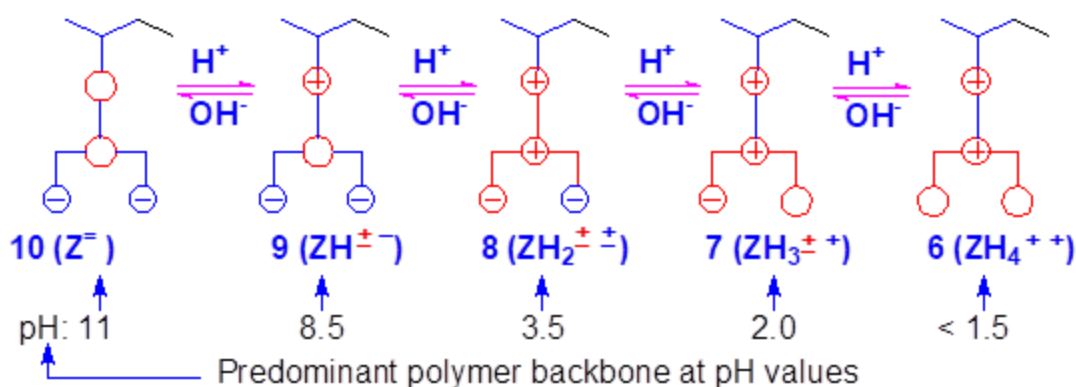
Table 2.2 Critical Salt Concentration required for water-solubility of PBZ 8 at 23 °C.

Salt	CSC (M)
NaCl	0.342
NaBr	0.194
NaI	0.0803
HCl	0.0173
CaCl ₂	0.509

The most polarizable Γ^- is the most effective ion in disrupting the zwitterionic interactions thereby promoting water-solubility in 0.0803 M NaI. The presence of cationic units and depletion of zwitterionic motifs promotes water-solubility. Note that Ca^{2+} usually precipitates anionic polyelectrolytes, however it promoted water-solubility of PBZ **8**.

pH-dependent dynamic equilibria involving polymers **6-10** having different charge types (Scheme 2.1) are described in Scheme 2.3. Note the poly(bis-cation) (++) **6** having four acidic protons is denoted as ZH_4^{++} , while deprotonation of all exchangeable protons leads to poly(bis-anion) **10** depicted as Z^- . Apparent pK_a values (*vide infra*) of all four acidic centers are approximated to be 10.5, 5.9, 2.4 and < 2 as depicted on the structure of ZH_4^{++} (Scheme 2.3). The polymer backbones of **6-10** are approximated to be predominant at pH values of < 1.5 , 2.0, 3.5, 8.5 and 11, respectively, as calculated from their pK_a values (*vide infra*).

The solubility in 0.0173 M HCl (pH 1.76) has to be dealt within the context of PBZ **8** ($\text{ZH}_2^{\pm}$) + $\text{H}^+ \rightleftharpoons \text{PZC } 7$ ($\text{ZH}_2^{\pm+}$) equilibrium (Scheme 2.3). A solution of PBZ **8** (100 mg) in 0.5 M NaCl (200 mL) was found to have a pH of 4.05. Titration with 0.1026 M HCl revealed that the solution became cloudy at a pH of 3.03 and clear at 1.87. In the absence of NaCl, in a similar experiment, PBZ **8** was found to be water-insoluble in the pH-range 2.15-3.93. At pHs below 2.15 and above 3.93, the polymer remains soluble because of increasing participation of PBC (++) **6** and poly(zwitterion/anion) (PZA) ($\pm -$) **9**, respectively, in the pH- responsive equilibria (Scheme 2.3). At pH 2.15, the degree of protonation (α) for the dominant equilibrium: $\text{PZC } 7$ ($\text{ZH}_3^{\pm+}$) + $\text{H}^+ \rightleftharpoons \text{PBC } 6$ (ZH_4^{++}) was calculated to be 0.10. Therefore, for solubility, the polymer backbone must contain ≥ 10 mol% repeating units in the bis-cationic form of PBC **6**. Likewise, at pH 3.93, the calculated α value of 0.83 for the dominant equilibrium $\text{PZA } 9$ ($\text{ZH}^{\pm-}$) + $\text{H}^+ \rightleftharpoons \text{PBZ } 8$ ($\text{ZH}_2^{\pm\pm}$), suggest that for solubility, the polymer backbone must contain ≤ 83 mol% repeating units in the bis-zwitterionic form of PBZ **8**. More than 83 mol% bis-zwitterionic form thus leads to insolubility. In summary, PBC (++) **6**, PZA ($\pm -$) **9**, PBA ($--$) **10** are water-soluble, while PBZ ($\pm \pm$) **8** and PZC ($\pm +$) **7** are water-insoluble.



$$\log K_i = \text{pH} - \log [(1 - \alpha)/\alpha] \quad (2)$$

$$\text{pH} = \log K_i^0 + n_i \log [(1 - \alpha)/\alpha] \quad (3)$$

$$\log K_i = \log K_i^0 + (n_i - 1) \log [(1 - \alpha)/\alpha] \quad (4)$$

$\log K_i$ of protonation constant of base = pK_i of the conjugate acid

Scheme 2.3 pH-induced changes in the charge types and densities in the backbone of 6-10 and protonation constants (K_i) of the basic centers.

2.4.3. Basicity Constant

The pH versus $\log[(1-\alpha)/\alpha]$ gave the intercept value (where $\alpha = 0.5$) as $\log K^0$ and slope as n as per Henderson–Hasselbalch Equations (2-4) (Scheme 2.3). Here, n describes the deviation of K with the α ; for small molecule like a monomer, $n = 1$, whereas any deviation from 1 would indicate the ‘apparent’ nature of the basicity constant; $n > 1$ and < 1 describes the progressive decrease and increase of the basicity constant with increasing α (Scheme 2.3, Equation (4)). Unlike a monomer, the protonation tendency of a basic centre in a repeating unit is influenced by its immediate neighbor as well as the overall α . An already protonated center would usually discourage the protonation of its neighbor since the average electron density, which encourages protonation, decreases as α increases.

For the polymer, $\log K^0_1$ and $\log K^0_2$ for the ring-nitrogen in PDE **10** and pendant-nitrogen in PZA **9** were determined to be 10.57 and 5.89, respectively (Scheme 2.3, Table 2.3), with the corresponding n_1 and n_2 values of 0.57 and 2.08. Log K of a basic center is the pK of the conjugate acid. As such, $\log K^0$ values of 10.57 and 5.89 were assigned to the pK of the ring NH^+ and pendent NH^+ , respectively. The pendent nitrogen attached to the $(\text{CH}_2\text{CO}_2^-)_2$ is expected to have greater acidity owing to the adjacent electron-withdrawing motifs. Log K^0_3 could not be determined because of insolubility of polymer PBZ ($\pm \pm$) **8**. Log K^0_4 involving the protonation of the weakest basic CO_2^- was not determined since it would require a large volume of HCl solution to protonate the CO_2^- to a meaningful extent.

Table 2.3 Protonation of PBZ 8 ($\text{ZH}_2^{\pm\pm}$) and monomer 5 (ZH_4^{++}) in salt-free water at 23 °C.

run	$\text{ZH}_2^{\pm\pm}$ (mmol)	C_T^a (mol dm ⁻³)	α -range	pH-range	Points _b	Log $K_i^{\circ c}$	n_i^c	$R^2,^d$
PBZ 8 ($\text{ZH}_2^{\pm\pm}$)								
1	0.3121($\text{ZH}_2^{\pm\pm}$)	0.1016	0.73-0.089	4.93-8.01	17	5.90	2.11	0.999
2	0.3902 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.73-0.10	4.81-7.65	18	5.84	2.07	0.992
3	0.4682 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.06-0.18	4.94-7.57	21	5.92	2.07	0.997
Average						5.89 (4)	2.08 (2)	
Log $K_2^e = 5.89 + 1.08 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^{\pm\pm}$								
1	0.3121($\text{ZH}_2^{\pm\pm}$)	0.1016	0.93-0.32	9.80-10.6	13	10.46	0.566	0.994
2	0.3902 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.89-0.31	10.09-10.	14	10.67	0.611	0.997
3	0.4682 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.94-0.18	9.90-10.8	16	10.57	0.540	0.995
Average						10.57 (11)	0.57 (4)	
Log $K_1^e = 10.57 - 0.43 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^- + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								
Monomer 5 (ZH_4^{++})								
1	0.3037 (ZH_4^{++})	0.1016	0.42-0.14	2.62-3.28	13	2.42	1.04	0.981
2	0.3645 (ZH_4^{++})	0.1016	0.44-0.11	2.55-3.42	13	2.43	1.08	0.993
Average						2.42 (1)	1.06 (3)	
Log $K_3^e = 2.42 + 0.06 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_2^{\pm\pm} + \text{H}^+ \xrightleftharpoons{K_3} \text{ZH}_3^{\pm+}$								
1	0.3037 (ZH_4^{++})	0.1016	0.90-0.16	4.19-5.95	11	5.11	1.03	0.9909
2	0.3645 (ZH_4^{++})	0.1016	0.94-0.18	4.21-5.70	13	5.08	1.04	0.9978
Average						5.10 (2)	1.04 (1)	
Log $K_2^e = 5.10 + 0.06 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^{\pm\pm}$								
1	0.3037 (ZH_4^{++})	0.1016	0.92-0.31	9.27-10.6	11	10.29	0.969	0.989
2	0.3645 (ZH_4^{++})	0.1016	0.94-0.24	9.15-10.8	13	10.32	0.971	0.997
Average						10.30 (2)	0.970	0.995
Log $K_1^e = 10.30 - 0.03 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^- + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								

^a Titration with NaOH. ^b Data points used. ^c Parentheses include the standard deviations in the last digit. ^d R = Correlation coefficient. ^e $\log K_i = \log K_i^{\circ} + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

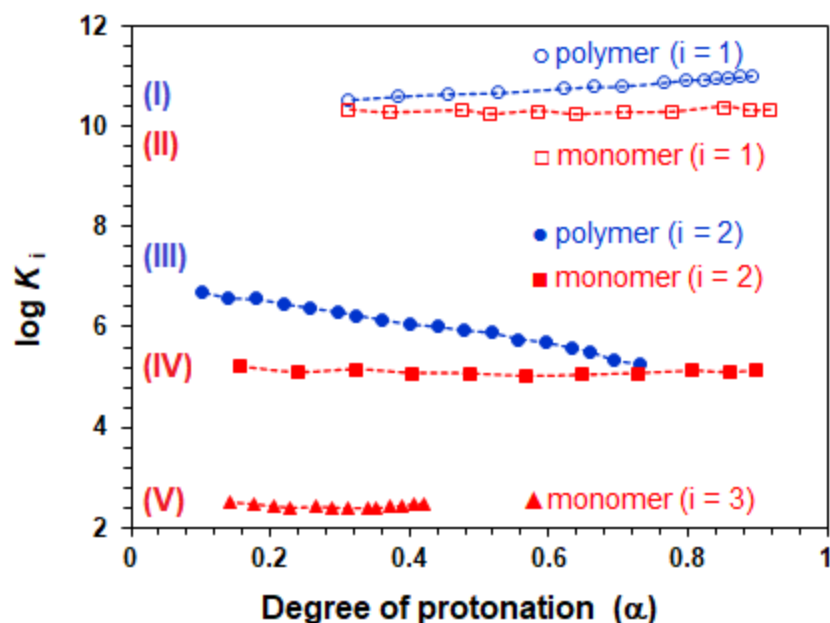
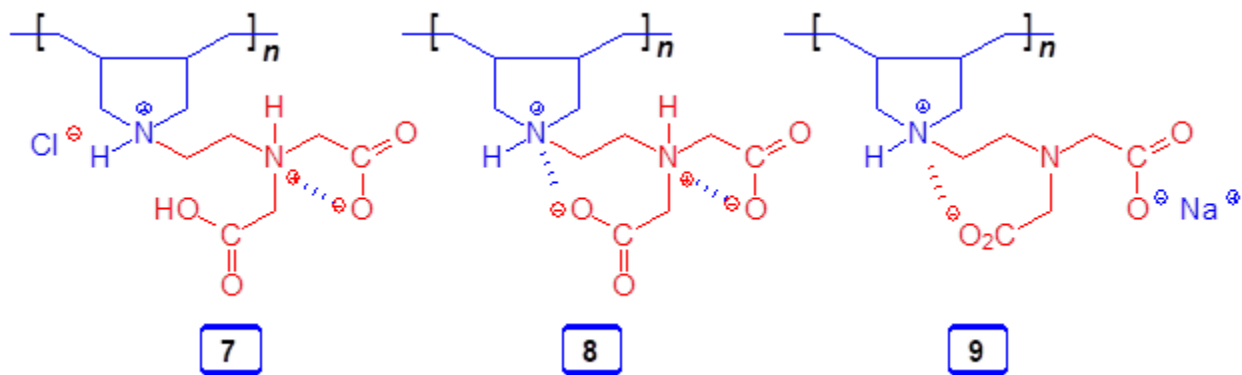


Figure 2.4 Plot for the apparent $\log K_i$ versus degree of protonation (α) in salt-free water for (I) $\circ$ PBZ 8 ($i = 1$) ($\log K_1$), (II) $\square$ monomer 5 ($i = 1$) ($\log K_1$), (III) $\bullet$ PBZ 8 ($i = 2$) ($\log K_2$), (IV) $\blacksquare$ monomer 5 ($i = 2$) ($\log K_2$), and (V) $\blacktriangle$ monomer 5 ($i = 3$). [Data for runs 2, Table 3].



Scheme 2.4 Zwitterionic interactions in PZC 7, PBZ 8 and PZA 9.

The variation of $\log K_1$ versus α plot (Fig. 2.4 I) demonstrates the increase of basicity with progressive increase of α as dictated by $n_1 < 1$. Transformation of PBA (=) **10** to PZA **9** ($\pm -$) is an entropy-driven process [120]. The dipolar motifs in PZA **9** ($\pm -$) is separated by six σ bonds between NH^+ and O^- (Scheme 2.4). Increased distance would lead to increased dipole moment, hence increased hydrophilicity and hydration [92,121,122]. Thus, with each protonation of PBA (=) **10**, the average number of water molecules per repeating unit increases. The progressive protonation would lead to release of greater number of water molecules of hydration, thereby leading to an entropy-driven increase of $\log K_1$ values with increasing α [123,124]. For the transformation of PZA **9** ($\pm -$) to PBZ **8** ($\pm \pm$), the latter would demonstrate strong zwitterionic interactions, where the intervention of only three σ bonds in between the charge centers of the newly formed dipolar motifs would lead to a decreased dipole moment, hence increased hydrophobicity. Average number of water molecules per each repeating unit will be lesser and lesser with increasing α , thereby $\log K_2$ will be decreased with the progressive formation of a collapsed-coil conformation in for PBZ **8** ($\pm \pm$) (Fig. 2.4 III). It makes sense since **8** is so hydrophobic that it becomes water-insoluble. The $\log K^0_1$, $\log K^0_2$ and $\log K^0_3$ for monomer **5** (++) were found to be 10.3, 5.1 and 2.42, respectively, with n values of close to unity as expected for a small molecule (Table 2.3). As expected, $\log K^0$ s remain constant with the increase of α (Fig. 2.4 II, IV, V). Note that $\text{p}K_1$ for ring NH^+ and $\text{p}K_2$ for pendant NH^+ and $\text{p}K_3$ for one of the CO_2H are thus determined to be 10.3, 5.1 and 2.42, respectively. $\text{p}K_4$ for the remaining most acidic CO_2H was not determined since it would require a large volume of HCl solution to protonate the weakly basic CO_2^- .

2.4.4. Measurement of Viscosity

Viscosity plots of PBZ **8** (entry 1, Table 2.1) are displayed in Fig. 2.5. Increase of viscosity with the increase of NaCl concentrations demonstrate the anti-polyelectrolyte effect owing to the presence of zwitterionic motifs ((Fig. 2.5 (e) vs. (f)). As discussed earlier (*vide supra*), with increasing NaCl concentrations, the charge imbalance in favour of the negative charge in the electroneutral PBZ **8** increases owing to greater neutralization of the positive charges by Cl⁻ ions as compared to Na⁺ ions neutralizing CO₂⁻ (Scheme 2.2) [125].

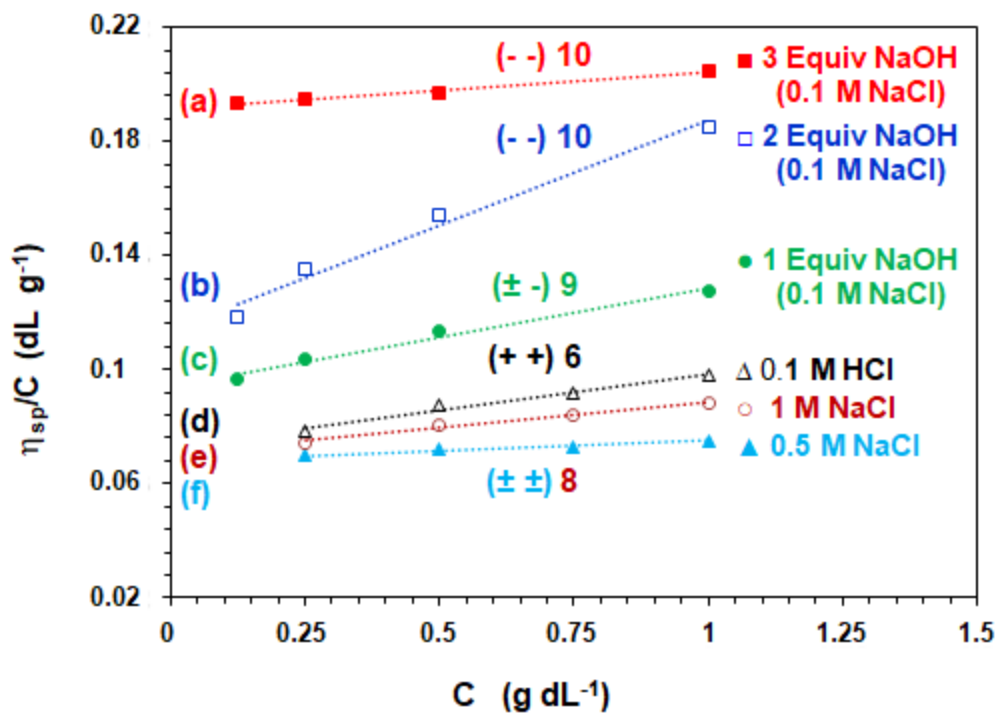


Figure 2.5 The viscosity behavior at 30 °C of PBZ 8 in (a) $\blacksquare$ 0.1 M NaCl + 3 equivs NaOH, (b) $\square$ 0.1 M NaCl + 2 equivs NaOH, (c) $\bullet$ 0.1 M NaCl + 1 equiv NaOH, (d) $\triangle$ 0.1 M HCl, (e) $\circ$ 1.0 M NaCl, and (f) $\blacktriangle$ 0.5 M NaCl.

The increase in NaCl concentrations enhances the residual (-)ve charge on the dipole thereby increasing repulsion, hydrodynamic volume, hence the viscosity. The viscosity value of PBZ 8 in 0.1 M HCl, where it is likely to be present as PBC 6, is found to be higher than in 0.5 and 1 M NaCl (Fig. 2.5d). In the presence NaOH (1, 2 and 3 equivalents), the viscosity values increase because of increasing presence of anionic motifs in the polymer backbone ((Fig. 2.5 (a)-(c)) as a result of participation of PZA 9 ($\pm -$) and poly(bis-anion) (PBA 10) (=) (Schemes 2.1 and 2.3). While the electroneutral PZB 8 has minimum excluded volume and collapsed coil conformation, the charge imbalances in 9 and 10 and their magnitudes lead to increasing excluded volumes, hence increasing viscosity values [126,127].

2.4.5. Scale inhibition study

Membrane fouling in a RO plant, in which an inlet feed produces pure water (30%) and reject brine (70%), results from the deposition of CaSO_4 and CaCO_3 , etc. as a result of supersaturation of the corresponding ions in the concentrated reject brine. A 30-min residence time in the osmosis chamber has to be negotiated with the help of an antiscalant to mitigate scale formation. A supersaturated solution containing three times the concentration of Ca^{2+} , and SO_4^{2-} , found in the reject brine of a local RO plant [128], was examined using conductometry in the absence and presence of various concentrations (2.5 – 20 ppm) of the as-synthesized PBZ **8**. A sudden decrease of conductance, after an induction time, indicates the depletion of the ions with the formation of $\text{CaSO}_4(\text{s})$ as can also be observed visually (Fig. 2.6). The percent scale inhibition (PSI) (Equation (5)) at various times and induction times are given in Table 2.4. The ionic conductance is reflective of ionic concentration. Even at a meagre concentration of 2.5 ppm of PBZ **8** (entry 5, Table 2.4), the PSI was found to be $\approx 100\%$ for a duration of 30 min. At higher concentrations, both PSI and induction times increase significantly. Note that, like the blank, immediate precipitation resulted in the presence of 20 ppm of monomer **5**.

$$\text{PSI} = \frac{[\text{Ca}^{2+}]_{\text{inhibited}}(t) - [\text{Ca}^{2+}]_{\text{blank}}(t)}{[\text{Ca}^{2+}]_{\text{inhibited}}(t_0) - [\text{Ca}^{2+}]_{\text{blank}}(t)} \times 100 \quad (5)$$

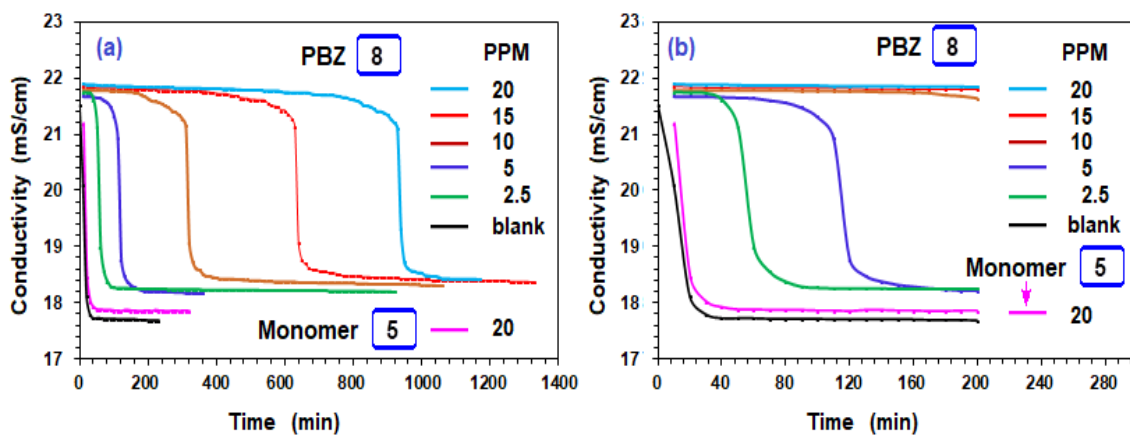


Figure 2.6 (a) Conductivity of a supersaturated solution of CaSO_4 in the presence (2.5, 5, 10, 15, 20 ppm) of PBZ 8 and monomer 5 (20 ppm) and in the absence (blank) of antiscalant and (b) same plot for a shorter scale of 200 min.

The significant antiscalant activity of the polymer is attributed to its ability to complex with Ca^{2+} and keep it in solution. At the time of nucleation of crystal, an antiscalant is adsorbed on the surface and change its morphology and hinders further growth, thereby preventing scale-growth [129-131].

Table 2.4 Scale inhibition using PBZ **8** and monomer **5** in a supersaturated CaSO_4 solution at 40 °C.

Entry	Sample (ppm)	Percent inhibition at times (min) of						Induction time (min)
		30	60	120	180	300	360	
PBZ 8								
1	20	100	99	99	99	98	98	900
2	15	100	99	99	99	98	98	570
3	10	100	100	100	98	88	–	300
4	5	100	99	27	14	–	–	90
5	2.5	100 ^b	32	14	–	–	–	45
Monomer 5								
6	20	6	4	–	–	–	–	5

^aThree times the concentration of Ca^{2+} and SO_4^{2-} in the reject brine of a RO plant.

^bThe percent inhibition at 40 and 50 min are 97 and 84%, respectively.

2.4.6. PBZ **8** as a corrosion inhibitor

The results of the corrosion inhibition tests by gravimetric weight-loss method are given in [Table 2.5](#). Note that the method adapted is the simplest yet most reliable as it examines the weight loss for a longer duration of 6 h as compared to shorter time taken to carry out corrosion inhibition tests by electrochemical techniques. As evinced from the Table, inhibition efficiency ($\eta\%$) increases with the increase in the inhibitor concentrations, while it becomes asymptotic after 10 ppm of PBZ **8**, confirming the completion of the surface coverage. The results are highly gratifying as a meagre concentration of 10 ppm gave a $\eta\%$ 90, while at 100 ppm it became 96. Iodide ions are known to boost inhibition efficiency, as such inhibition test carried out using a mixture of 20 ppm PBZ **8** and 800 ppm KI gave a protection of 99%, while the polymer and KI alone gave $\eta\%$ of 90 and 44, respectively. The synergism parameter S_θ is calculated using Equation (6) [132]:

$$S_\theta = \frac{1 - (\theta_1 + \theta_2 - \theta_1\theta_2)}{1 - \theta_{1+2}} \quad (6)$$

where θ_1 and θ_2 are the degree of surface coverages which are equated to fractional inhibition efficiencies ($\eta\%/100$) of PBZ **8**, and iodide ions, respectively, while θ_{1+2} is the degree of surface coverage of PBZ **8** + KI mixture. Generally, $S_\theta > 1$ and < 1 signify cooperative co-adsorption (i.e. synergistic effect) and competitive co-adsorption (i.e. antagonistic effect), respectively [132,133]. The S_θ value was calculated to be 7.11 thereby implying that the polymer+KI mixture demonstrates synergistic effect in the mitigation of corrosion of mild steel.

Table 2.5 Inhibition efficiency (IE) ($\eta\%$) imparted by PBZ **8** to arrest corrosion of mild steel in 1 M HCl at 60 °C for an immersion time of 6 h.

Entry	Sample (ppm)	KI (ppm)	IE ($\eta\%$)
PBZ 8			
1	1	–	11.1 $\pm$ 1.1
2	3	–	44.5 $\pm$ 0.7
3	4	–	57.2 $\pm$ 0.7
4	5	–	70.1 $\pm$ 0.5
5	10	–	89.9 $\pm$ 0.1
6	20	–	90.4 $\pm$ 0.4
7	50	–	93.0 $\pm$ 0.8
8	100	–	95.9 $\pm$ 0.2
PBZ 8 and KI			
9	–	800	41.4 $\pm$ 1.3
10	20	800	99.1 $\pm$ 0.4
Monomer 5			
11	5	–	35.9 $\pm$ 1.3
12	10	–	53.6 $\pm$ 1.1

Note that, at 10 ppm concentration, PBZ **8** performed much better than its monomer **5** imparting inhibition efficiency ($\eta\%$) of 89.9 and 53.6, respectively ([Table 2.5](#)). Two things work in favor of the polymer: (i) energetically unfavorable entropy-loss for the adsorption of monomer is much greater than that of the polymer and (ii) in the adsorption $\rightleftharpoons$ desorption equilibrium, the polymer greatly favors the adsorption process since its multiple adsorption sites lock onto the metal surface resist desorption.

The surface coverage (θ) data in the concentration range 1-10 ppm were fitted into several isotherm models listed below and the linear plots are shown in [Fig. 2.7](#).

$$\text{Temkin:} \quad K_{ads} C = e^{f\theta} \quad (7)$$

$$\text{Langmuir:} \quad \frac{\theta}{1-\theta} = K_{ads} C \quad (8)$$

$$\text{Frumkin [134]:} \quad K_{ads} C = \frac{\theta}{1-\theta} e^{-2a\theta} \quad (9)$$

$$\text{Freundlich [135]:} \quad \theta = K_{ads} C^n \quad (10)$$

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G^0_{ads}}{RT}} \quad (11)$$

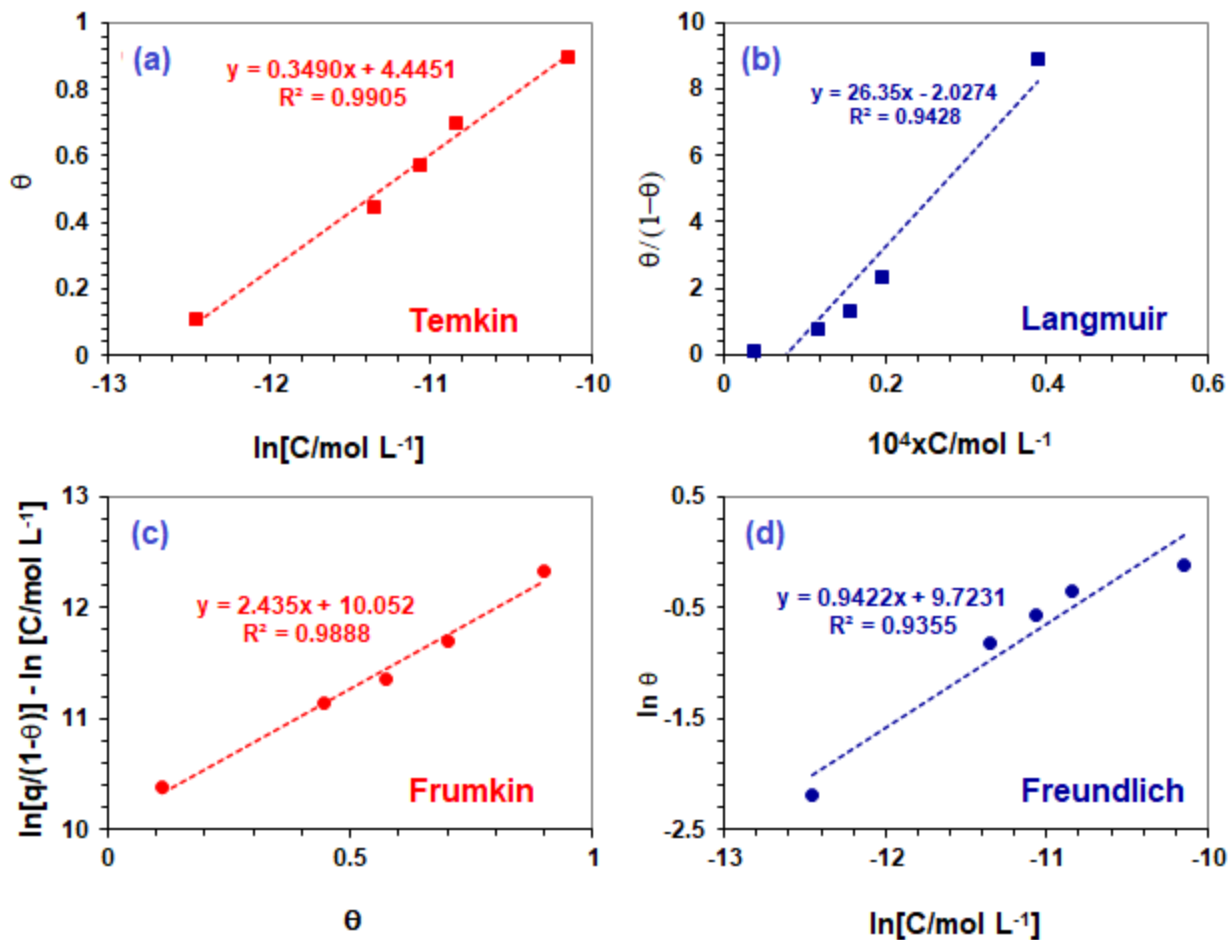
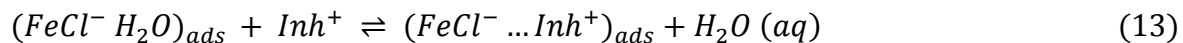
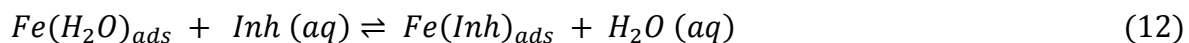


Figure 2.7 (a) Temkin, (b) Langmuir, (c) Frumkin, and (d) Freundlich adsorption isotherms of PBZ 8 in 1 M HCl at 60 °C.

The C denotes concentration in mol L^{-1} , K_{ads} is the adsorption equilibrium constant. The R^2 values indicate that the data fitted Temkin and Frumkin isotherms well (Fig. 2.7). From the slope $(1/f)$ and intercept $(1/f)\ln K_{\text{ads}}$, the f and K_{ads} were found to be 2.87 and $3.40 \times 10^5 \text{ L mol}^{-1}$, respectively. The

free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$), calculated using Equation (11), where 55.5 is the molar concentration of water in solution [134] was found to be $-46.4 \text{ kJ mol}^{-1}$. The factor 55.5 arises from the fact that the adsorption of an inhibitor (Inh) at a metal/aqueous interface may result from the displacement of the adsorbed water molecules (Equation (12)) and/or consecutive adsorption of Cl^- and cationic inhibitor (Inh^+) (Equation (13)) on the metal surface with the subsequent entrainment of water coverage [136]:



While $\Delta G^{\circ}_{\text{ads}}$ value less negative than -20 kJ mol^{-1} is attributed to physisorption on the metal surface, the current value may be attributed to the prevalence of both electrostatic adsorption and chemisorption [137,138]. While physisorption would correspond to the adsorption of cationic motifs of the polymer on the layer of Cl^- ions covering the Fe-surface, the interaction of carboxyl motifs with the d-orbitals of iron or accumulated Fe^{2+} on the anodic sites to form coordinate type of bond. The low value (2.87) for the molecular interaction constant f signifies that the columbic repulsive forces between positive nitrogen are not significant [139]. The small and positive value of 1.22 for attraction constant ' a ' extracted from the

Frumkin isotherm (Fig. 2.7) provides evidence of mutual attraction between adsorbed organic molecules [140], the negative values would have signified repulsion.

2.5 Conclusions

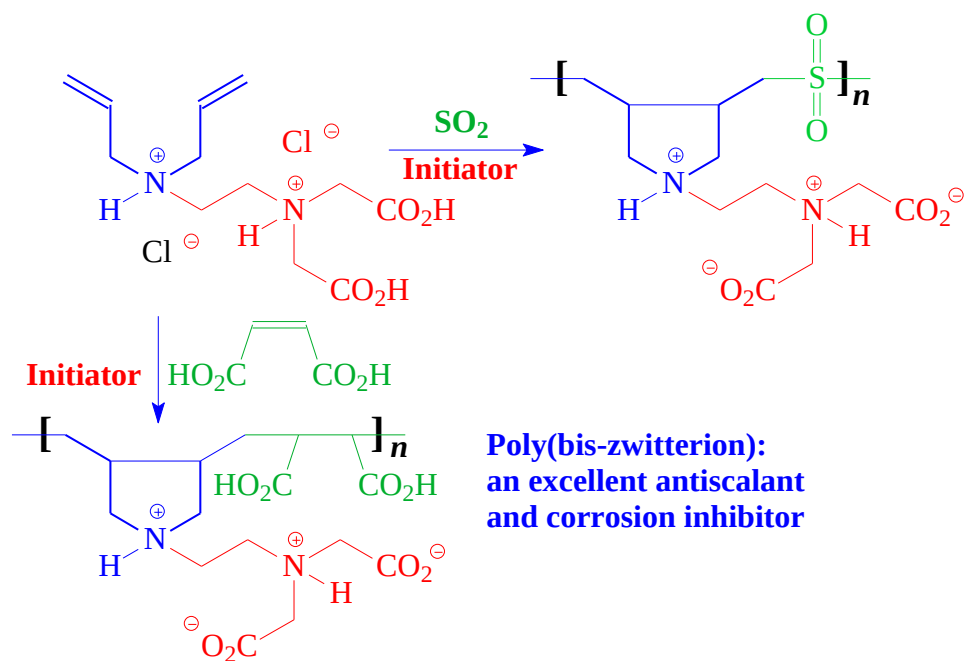
Commercially available, 2-bromoethylamine hydrobromide **1**, in a one-pot, two-step reaction involving ethyl bromoacetate and diallylamine afforded monomer precursor **4** (82.5%), which upon ester hydrolysis gave bis-cationic diallylamine salt monomer **5**, containing residue of chelating motifs of *N*-(2-aminoethyl)iminodiacetic acid, in excellent yield (87%). Monomer **5** upon cyclopolymerization initiated by azoinitiator AMPD gave PBZ **8**, a unique polymer having bis-zwitterionic motifs in each repeating unit. The polymer is water-insoluble, but soluble in the presence of salts like NaCl, NaBr, NaI, CaCl₂; - the CSCs were determined to be 0.342, 0.194, 0.0803, and 0.509 M, respectively. PBZ **8** displayed antipolyelectrolyte behavior (a manifestation of zwitterionic interactions) as its viscosity increased with the increase in salt (NaCl) concentrations. PBZ **8** with pHPZC at 3.85 was found to be water-insoluble in the pH-range 2.15-3.93, where bis-zwitterionic motifs ($\pm \pm$) predominates in the polymer chain. In either side of the pH-window, the polymer remains soluble because of increasing participation of cationic and anionic motifs in the pH-responsive equilibria: $(+ +) \mathbf{6} \rightleftharpoons (\pm +) \mathbf{7} \rightleftharpoons (\pm \pm) \mathbf{8} \rightleftharpoons (\pm -) \mathbf{9} \rightleftharpoons (=) \mathbf{10}$. The ‘apparent’ pK_a of two cationic centers involving NH⁺ in **8** and **9** was determined to be 5.89 and 10.57, respectively. PBZ **8** was found to be an excellent antiscalant to inhibit scale formation; at a concentration of 2.5 ppm, it imparted $\approx$ 100% inhibition of CaSO₄(s) scale formation from its super-saturated solution for 30 min which is the usual residence time of brackish water in the reverse osmosis chamber. Interestingly, PBZ **8** at a concentration of 20 ppm in the

presence of KI imparted synergistic 99% inhibition of mild steel corrosion in 1 M HCl at 60 °C for a duration of 6 h.

chapter 3

Synthesis and application of alternate cyclopolymers of β -diallylaminoethyliminodiacetic acid with maleic acid and sulfur dioxide

GRAPHICAL ABSTRACT



3.1 Abstract

A bis-cationic (+ +) diallyl monomer $[(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{NH}^+(\text{CH}_2)_2\text{NH}^+(\text{CH}_2\text{CO}_2\text{H})_2 \cdot 2\text{Cl}^-]$ (**I**) was prepared by a one-pot, two-step reaction of 2-bromoethylamine hydrobromide, ethyl bromoacetate and diallylamine followed by ester hydrolysis. **I** underwent alternate copolymerization with SO_2 and maleic acid to give poly(bis-zwitterion) (PBZ) ($\pm \pm$) **II**, and **III**, respectively. Both the PBZs contained the chelating motifs of *N*-(2-aminoethyl)iminodiacetic acid $[\text{NH}^+(\text{CH}_2)_2\text{NH}^+(\text{CH}_2\text{CO}_2^-)_2]$ embedded in the pyrroline ring skeleton of each containing repeating unit. Both the PBZs were water-insoluble, however they became water-soluble in the presence of added salts like NaCl. PBZs **II** and **III**, having pH of 2.4 at point of zero charge, became water soluble outside the pH-windows of 0.81-4.46 and 1.49-3.35, respectively, whereby the electroneutral pH-responsive polymers become charge-imbalanced. The ‘apparent’ pK_a s of the two NH^+ centers in **II** were determined to be 5.18 and 9.92. At a concentration 2.5 ppm, antiscalant PBZ **III** imparted 99% inhibition of CaSO_4 scale formation for over 180 min from its supersaturated solution, while at 1.5 ppm inhibition efficiency was found to be 98% for 50 min. PBZ **II** at the concentrations of 20 and 10 ppm demonstrated CaCO_3 scale inhibition of 98% for over 240 min and 95% for over 90 min, respectively. At a concentration 20 ppm **III** along with 400 ppm KI, it demonstrated an outstanding synergistic 98% inhibition of mild steel corrosion in 1 M HCl at 60 °C in 1 M HCl for a duration of 24 h.

Keywords

Alternate Cyclopolymerization
pH-responsive polymers
Diallylamine salts
Antiscalant

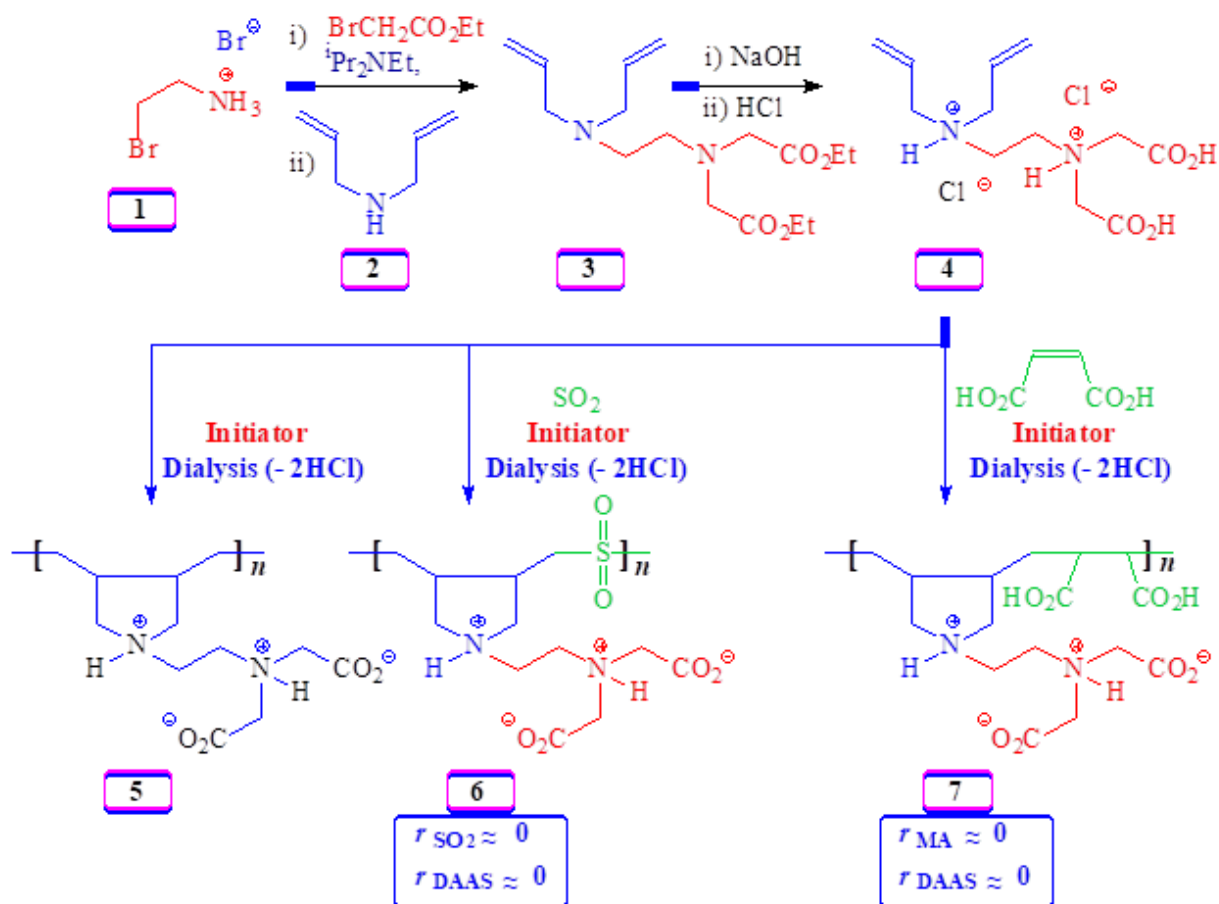
.Mild steel corrosion
N-(2-aminoethyl)iminodiacetic acid

3.2 Introduction

Butler's cyclopolymerization protocol involving of diallyamine derivatives (DAD) $[(CH_2=CH-CH_2)_2N^+R^1R^2 Cl^-]$ as monomers has etched a place of distinction in the synthesis of industrially important polymers whose backbones are embedded with five-membered pyrrolidine ring[91,92,95]. The macromolecular backbone, embedded with five-membered pyrrolidine ring, represents the eighth most important synthetic polymer architecture. Poly(diallyldimethylammonium chloride) accounts for over 1000 patents and publications; Millions of pounds of the polymer are produced annually for various applications, including water treatment[91]. Judicious choice of the substituents (R^1 , R^2) in the DAD salts has led to the incorporation of anionic, zwitterionic ($\pm$) and ampholytic (+ -) charges on the pH-responsive polymer backbone[141,142]. Copolymerization of DAA salts with sulfur dioxide[143] or maleic acid (MA)[144,145] invariably leads to alternate copolymers as a result of each monomeric pairs having reactivity ratios of zeros (i.e., $r_1 \approx 0$, $r_2 \approx 0$).

N-(2-Aminoethyl)iminodiacetic acid $[H_2NCH_2CH_2NH(CH_2CO_2H)_2]$ (AEIDA), like ethylenediaminetetraacetic acid (EDTA), is an important chelating ligand [98]. The current chapter describes the synthesis of two alternate copolymers of AEIDA-derived monomer bis-cationic monomer **4** with SO_2 and maleic acid to synthesize pH-responsive new poly(bis-zwitterion) (PBZ) ($\pm \pm$) **6** and **7** via Butler's cyclopolymerization protocol, whereby each repeating unit has the bis-zwitterionic motifs of AEIDA in the form: $NH^+CH_2CH_2NH^+(CH_2CO_2^-)_2$ (Scheme 3.1). By means of homopolymerization of monomer **4**, we have introduced PBZ **5**, the first example of a cyclopolymer, whereby each repeating unit has the bis-zwitterionic dipoles, and where the integrity of all four original

functionalities of AEIDA (i.e. two unquenched nitrogen valency and two CO₂H groups) has been kept intact.



Scheme3. 1 Alternate cyclopolymerization of a diallylamine salt containing *N*-(2-aminoethyl)iminodiacetic (AEIDA) motifs with SO₂ and maleic acid.

The pH-responsive bis-zwitterionic motifs in these polymers are expected to exhibit interesting solution properties. The polymers may have the potential for use as antiscalant in reverse osmosis (RO) desalination plants to arrest membrane fouling by minimizing scale deposition, and inhibitor of mild steel corrosion in oilfield applications. Since chemical formulation used in oilfield applications requires simultaneous use of antiscalants and corrosion inhibitors

As of 2018, over 95 million $\text{m}^3 \text{ day}^{-1}$ of desalinated water for human consumption is produced using 15,908 operational desalination plants[146]. The contribution of reverse osmosis (RO) process to clean brackish and seawater accounts for about 63% of the world desalting capacity[147]. In RO desalination plants, deposition of scale (i.e., the precipitation of low soluble salts, like CaCO_3 , SrCO_3 , CaSO_4 , BaSO_4 , SrSO_4 , etc.) on the membrane surface leads to a decline in the permeate flux. Small doses of antiscalants are used to mitigate scaling, which upon adsorption disrupt the nucleation process for scale (crystal) formation thereby changing its morphology and retarding the crystal growth[129,130,148]. Different types of scale inhibitors (phosphonate, polyphosphate, polyaspartic acid, copolymers of acrylic acid/methacrylic acid, acrylic acid/maleic anhydride, etc.) have been used to mitigate CaCO_3 and CaSO_4 precipitations onto the membrane surface at a dosage of 10 mg L^{-1} using simulated seawater[149-152].

Antiscalants are also used in oilfield applications to mitigate formation of CaCO_3 scale which causes obstruction of pipes as well as reduction of heat transfer efficiency in cooling systems in areas of energy, water, and food industries[153]. In oil reservoirs, mixing of injection water with formation water leads to the scale deposition, which reduces petroleum production.

Sometimes, biofilm growth (biofouling) on RO membrane surfaces owing to the nutritional contribution of some polyphosphonate- and polyacrylate-based antiscalants, may adversely affect the membrane performance[154,155].

Phosphorus-based antiscalants are widely used in most RO desalination plants owing to their excellent efficacies. However, they are neither biodegradable nor environmentally friendly; as such the effluence of reject-brine disposed in the marine ecosystems leads to eutrophication problems[151,156].

The excellent chelating properties of adsorbents functionalized with multidentate ligands of aminocarboxylic acid of iminodiacetic acid $[\text{NH}(\text{CH}_2\text{CO}_2\text{H})_2]$ (IDA)[99,102,104,157], EDTA[99,101], ethylenediamine-*N,N'*-diacetate[99,100], and ethylenediamine-*N,N'*-diacetate[99,100] in trapping toxic metal ions are well documented. By the formation of soluble Ca(II)-complex, the chelating motifs of antiscalants like EDTA help keep the Ca(II) in solution, thereby mitigating the scale formation on the membrane surface in desalination plants[60,158].

In oilfield applications, chemical formulations contain the antiscalant additives to arrest scale formation, and corrosion inhibitors protect mild steel during oil well acidizing. However, their incompatibility may lead to competitive adsorption behavior which can adversely impact each other's performance[159]. The global cost due to corrosion - estimated to be 2.5 trillion US dollars in 2016[75] - could be reduced by 15-35%[76] by the use of organic corrosion inhibitors containing lone pair donating O, N, S which mitigate corrosion attack on mild steel and iron during industrial acid cleaning, acid pickling, and oil well acidizing[77,78]. EDTA[84,85] and IDA[86,160] have been used to mitigate mild steel corrosion in HCl media with some success. Polymers, as compared to small molecules,

having multiple anchoring sites can adsorb strongly to cover mild steel surface thereby restraining corrosive attack by forming metal (Fe^{2+})-polymer complex[79-83].

The above discussion dealt to some extent the importance of aminoacetate chelating motifs. In search of phosphorus-free antiscalants to achieve stable membrane performance, herein we describe the synthesis, solution properties, antiscalant behavior, and corrosion inhibition activity of the newly synthesized PBZs **6** and **7** with the anticipation of an exciting outcome.

3.3 Experimental

3.3.1 Materials

MA **1** from BDH Chemicals Ltd. and ammonium persulfate (APS) from Sigma-Aldrich were purchased. 2,2'-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform-ethanol mixture. Bis-cationic monomer α -diallylaminoethyliminodiacetic acid dihydrochloride (**4**) was prepared as described (Scheme 3.1)[161]. Dimethylsulfoxide (DMSO) was dried over calcium hydride and distilled at 64 – 65°C (4 mmHg). Millipore water (double distilled, 18.2 M Ω ·cm) were used. Dialyses were performed in spectra/Por membranes of MWCO of 1000 and 6000–8000 both from Spectrum Laboratories, Inc.

3.3.2 Physical Methods

A Perkin Elmer Elemental Analyzer Series 11/2400 (Waltham, Massachusetts) was utilized to find atomic compositions. An FTIR spectrometer (Nicolet 6700, Thermo Electron Corporation) was utilized to record IR spectra. Thermogravimetric analyses (TGA) under N₂ flow (50 mL min⁻¹) were performed in an SDT analyzer (Q600: TA instruments). Viscosity measurements were performed in an Ubbelohde viscometer (Viscometer Constant = 0.005 cSt/s) in the presence of N₂ atmosphere at 30.0±0.1°C as controlled by a water bath CT72/P, SI Analytics, Germany. Double distilled water, purged with N₂ at 90 °C for 15 min to make it CO₂-free, was used for viscosity measurements; the presence of CO₂ in the air may otherwise affect the viscosity values especially in the alkaline solutions. ¹H and ¹³C NMR spectra in D₂O were recorded on a Bruker Avance^{III} 400 MHz spectrometer, and the ¹H and ¹³C chemical shifts in D₂O were referenced with sodium 3-trimethylsilylpropionate-2,2,3,3-d₄ (TSP-deuterated, δ 0 ppm) and dioxane (δ 67.4 ppm). An Orion Versastar Conductometer (Thermo Scientific) was used for conductance measurements. pH measurements were performed by a Sartorius pH meter. Quattro ESEM-FEG integrated with energy dispersive x-ray spectrometer (EDX, Oxford Instruments) from ThermoFisherTM Scientific was utilized to examine the surface morphology of the samples.

Size Exclusion chromatography (SEC) was performed on an Agilent Technologies 1260 infinity II high performance liquid chromatograph equipped with a Refractive index detector and two columns (PL aquagel-OH MIXED – H 8 μm) in series. A solution of 0.05 M NaNO_3 + 0.5M NaCl was used as eluant at a flow rate of 1.0 mL/min at 35 $^\circ\text{C}$. A sample solution of 2 mg/mL was prepared in 0.05 M NaNO_3 containing minimum amount of NaHCO_3 to dissolve it and filtered using 0.45 μm syringe filters. The resulting solution (50 μL) was injected into the GPC columns and chromatographic data was analyzed using data analysis tool. The equipment was calibrated using nine polyethylene oxide (PEO) standards.

3.3.3 Alternate copolymerization of monomer 4 with SO_2

To a mixture of monomer **4** (4.0 g, 12.2 mmol) in DMSO (6.0 g) was absorbed SO_2 (0.895 g, 14.0 mmol). The heterogeneous mixture became homogeneous upon addition of SO_2 . Initiator AIBN (120 mg) was added and the mixture was heated at 75 $^\circ\text{C}$ for 12 h. The thick mixture was transferred to a dialysis bag (MWCO: 6000-8000) with the help of 1 M HCl , and dialyzed against deionized water for 48 h. The polymer started separating as a solid and settled down in the dialysis bag. The white solid was dried under vacuum to a constant weight (3.5 g, 90%) to obtain **5**. (Found: C, 44.5; H, 6.1; N, 8.5; S, 9.8%. $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$ requires C, 44.99; H, 6.29; N, 8.74; S, 10.01%); ν_{max} (KBr): 3562, 3031, 2973, 2923, 2501 (br), 1728, 1633, 1459, 1404, 1306, 1215, 1125, 1010, 834, 698, 605, and 507 cm^{-1} .

3.3.4 Alternate copolymerization of monomer 4 with maleic acid

A solution of monomer **4** (4.1 g, 12.5 mmol) and maleic acid (1.73 g, 15.0 mmol) in water (2.4 g) was heated to 100 °C, and initiator APS (800 mg) was added in two portions over a duration of 4 min. Exothermic polymerization proceed and the mixture was continued heat at 100 for 20 min. Thereafter, the thick mixture was transferred to a dialysis bag (MWCO: 1000) with the help of 1 M HCl, and dialyzed against 0.3 M HCl (2 h) to remove any maleate counterion followed by dialysis against deionized water for 36 h. The polymer started separating as a solid and settled down in the dialysis bag. The whole aqueous mixture was freeze-dried to obtain polymer **6** as a white solid (3.3 g, 71%). (Found: C, 51.2; H, 6.3; N, 7.2%. $C_{16}H_{24}N_2O_8$ requires C, 51.61; H, 6.50; N, 7.52%); $\nu_{\max}$ (KBr): 3458-2955 (br), 3031, 2961, 1740, 1613, 1463, 1399, 1181, 1074, 1053, 971, 901, 797, 696, 606, and 569 cm^{-1} .

3.3.5 Measurement of critical salt concentration (CSC)

The concentrations of several salts required to promote water-solubility of PBZ **6** and **7** were determined at 23 °C in triplicate with accuracies of 1-2%. An aqueous solution of 1% wt/wt of the polymers in the presence of sufficient concentration of a salt was titrated with deionized water to reach the first cloud point. The concentration of the salt at this point becomes its CSC value.

3.3.6 Protonation constants (K_i)

The protonation constants (K_i) of various basic nitrogen centers in the synthesized polymers were determined using procedure detailed elsewhere^[145]. Thus, as described in [Table 3.2](#), a certain mmol of PBZ **6** and **7** were dissolved in CO₂-free water (200 mL) and its pH value was recorded after each addition of 0.1 - 0.15 mL of titrant NaOH.

3.3.7 Antiscalant behavior of the synthesized polymers

The antiscalant efficiency of the polymers were determined using procedure as detailed elsewhere[110]. Thus, a 12600 ppm SO_4^{2-} (60 mL, prepared using Na_2SO_4) containing 2x ppm polymer at 40 ± 1 °C was added a 5200 ppm Ca^{2+} (60 mL, prepared using CaCl_2) at 40 ± 1 °C. The resultant supersaturated (with respect to CaSO_4) solution - thus containing 6300 ppm SO_4^{2-} , 2600 ppm Ca^{2+} and x ppm (in the range 1-10 ppm) the antiscalant (polymer) - was then stirred at 300 rpm using a magnetic stir-bar at 40 ± 1 °C. The conductivity of the solution was then measured at 1 min, after and thereafter at every 10 min interval as programmed in the instrument. The stock solutions (1000 ppm) of the polymers were prepared by dissolving them in water (2 mL) by treating with a minimum amount of NaHCO_3 and thereafter diluting in a volumetric flask. easured at 1 min after addition, 10 min interval. A sudden decrease of conductance after an induction time indicates a significant decrease of ionic concentrations leading to turbidity and crystal formation which can be seen visually.

A supersaturated solution of CaCO_3 was prepared by adding a 2600 ppm Ca^{2+} (60 mL, prepared using CaCl_2) at 40 ± 1 °C to a solution of 2050 ppm HCO_3^- (60 mL, prepared using NaHCO_3) containing 2x ppm polymer from the stock solution as prepared above at 40 ± 1 °C. The resultant solution has thus contained 1025 ppm in HCO_3^- , 1300 ppm Ca^{2+} , and x ppm polymer.

3.3.8 Corrosion inhibition of mild steel in 1 M HCl by the synthesized polymers 6 and 7

The corrosion inhibition tests were carried out in triplicate by hanging mild steel coupons of $2.9 \times 2.9 \times 0.7 \text{ cm}^3$ dimension on corrosive environment of 1 M HCl (250 mL) in the absence (blank) and presence of (2.5, 10, 20, and 50 ppm) of PBZ **6** and **7** at 60 °C for 24 h as described[110]. The mild steel has the following elemental composition (wt%): 0.33 (C), 0.39 (Si), 0.84 (Mn), 0.033 (S), 0.16 (Cr), 0.03 (Mo), 0.075 (Ni), 0.043 (Al), 0.014 (Co), 0.15 (Cu), 0.015 (Wu), 97.8 (Fe).

For the coupons of similar masses, gravimetric weight-loss data were used to calculate the percent inhibition (%*h*) using equation (1):

$$\% \eta = \frac{W_{lb} - W_{li}}{W_{lb}} \times 100 \quad (1)$$

where W_{lb} and W_{li} represent weight-loss in the absence (blank) and presence of inhibitor, respectively. In cases where the coupons are not of similar masses, the weight losses were calculated by a relative weight-loss method[110]. The average percent inhibition efficiency is found to have a standard deviation of 0.5–1.4%.

3.4 Results and discussion

3.4.1 Synthesis and characterization of polymers 6 and 7

Bis-cationic monomer **4** was synthesized by basic hydrolysis and acidification of tertiary amine **3**, which in turn was generated by a one-pot two-step process of reacting 2-bromoethylamine hydrobromide **1** with ethyl bromoacetate followed by alkylation of diallylamine **2** with the intermediate $(\text{EtO}_2\text{C})_2\text{NCH}_2\text{CH}_2\text{Br}$ (Scheme 3.1). Monomer **4** underwent AIBN-initiated alternate cyclopolymerization with SO_2 to afford poly(bis-zwitterion-*alt*- SO_2) **6** in excellent yield (90%). During dialysis, the water-soluble polymer containing bis-cationic repeating units was converted to water-insoluble bis-zwitterionic **6** with the depletion of two equivalents of HCl . The elemental analysis indicated the absence of Cl^- ions, however their complete removal cannot be ascertained since the SEM and EDX analyses revealed the presence of minute amount of Cl (Fig. 3.1).

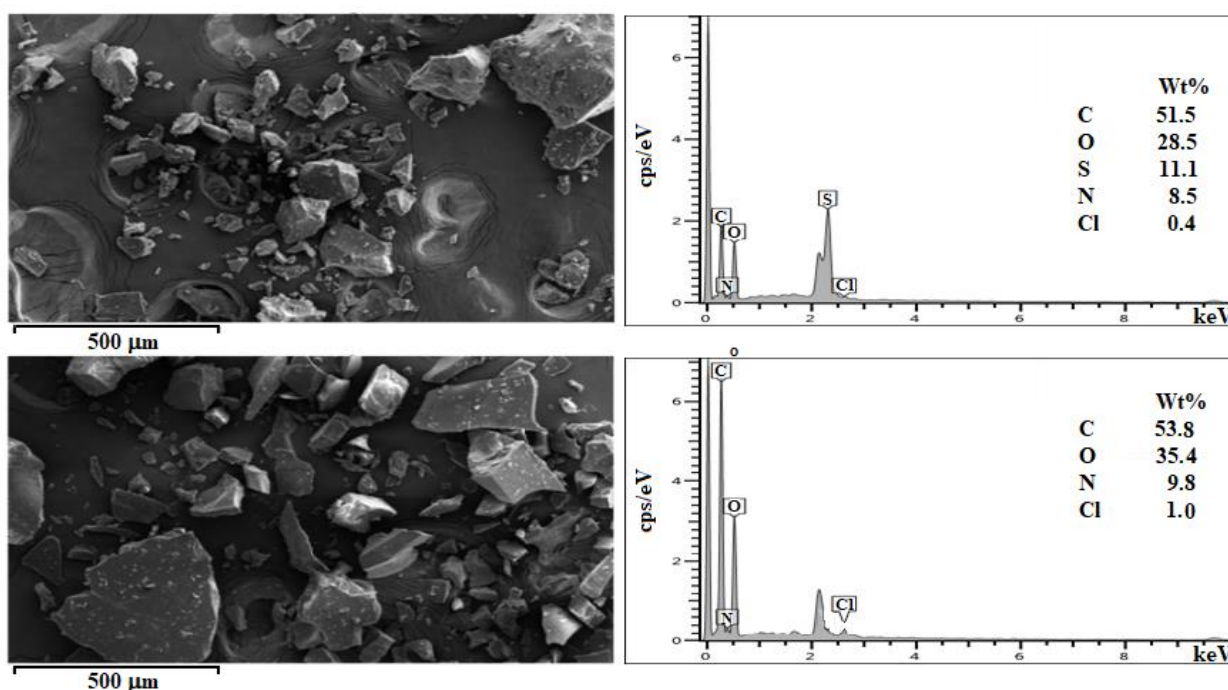


Figure3. 1 SEM and EDX analysis for PBZs 6 and 7.

The pH at point of zero charge (pHPZC) was determined by a pH-drift method. Thus, polymers **6** or **7** (50 mg) was added to a series of a 0.1 M NaNO₃ (10 mL) of known initial pHs and after stirring for 6 h at room temperature (23 °C), the final pHs were recorded. A plot of ΔpH [(i.e. pH (final) – pH (initial))] versus pH (initial) was used to determine pHPZC value at which ΔpH becomes zero (Fig. 3.2a). Both the polymers were found to have a similar pHPZC value of 2.4, implying that the polymers will have net positive and negative charge below and above the pH 2.4, respectively.

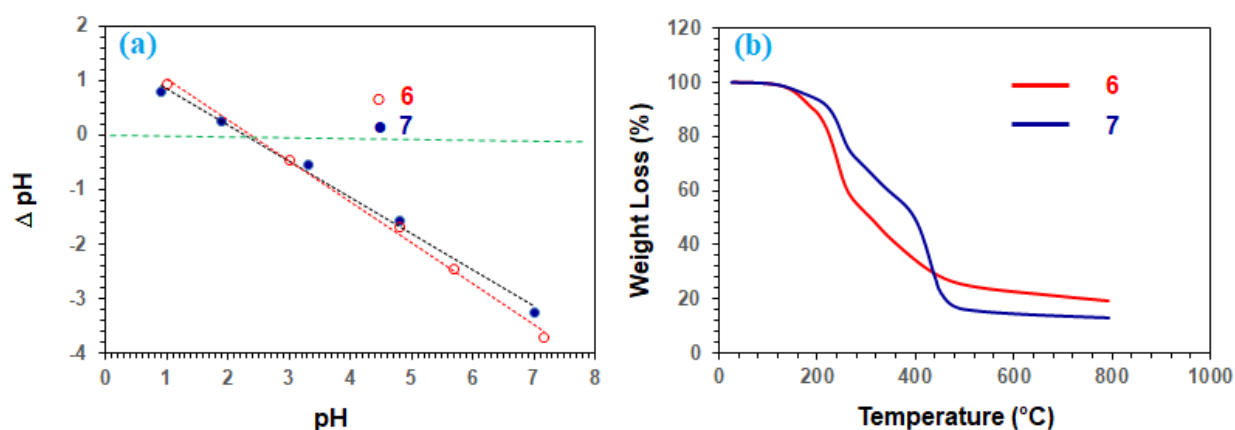


Figure3. 2 (a) pH versus ΔpH plot to determine pH of point of zero charge for PBZs 6 and 7; (b) TGA curves of 6 and 7.

The TGA curves of the polymers are shown in Fig. 3.2b. PBZ **6** was stable up to 165 °C, a weight-loss of 5% was attributed to the removal of moisture. Thereafter a gradual, a steep, followed by another gradual loss account for an overall loss of 70% in the temperature range 165-490 °C. The zwitterionic pendant, SO₂ and pyrrolidine backbone constitute for 50%, 20% and 30% mass, respectively. Therefore the 70% weight-loss may be attributed to the removal of zwitterionic pendant and SO₂, whereby the steep loss of $\approx 24\%$ in the range 225-275 °C belongs to removal of SO₂. A steep loss of 28% in the temperature range 215-275 could be accounted for the release of SO₂. The gradual loss after 490 °C (6%) and the residual mass (19%) could be attributed to nitrogenous fraction of the backbone.

Similarly, in case of PBZ **7**, a loss of 5% up to 190 °C is attributed to the moisture loss. A 47% loss in the temperature range 190-400 °C is accounted mainly for the removal of maleic acid unit and part of zwitterionic pendant[144,162]. A loss of 33% in the range 400-490 °C is attributed mainly to the loss of the zwitterionic pendant and gradual decomposition of nitrogenous pendant.

IR bands 1306 and 1125 cm⁻¹ were assigned to the asymmetric and symmetric vibrations of SO₂ unit in polymer **6**, while the bands at 1404 and 1633 cm⁻¹ were assigned to the symmetric and anti-symmetric stretching[111] of COO⁻ in the zwitterionic form. The presence of a minor band at 1728 cm⁻¹ could be accounted for the presence of CO₂H arising out of incomplete depletion of HCl during dialysis (vide supra) and/or the equilibration: $\text{NH}^+\text{CH}_2\text{CO}_2^- \rightleftharpoons \text{NCH}_2\text{CO}_2\text{H}$. The absorption bands at 1740 and 1613 cm⁻¹ are attributed to the C=O stretch of CO₂H and CO₂⁻ in PBZ **7**[163].

The NMR spectra of polymers **6** and **7** along with monomer **4** are displayed in Figs. 3.3 and 3.4. ¹H spectrum revealed the disappearance of alkene proton signals confirming the transformation to the alternate copolymers (Fig. 3.3b,c).

Complete absence of residual alkene protons (δ5.5-6 ppm) (Fig. 3.3a) suggests the termination of polymerization by degradation chain transfer involving abstraction of allylic hydrogen to stable allylic radicals which are unable re-initiate propagation[112]. Likewise, alkene carbon signals at δ126.4 and 128.5 ppm (Fig. 3.4a) disappeared upon undergoing polymerization to **6** and **7** as seen in Fig. 3.4b, c. The incorporation of maleic acid in **7** is confirmed by the presence of carbonyl signal at δ180.2 ppm (Fig. 3.4c). For the microstructure, the substituents in the copolymer **6** are found to be *cis*- and *trans*-disposed in a 3:1 ratio as determined by the signals of carbon marked 'b', which are free of any overlapping signals (Fig. 4b)[115,164].

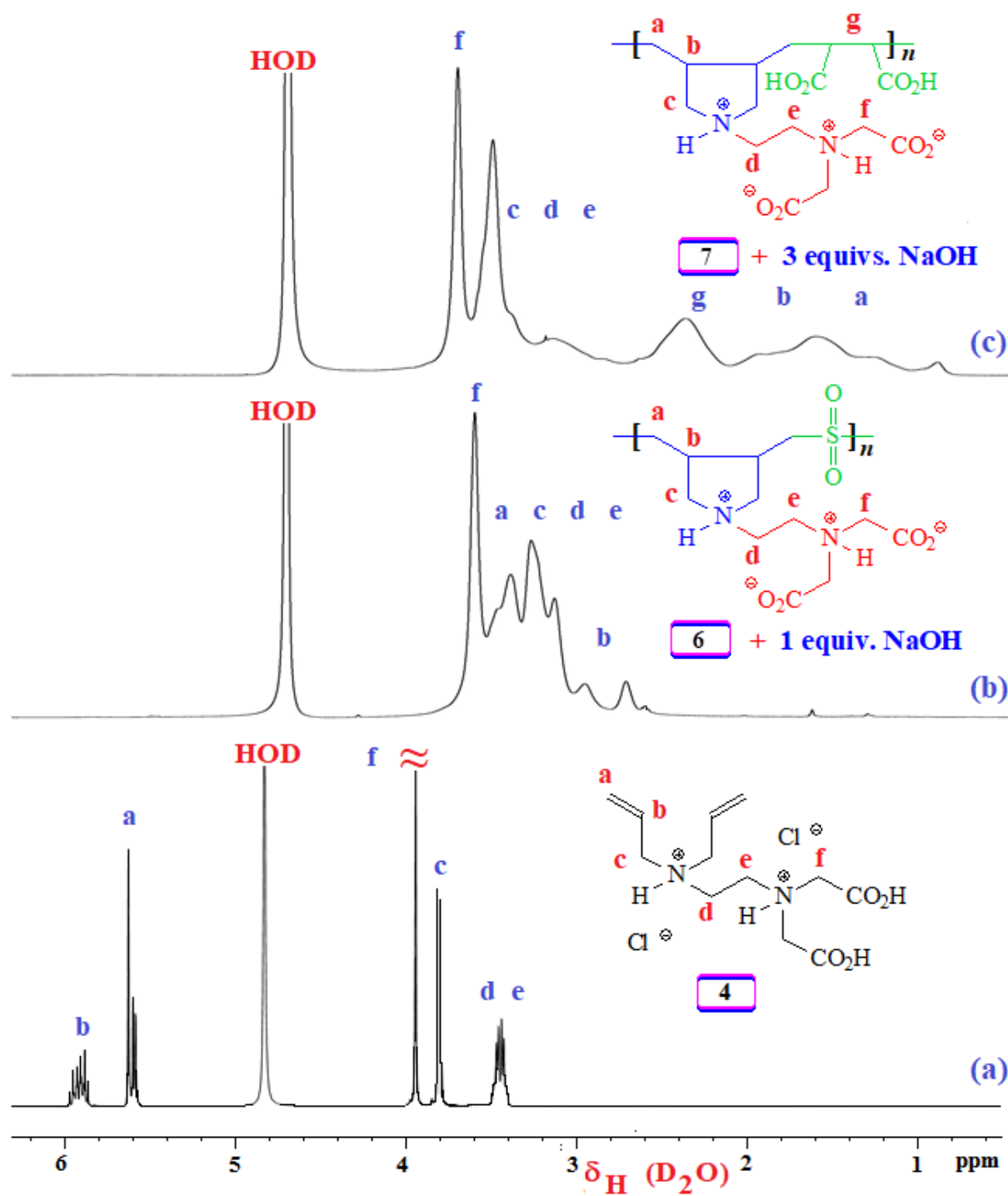


Figure 3. ^1H NMR spectra of (a) monomer 4 (b) 6 (+ 1 equiv. NaOH), and (c) 7 (+ 3 equivs. NaOH) in D_2O .

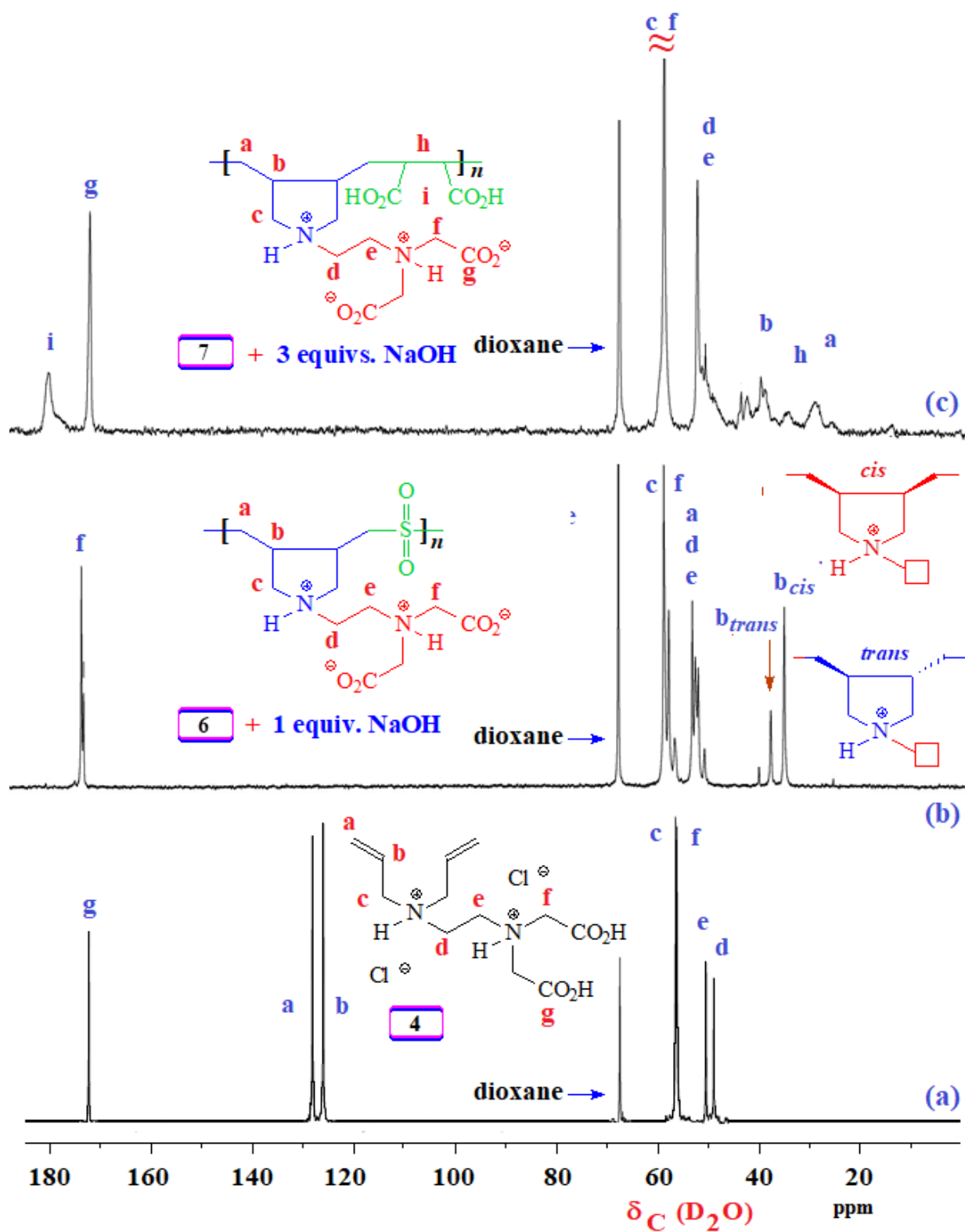
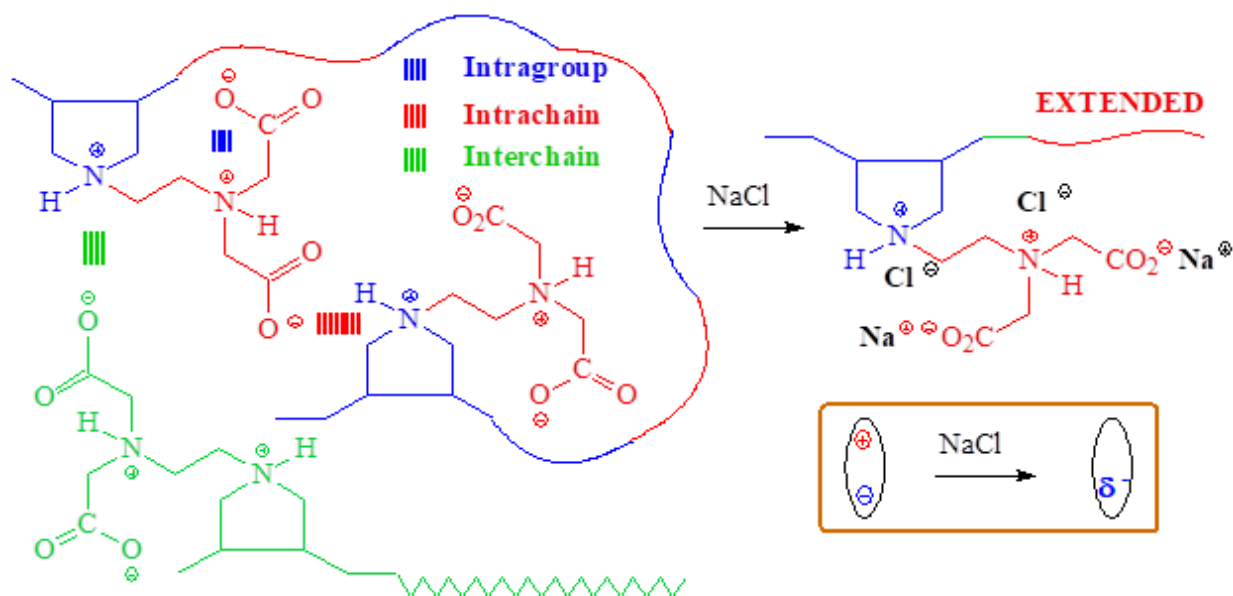


Figure 3. 4 ^{13}C NMR spectra of (a) monomer 4 (b) 6 (+ 1 equiv. NaOH), and (c) 7 (+ 3 equivs. NaOH) in D_2O .

Molar masses of polymers by GPC are usually difficult as the aminocarboxylate motifs tend to stick to the column materials[144]. However, the $\bar{M}_w$ and PDI values of PBZ **6** were found to be 34,900 g mol⁻¹ and 1.42, respectively, while the corresponding values for PBZ **7** were determined to be 6650 g mol⁻¹ and 1.36. The signal of the (CH₃)₂C(CN) moiety (originating from the AIBN initiator) attached to the chain end is displayed as a singlet at 1.31 ppm and was free of any overlapping signal. Careful integration of the peak indicated the number average degree of polymerization to be about 72 which corresponds to an $\bar{M}_n$. Value of 23,500 g mol⁻¹, while its corresponding value from GPC was found to be 24,540 g mol⁻¹.

3.4.2 Solubility behavior

Water-insolubility of poly(bis-zwitterion) **6** and **7** is a manifestation of intragroup, inter-, and intra-chain interactions of the zwitterionic dipoles, which transforms the polymer backbones from semicoil to globular conformation[96,118] (Scheme 3.2). However, the polymers were found to water-soluble in presence of added salts like NaCl. The Cl^- ions bind strongly to the positive nitrogens, while Na^+ ions having larger hydration shell are not effective enough to neutralize the negative charges on the carboxyls. Thus, zwitterionic dipoles upon interaction with NaCl will have slightly excess negative charge, the repulsion among them leads to an expanded conformation and increased hydration thus leads to water-solubility (Scheme 3.2).



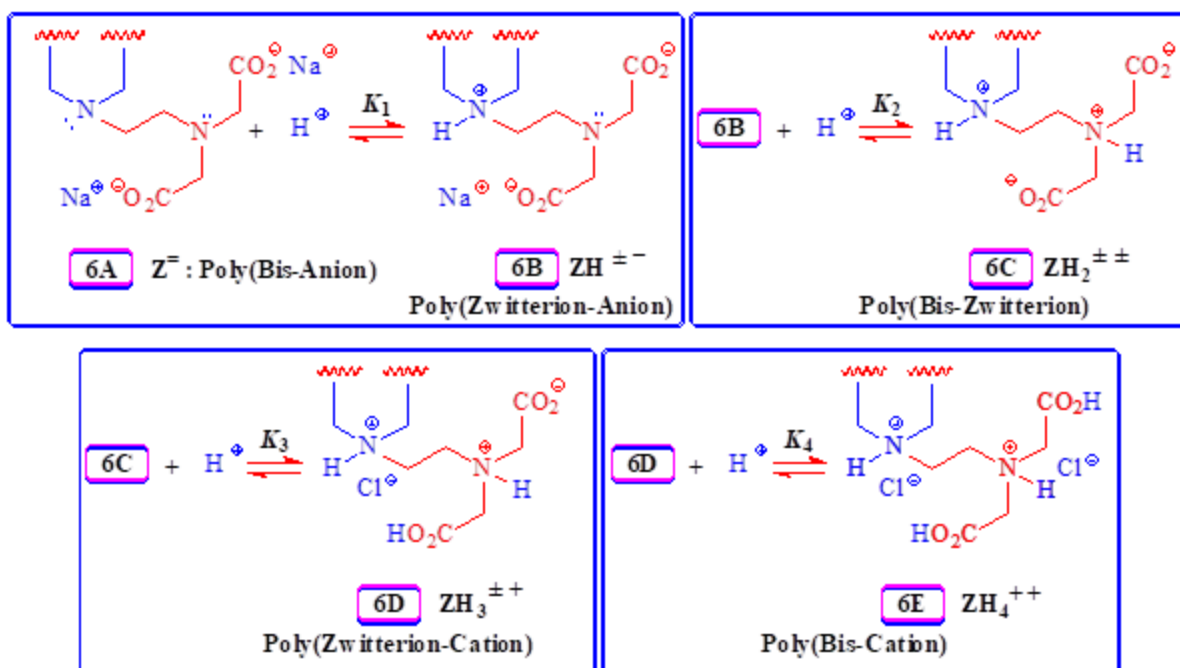
Scheme3. 2 Intragroup, intra- and interchain zwitterionic interactions in PBZ **8** and their disruptions in the presence of NaCl.

CSC of various salts required to promote water-solubility of **6** and **7** is given in [Table 3.1](#). As compared to **7**, stronger zwitterionic interactions were observed for polymer **6** which required greater concentration of the salts to promote solubility. Among the alkali metal salts, NaI has the lowest CSC values; iodide being the most polarizable can neutralize the positive nitrogens most effectively, thereby placing the greatest amount of excess negative charge on the zwitterionic dipoles. Overall excess negative charge leads to greater hydration and solubility. Note that Ca^{2+} usually precipitates anionic polyelectrolytes, however it promoted water-solubility of the polymers. Polymers **6** and **7** were found to be soluble in 0.109 M and 0.0380 M HCl, respectively, where the bis-zwitterions ($\text{ZH}_2^{\pm\pm}$) upon protonation is transformed to zwitterion/cation ($\text{ZH}_3^{\pm+}$) and bis-cation (ZH_3^{++}) motifs, which renders the polymers water-solubility.

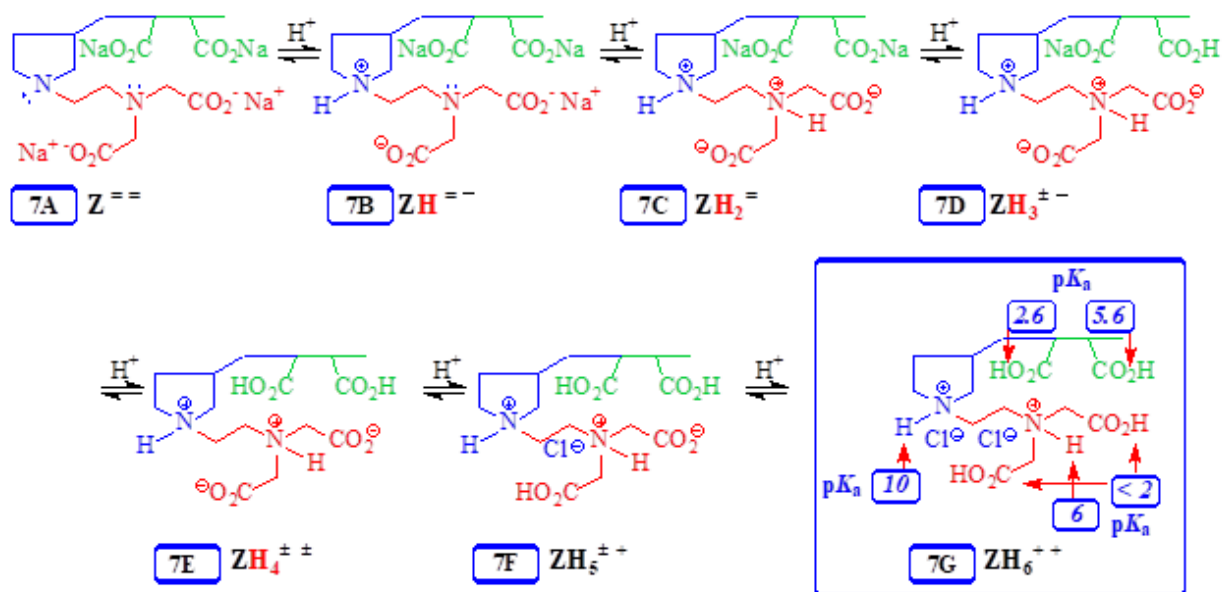
Table 3. 1 Critical Salt Concentration required for water-solubility of PBZ **6** and PBZ **7** at 23 °C

Salt	PZ 5 : CSC (M)	PZ 6 : CSC (M)
NaCl	3.97	2.77
NaBr	2.87	1.60
NaI	2.03	1.22
CaCl ₂	2.62	2.71
HCl	0.109	0.0380

The polymers, as expected, became water-soluble in the presence of NaOH owing to the transformation of bis-zwitterionic ($\text{ZH}_2^{+\pm}$) motifs to zwitterion-anion ($\text{ZH}^{\pm -}$) bis-anionic (Z^-). A solution of polymer **6** (100 mg) in water (200 mL) in the presence of a sufficient concentration of NaOH was titrated with 0.1026 M HCl. The first cloud point appeared at a pH of 4.46. At this pH, the dominant equilibration involving: poly(zwitterion-anion) **6B** ($\text{ZH}^{\pm -}$) + $\text{H}^+ \rightleftharpoons$ poly(bis-zwitterion) **6C** ($\text{ZH}_2^{+\pm}$) (Scheme 3.2) led to the degree of protonation (a) value of 0.62 as calculated using modified Henderson-Hasselbalch equation (Eq. 3) (*vide infra*). The polymer backbone containing >62 mol% bis-zwitterionic motifs thus becomes water-insoluble. The mixture remains cloudy upon further addition of 1.035 M HCl until it reached the pH value of 0.81. PBZ **6** is thus found to be water-soluble outside the pH-window of 0.81-4.46. At the pH value of 0.81, the dominant equilibration involving: poly(zwitterion-cation) **6D** ($\text{ZH}_3^{+ +}$) + $\text{H}^+ \rightleftharpoons$ poly(bis-cation) **6E** ($\text{ZH}_4^{+ +}$) (Scheme 3.3), revealed that the polymer backbone containing < 10 mol% bis-cationic motifs becomes water-insoluble. The increasing proportion of zwitterionic-cationic and bis-zwitterionic motifs thus leads to water-insolubility. Similar experiment with PBZ **7** revealed its water-insolubility inside the pH window of 1.49-3.35; outside the window, the polymer **7** remains soluble. PBZ **7** at $\text{pH} \leq 3.35$ becomes insoluble; approximate calculation revealed that for the **7D** $\rightleftharpoons$ **7E**, ≥ 11 mol% of one of the CO_2H in **7E** must be ionized to impart solubility (Scheme 3.4). PBZ **7** at $\text{pH} \leq 1.49$, polymer becomes water-soluble because of shifting **7E** $\rightleftharpoons$ **7F** to the right containing the zwitterionic-cationic motifs in **7F** protonated to the extent of ≥ 90 mol% repeating units.



Scheme3. 3 pH-induced changes in the charge types and densities in the backbone of PBZ 6.



Scheme3. 4 pH-induced changes in the charge types and densities in the backbone of PBZ 7 and protonation constants (K_i) of the basic centers.

3.4.3 Measurement of Viscosity

Viscosity plots of PBZ **6** and PBZ **7** are shown in Fig. 3.5. The viscosity plot of PBZ **6** ($\text{ZH}_2^{\pm\pm}$) in salt-free water in the presence of 2 equivalents NaOH is concave upwards showing because of the presence of bis-anionic motifs as depicted in **6A** (Z^-) (Fig. 3.5a-i). The viscosity plots in 0.1 M NaCl in the presence of 2 and 1 equivalents of NaOH became linear owing to polyelectrolyte effect. The shielding of the anionic and cationic charges by respective charge neutralization by Na^+ and Cl^- ions reduces the repulsion among similar charges thereby reducing hydrodynamic volume hence viscosity values (Fig. 3.5a-ii, iii). The greater excess negative charges in the presence of 2 equivalents NaOH leads to higher viscosity values. The viscosity plot in the presence of 0.15 M HCl is displayed in (Fig. 3.5a-iv). The intrinsic viscosity $[\eta]$ in 0.1 M NaCl in the presence of 2 and 1 equivalent NaOH and in 0.15 M HCl was found to be 0.771, 0.252 and 0.159 dL g^{-1} , respectively. Note that the linear portions of the plots were used for the determination of $[\eta]$; at lower concentration the plots bend downward owing to a decrease in the charge imbalance arising out of the increasing hydrolysis at lower dilution involving:



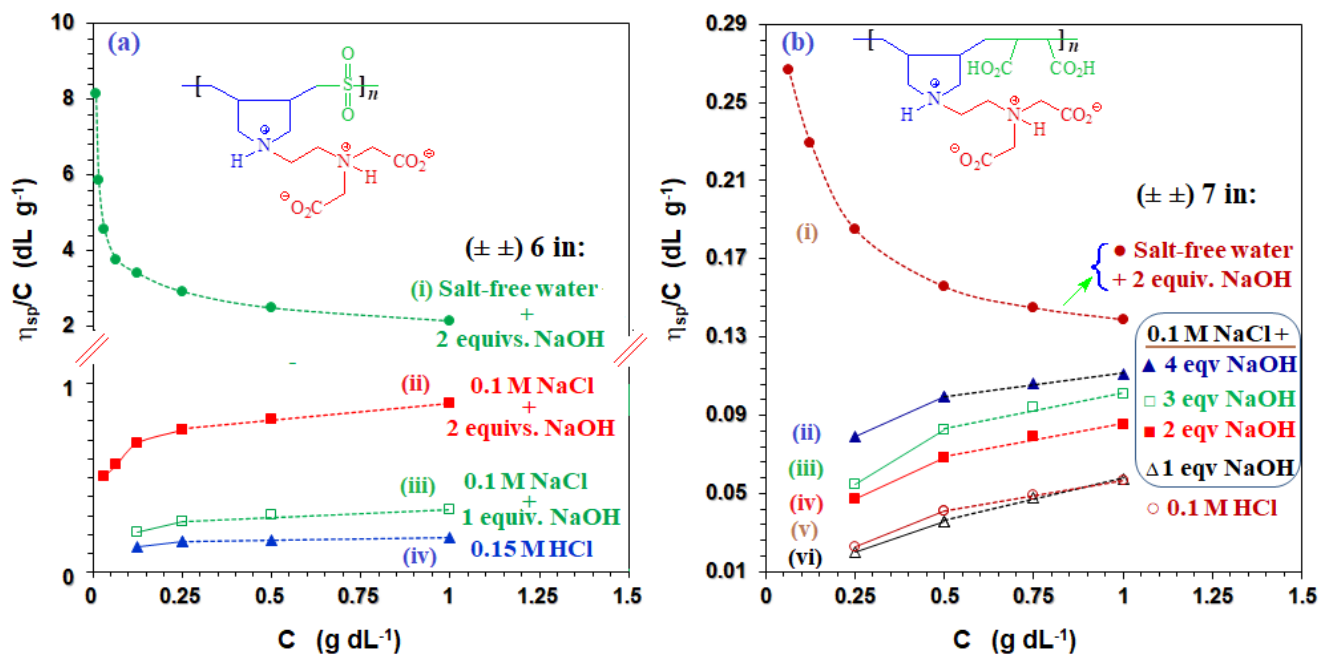


Figure 3.5 (a) The viscosity behavior at 30 °C of PBZ 6 in (a) (i) ● salt-free water + 2 equivs. NaOH, (ii) ■ 0.1 M NaCl + 2 equivs. NaOH, (iii) □ 0.1 M NaCl + 1 equiv. NaOH, (iv) ▲ 0.15 M HCl; PBZ 7 in (b) (i) ● salt-free water + 2 equivs. NaOH, (ii) ▲ 0.1 M NaCl + 4 equivs. NaOH, (iii) □ 0.1 M NaCl + 3 equiv. NaOH, (iv) ■ 0.1 M NaCl + 2 equivs. NaOH, (v) ○ 0.15 M HCl; (vi) △ 0.1 M NaCl + 1 equiv. NaOH.

PBZ **7** ($\text{ZH}_2^{\pm\pm})(\text{CO}_2\text{H})_2$ (depicted as **7E** in [Scheme 3.4](#)) in the presence of 2 equivalents of NaOH would lead to the generation of **7C** ($\text{ZH}_2^{\pm\pm})(\text{CO}_2^-)_2$; as expected its viscosity plot became concave upward ([Fig. 3.5b-i](#)), while became linear in the presence of 0.1 M NaCl ([Fig. 3.5b-ii-v](#)). The $[\eta]$ values in 0.1 M NaCl in the presence of 4, 3, 2, and 1 equivalent NaOH and in 0.15 HCl was found to be 0.0883, 0.0647, 0.0513, 0.0144 and 0.0252 dL g⁻¹, respectively. Note that like PBZ **6**, the plots for PBZ **7** bend downward because of the decrease in the charge imbalance leading to excessive decrease in reduced viscosities.

3.4.4 Basicity Constant

For a small acid molecule like a monomer, the protonation or basicity constant K involving the equilibrium in a dilute solution: $[A^- + H_3O^+ \rightleftharpoons HA + H_2O]$, pH, and degree of protonation a is related by Henderson–Hasselbalch equation (1). However, for a polymer molecule, K becomes apparent and changes with a as a result of decreasing (-) charges in the polymer backbone that impart electrostatic attraction for protonation. The tendency to protonate a basic center is thus influenced by charge-type on its neighboring repeating unit, a , as well as other factors. Modified equation 2 incorporate polelectrolytic index n ; whereby a pH versus $\log[(1-a)/a]$ plot gives the intercept value (where $a = 0.5$) as $\log K^0$ and slope as n which describes the deviation of K with the a and has a value of 1 for a small molecule giving real basicity constant K (eq 3). For $n > 1$ or < 1 , there will be a progressive decrease or increase of K with increasing a as dictated by eq 3.

$$\log K_i = pH - \log \left[\frac{(1 - \alpha)}{\alpha} \right] \quad (1)$$

$$pH = \log K_i^0 + n_i \log \left[\frac{(1 - \alpha)}{\alpha} \right] \quad (2)$$

$$\log K_i = \log K_i^0 + (n_i - 1) \log \left[\frac{(1 - \alpha)}{\alpha} \right] \quad (3)$$

For the polymer, $\log K^0_1$ and $\log K^0_2$, assigned to the protonation of the ring nitrogens in PBA **6A** and pendant nitrogens in PZA **6B**, respectively, to be 9.92 and 5.18, respectively, with the corresponding n_1 and n_2 values of 0.80 and 1.47 ([Scheme 3.3](#), [Table 3.2](#)). Since, $\log K$ of a basic center is the pK of its conjugate acid, the lower pK value (5.18) was assigned to the pendant NH^+ owing to its attachment to electron-withdrawing $(CH_2CO_2^-)_2$ motifs. $\log K^0_3$ and $\log K^0_4$ were not determined because of insolubility of polymer PBZ ($\pm \pm$) **6C** and requirement of a large volume of HCl solution to protonate the CO_2^- of PZC ($\pm +$) **6D** to a meaningful extent.

Table 3. 2 Protonation of PBZ **6** ($\text{ZH}_2^{\pm\pm}$) in salt-free water at 23 °C

run	$\text{ZH}_2^{\pm\pm}$ (mmol)	C_T^a (mol dm^{-3})	α -range	pH-range	Point s^b	$\text{Log } K_1^{\circ c}$	n_1^c	$R^2,^d$
1	0.2497($\text{ZH}_2^{\pm\pm}$)	0.1016	0.47-0.10	5.25-6.54	11	5.20	1.49	0.993
2	0.3121 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.48-0.12	5.21-6.40	11	5.19	1.46	0.992
3	0.3746 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.45-	5.17-6.57	12	5.14	1.45	0.989
Average						5.18 (3)	1.47 (2)	
$\text{Log } K_2^e = 5.18 + 0.47 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^{\pm\pm}$								
1	0.2497($\text{ZH}_2^{\pm\pm}$)	0.1016	0.82-0.3	9.42-10.1	12	9.93	0.787	0.997
2	0.3121 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.80-0.2	9.46-10.2	13	9.94	0.796	0.995
3	0.3746 ($\text{ZH}_2^{\pm\pm}$)	0.1016	0.94-0.1	9.42-10.3	14	9.88	0.807	0.990
Average						9.92 (3)	0.80 (1)	
$\text{Log } K_1^e = 9.92 - 0.20 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^- + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								

^a Titration with NaOH. ^b Data points used.^c Parentheses include the standard deviations in the last digit.^d R = Correlation coefficient. ^e $\log K_i = \log K_i^{\circ} + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

A value of $n_1 < 1$ dictates the progressive increase of $\log K_1$ with increasing a in the protonation of the basic ring-nitrogen in PBA (=) **6A** leading to the zwitterion-anionic motifs of (Fig. 3.6 I). The higher dipole moment of the zwitterionic motifs (NH^+ and O^-), separated by a long distance of six σ bonds, leads to an increased hydrophilicity[95,121,122] (Scheme 3.3). With the protonation of a nitrogen center in PBA (=) **6A**, the average number of water molecules per repeating unit increases.

As such, the next protonation would lead to the release of a greater number of water molecules of hydration, thereby leading to an entropy-driven [120] increase of $\log K_1$ values with increasing a [123,165]. The protonation of the pendant nitrogen in PZA **6B** ($\pm -$) leading to PBZ **6C** ($\pm \pm$), which demonstrates strong zwitterionic interactions because of the decreased distance, hence decreased dipole moment, between the zwitterionic centers. The progressive formation of a collapsed-coil conformation in PBZ **6C** ($\pm \pm$) will be less hydrophilic and thus have lesser number of water molecules per each repeating unit. Therefore, the entropically-disfavored protonation for an n_2 value of > 1 would lead to decreasing $\log K_2$ values with increasing a (Fig. 3.6 II).

The repeating unit of copolymer **7** has six protonation centers (two nitrogens and four CO_2^- groups); the pH-dependent dynamic equilibria are shown in Scheme 4. Approximate $\text{p}K_a$ values of all six acidic centers are depicted on the structure of ZH_6^{++} (Scheme 4). The solubility problem as well as the presence of four CO_2H groups in a repeating unit are not conducive to determine the protonation constants using the current protocol.

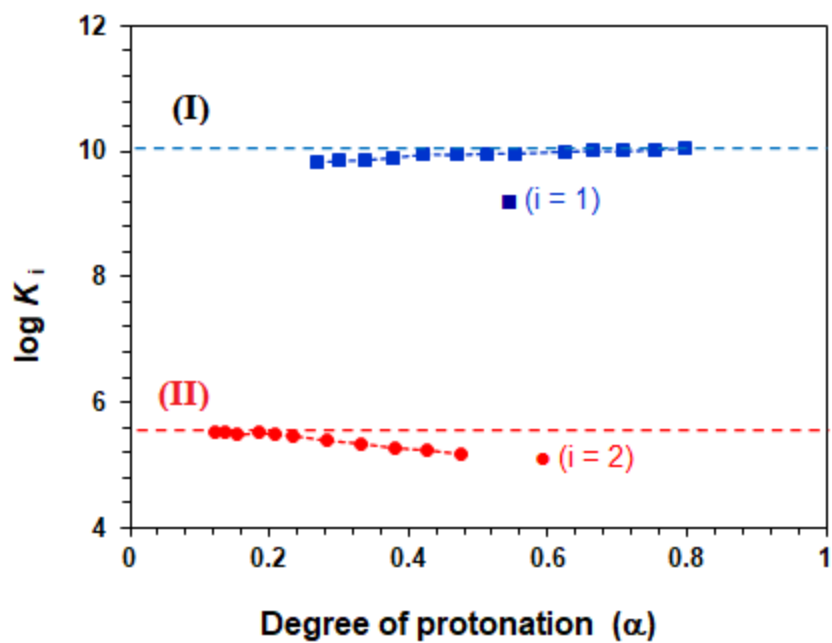


Figure3. 6 Plot for the apparent $\log K_i$ versus degree of protonation (α) in salt-free water for (I) ■ PBA 6A ($i = 1$) ($\log K_1$) and (II) ■ PZA 6B ($\log K_2$). [Data for runs 2, [Table 3.2](#)]

3.4.5 Scale inhibition study

Feed water in a RO plant resides for a duration of about 15 min producing pure water (70%) and reject brine containing Ca^{2+} , SO_4^{2-} , CO_3^{2-} , etc. which can precipitate onto the membrane, thereby reducing its efficacy. The purpose of added antiscalant is to mitigate the scale formation during the residence-time in the osmosis chamber. For the study, a supersaturated solution of CaSO_4 containing three times the concentration of Ca^{2+} , and SO_4^{2-} found in the reject brine of a local RO plant[128]. The conductivity of the supersaturated solution in the absence (blank) and presence of various concentrations of antiscalants PBZ 6 and 7 were monitored to find out the percent scale inhibition (PSI) using Eq. (5), where concentration of Ca^{2+} ions at various times (t) was related to its conductivity. A sudden decrease in conductivity after an induction time would signal the precipitation of CaSO_4 which can also be seen visually (Fig. 3.7).

$$PSI = \frac{[\text{Ca}^{2+}]_{inhibited(t)} - [\text{Ca}^{2+}]_{blank(t)}}{[\text{Ca}^{2+}]_{inhibited(t_0)} - [\text{Ca}^{2+}]_{blank(t)}} \times 100 \quad (5)$$

While precipitation happens within minutes in the blank solution, the induction time increases with the addition of the synthesized antiscalant as shown in Fig. 3.7.

The percent scale inhibition (PSI) (Equation (5)) at various times and induction times are given in Table 3.3. The ionic conductance is reflective of ionic concentration. Even at a meagre concentration of 1.5 ppm of PBZ 7 (entry 7 and footnote b, Table 3.3), the PSI was found to be 99 and 98% for a duration of 30 and 50 min, respectively.

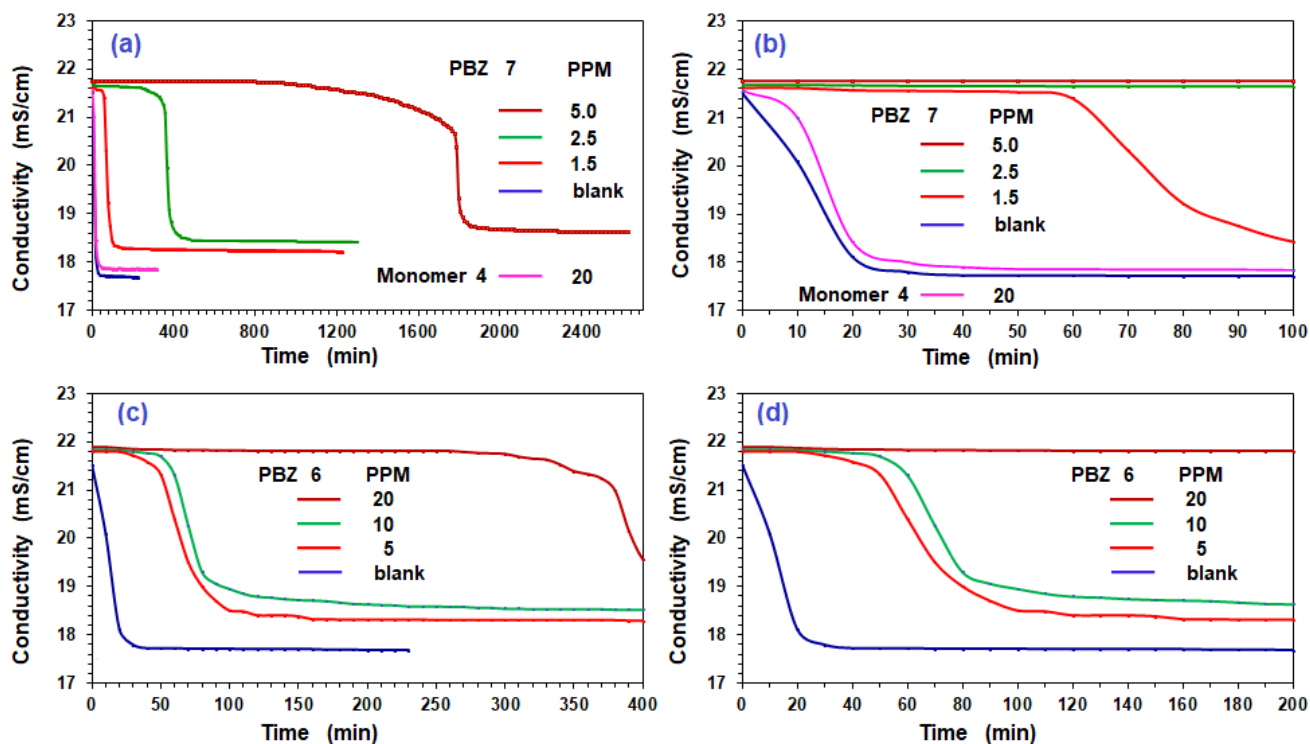


Figure3. 7 (a) Conductivity of a supersaturated solution of CaSO_4 in the presence (1.5, 2.5, 5 ppm) of PBZ 7 and monomer 5 (20 ppm) and in the absence (blank) of antiscalant, (b) expanded plot for a shorter scale of 100 min, (c) Conductivity of a supersaturated solution of CaSO_4 in the presence (5, 10, 20ppm) of PBZ 6, and (d) expanded plot (c) for a shorter scale of 200 min.

Usually, a residence time of less than 15 min is required for the saline water to stay inside a RO chamber, and as such an effective inhibitor at a specific concentration with an induction period of 15 min can prevent scale formation[166]. At higher concentrations, both PSI and induction times increase significantly. PBZ 7 was found to be superior to PBZ 6; while at 5 ppm concentration, PBZ 7 and PBZ 6 revealed induction times of 1780 and 40 min, respectively. Note that, like the blank, immediate precipitation resulted in the presence of 20 ppm of monomer 4. The significant antiscalant activity of PBZ 7 is attributed to its lower molar mass and ability to complex with Ca^{2+} and keep it in solution. At the time of nucleation of crystal, an antiscalant is adsorbed on the surface and change its morphology and hinders further growth, thereby preventing scale-growth[129,131,167-169].

PBZs 5, 6 and 7 are also tested as antiscalants for the inhibition of CaCO_3 scale formation from its supersaturated solution, and the results are plotted in Fig. 3.8. For over 240 min, PBZ 6 (20 ppm) maintained a PSI of 98%, while at 10 ppm concentration, it achieved a PSI of 95% for over 90 min. As the Figure shows, PBZ 6 performed better than PBZ 5 and 7.

Table 3. 3 Scale inhibition using PBZ **6**, PBZ **7**, and monomer **4** in a supersaturated^a CaSO₄ solution at 40 °C.

Entry	Sample (ppm)	Percent inhibition at times (min) of						Induction time (min)
		30	60	120	180	300	360	
PBZ 6								
1	20	99	99	98	98	97	87	370
2	10	99	87	27	24	—	—	60
3	5	98	66	24	15	—	—	40
PBZ 7								
4	5	100	100	100	100	100	100	1780
5	2.5	100	99	99	99	96	86	360
6	1.5	99 ^b	94	16	—	—	—	60
Monomer 4								
6	20	6	4	—	—	—	—	5

^aThree times the concentration of Ca²⁺ and SO₄²⁻ in the reject brine of a RO plant.

^bThe percent inhibition at 50 min was 98%.

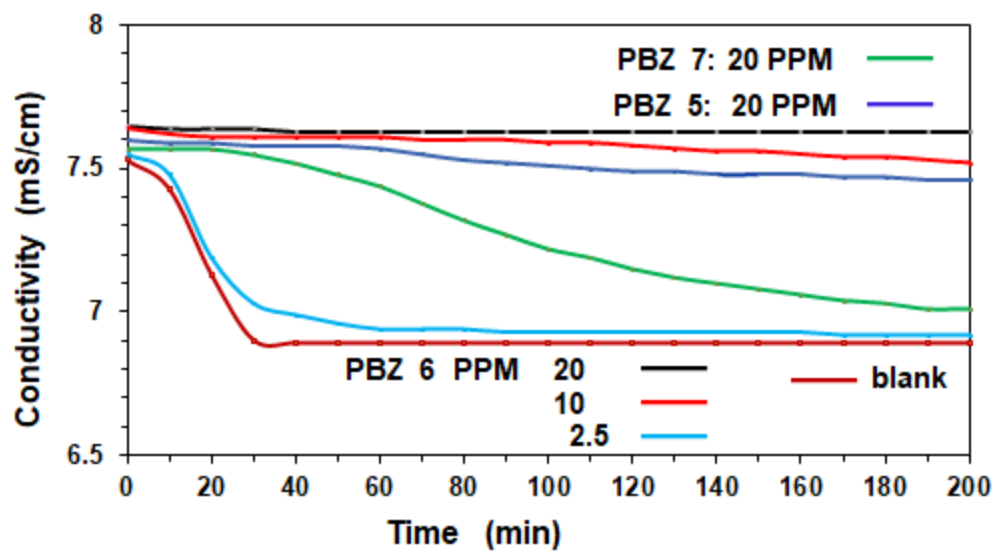


Figure3. 8(a) Conductivity of a supersaturated solution of NaHCO_3 in the presence (2.5, 10, 20 ppm) of PBZs 5, 6 and 7 and in the absence (blank) of antiscalants.

3.4.6 PBZs 6 and 7 as corrosion inhibitors

Gravimetric weight-loss method is the most reliable yet simple method to study corrosion inhibition as it examines corrosion loss for a longer duration (24 h in the current study) compared to shorter time required for electrochemical methods. As evident from [Table 3.5](#), inhibition efficiency (h%) (IE%) increases with increasing inhibitor concentrations. At a concentration of 50 ppm, PBZs **6** and **7** achieved impressive IE% of 92.5 and 95.7%, respectively. The presence of iodide ions is known to boost IE%, in the absence and presence of 400 ppm KI, the h% for 20 ppm PBZ **7** was found to be 90.5 and 98.3%. Note that a 400-ppm KI alone imparted a h% of 57.8%. The synergism parameter S_q is calculated using Equation (6)[132].

$$S_{\theta} = \frac{1 - (\theta_1 + \theta_2 - \theta_1\theta_2)}{1 - \theta_{1+2}} \quad (6)$$

where θ_1 , θ_2 and θ_{1+2} represent the degree of surface coverages which are equated to fractional inhibition efficiencies (h%/100) of PBZ **7**, KI, and (PBZ **7** + KI) mixture, respectively. While, $S_q > 1$ certifies cooperative co-adsorption (i.e. synergistic effect), $S_q < 1$ signifies competitive co-adsorption (i.e. antagonistic effect)[132,133]. The calculated S_q value of 2.35 demonstrates the synergistic effect of KI in a in the polymer+KI mixture in the mitigation of mild steel corrosion.

The PBZ **7** performed much better than PBZ **6** and monomer **4**; at 10 ppm concentrations, they imparted h% of 80.7, 45 and 34.4%, respectively ([Table 3.4](#)). The presence of high-density carboxyl motifs offering multiple adsorption sites provide stronger locking on the metal surface (thereby resisting desorption) by PBZ **7** as compared to PBZ **6** and monomer **4**.

Linear fitting of several isotherm models (Eqs, 7-10) (Temkin, Langmuir, Frumkin[134], and Freundlich[135]) with the surface coverage (q) data are presented in Fig. 3.9.

$$\text{Temkin:} \quad K_{ads} C = e^{f\theta} \quad (7)$$

$$\text{Langmuir:} \quad \frac{\theta}{1 - \theta} = K_{ads} C \quad (8)$$

$$\text{Frumkin:} \quad K_{ads} C = \frac{\theta}{1 - \theta} e^{-2a\theta} \quad (9)$$

$$\text{Freundlich:} \quad \theta = K_{ads} C^n \quad (10)$$

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G^0_{ads}}{RT}} \quad (11)$$

Table 3. 4Inhibition efficiency (IE) ($\eta\%$) imparted by PBZ **6** and PBZ **7** to arrest corrosion of mild steel in 1 M HCl at 60 °C for an immersion time of 24 h.

Entry	Sample (ppm)	KI (ppm)	IE (h%)
PBZ 6			
1	5	—	32.1
2	10	—	45.0 $\pm$ 0.6
3	20	—	67.3 $\pm$ 0.5
4	35	—	83.1 $\pm$ 0.5
5	50	—	92.3 $\pm$ 0.4
PBZ 7			
6	2.5		48.8 $\pm$ 1.1
7	5		67.4 $\pm$ 0.9
8	10		80.7 $\pm$ 0.5
9	20		90.5 $\pm$ 0.4
10	50		95.7 $\pm$ 0.4
PBZ 7 and KI			
11	—	400	57.8 $\pm$ 1.3
12	20	400	98.3 $\pm$ 0.6
Monomer 5			
13	5	—	33.2 $\pm$ 1.4
14	10	—	49.4 $\pm$ 1.1

In the Eqs. 7-10, C and K_{ads} represents concentration in mol L^{-1} and adsorption equilibrium constant, respectively, while. f and a denote interaction parameters. The data fitted the Langmuir model the best; the intercept value of $1.677 \times 10^5 \text{ L mol}^{-1}$ for K_{ads} was used to calculate the free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) using Equation (11) where 55.5 is the molar concentration of water in solution[134].

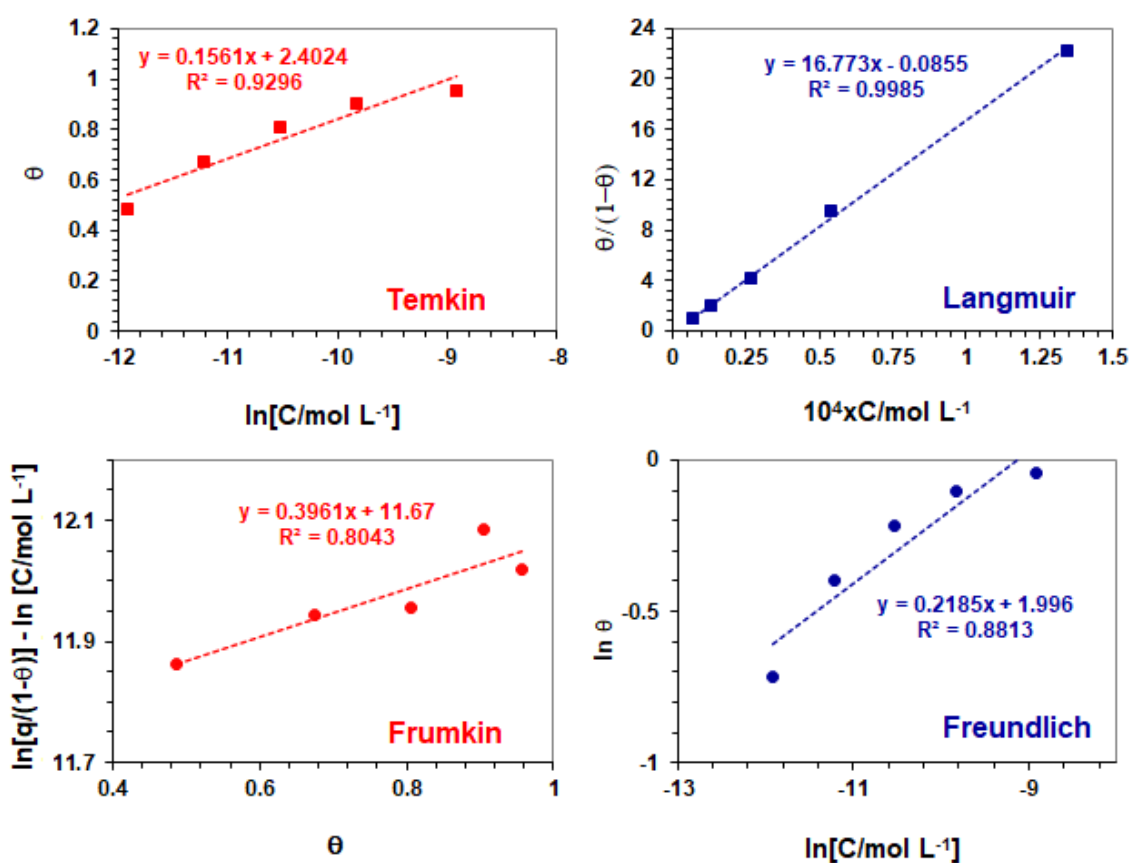
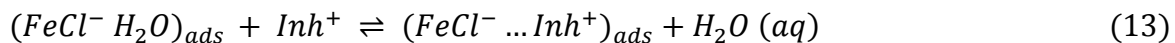
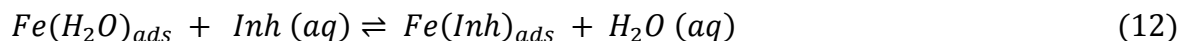


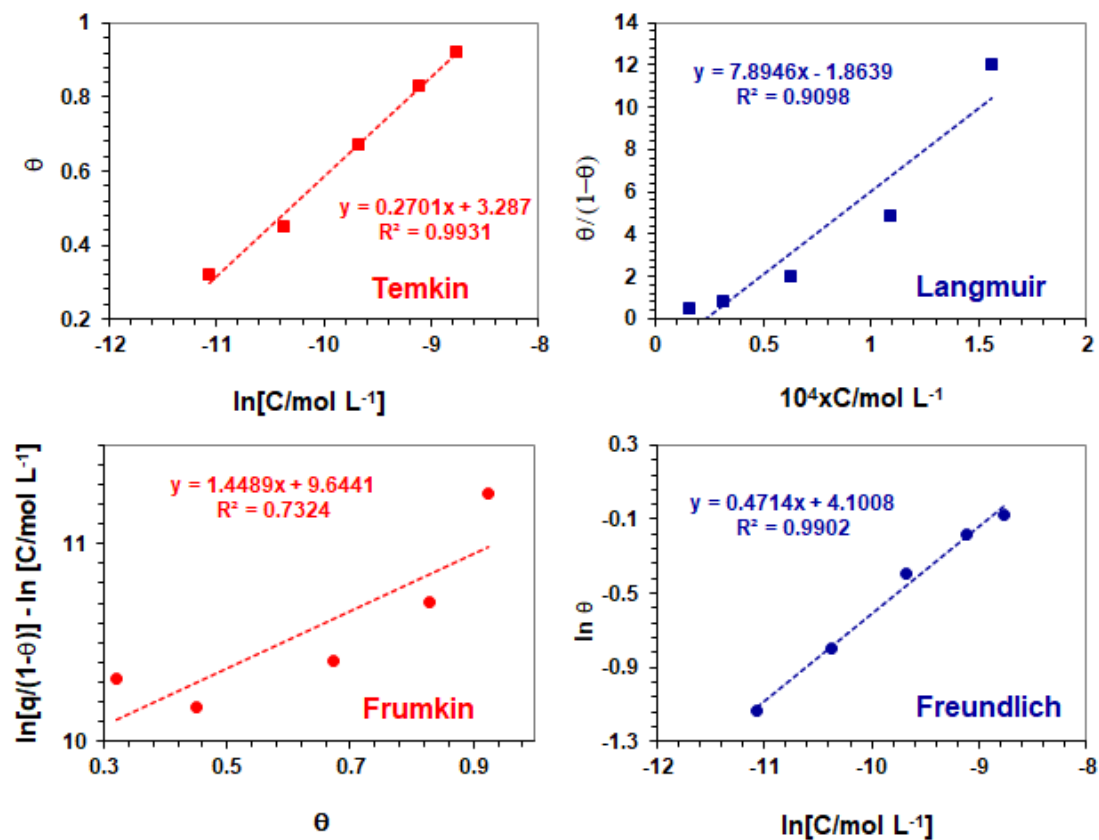
Figure3. 9(a) Temkin, **(b)** Langmuir, **(c)** Frumkin, and **(d)** Freundlich adsorption isotherms of PBZ 7 in 1 M HCl at 60 °C.

The factor 55.5 arises from the fact that the adsorption of an inhibitor (Inh) at a metal/aqueous interface may result from the displacement of the adsorbed water molecules (Equation (12)). The negative $\Delta G^{\circ}_{\text{ads}}$ value, found to be $-44.4 \text{ kJ mol}^{-1}$, implies the favorability of the adsorption process, and its magnitude may be attributed to the prevalence of both electrostatic adsorption and chemisorption[137,138].

Usually, $\Delta G^{\circ}_{\text{ads}}$ values less negative than -20 kJ mol^{-1} point toward physisorption involving the adsorption of cationic motifs of the polymer on the layer of Cl^{-} ions covering the Fe-surface (Eq 13)[136]. The interaction of carboxyl motifs with the d-orbitals of iron or accumulated Fe^{2+} on the anodic sites to form coordinate type of bond would represents chemisorption[137,138].



Temkin model fitted best with the gravimetric weight-loss data (Table 3.4) for PBZ **6** with a square of correlation coefficient (R^2) of 0.9931 (Figure 10 is not shown). From the slope ($1/f$) and intercept $(1/f)\ln K_{\text{ads}}$, the f , K_{ads} and $\Delta G^{\circ}_{\text{ads}}$ were found to be 3.70, $1.928 \times 10^5 \text{ L mol}^{-1}$ and $-44.8 \text{ kJ mol}^{-1}$, respectively.



3.5 Conclusions

Alternate copolymerization of monomer **4** with SO₂ (AIBN-initiated) and maleic acid (APS-initiated) afforded PBZs **6** and **7**, respectively, with corresponding yields of 90 and 71%. While both PBZs were insoluble in salt-free water, various salts like NaCl, NaBr, NaI, CaCl₂ and HCl imparted water-solubility. Both the polymers were found to have a similar pHPZC value of 2.4, implying that the polymers will have net positive and negative charge below and above the pH 2.4, respectively. PBZs **6** and **7** were found to be water-soluble outside the pH-windows of 0.81-4.46 and 1.49-3.35, respectively. The polymers remain soluble outside the pH-windows because of decreasing zwitterionic motifs and increasing charge-imbalanced backbones. The pK_a of NH⁺ centers in PBZ **6** was determined to be 5.18 and 9.92. Antiscalant PBZ **7** was very effective in preventing the formation of CaCO₃ and CaSO₄ scales. PBZ **7** at a concentration of 2.5 ppm, arrested formation of CaSO₄(s) scale with 99% efficacy for over 180 min, while in the presence of a meagre 1.5 ppm, the percent scale inhibitions were found to be 99 and 98% for over 30 and 50 min, respectively. Thus PBZ **7** is very suitable as a potent antiscalant since the usual residence time of brackish water in the RO chamber is about 15 min. PBZ **7** demonstrated superior antiscalant activities as compared to homopolymer PBZs **5** and SO₂-copolymer **7**. Interestingly, PBZ **6** at the concentrations of 20 and 10 ppm demonstrated CaCO₃ scale inhibition of 98% for over 240 min and 95% for over 90 min, respectively. Here, PBZ **6** performed better than PBZs **5** and **7**. The PBZs were turned out to be very good inhibitors of mild steel corrosion in 1 M HCl. A synergistic mixture of PBZ **7** (20 ppm) and KI (400 ppm) imparted 98% inhibition of mild steel corrosion.

Chapter 4

conclusion and future work

4.1 Conclusion

Monomers **16** (chapter1), which has been successfully synthesized, went free radical cyclopolymerization initiated by azoinitiator AMPD to afford poly biszwitterionic “PBZ” **17** in high yield, a unique polymer containing bis-zwitterionic motif in each repeating unit. The electrically neutral biszwitterionic polymer was found to be salt-free water insoluble. However, salts like NaCl, NaBr, and NaI imparted water solubility and increased viscosity, which is a typical antipolyelectrolyte behavior. Moreover, the pH-responsive polymer “PBZ” **17** with a point of zero charge “pHPZC” at 3.85 was found to be water-soluble outside the pH-range 2.15-3.93, wherein this pH range the electrically neutral bis-zwitterionic motifs ($\pm$) predominate in the polymer chain. Outside this pH-window, the polymer stays soluble because of increasing the participation of cationic or anionic motifs in the pH-responsive equilibria. The ‘apparent’ pK_a of two acidic proton centers containing NH^+ in **20** and **21** was determined to be 5.89 and 10.57, respectively. Regarding applications, poly biszwitterionic PBZ **17** was proved to be an effective antiscalant to inhibit scale formation, where at a concentration of 2.5 ppm, it imparted $\approx 100\%$ inhibition of $CaSO_4(s)$ scale formation from its super-saturated solution for 30 min, which is the usual residence time of brine water in the reverse osmosis chamber. Interestingly, the poly biszwitterionic PBZ **17** was found to be an excellent mild steel corrosion inhibitor at a concentration of 20 ppm in the existence of KI, where it imparted synergistic 99% inhibition of mild steel corrosion in 1 M HCl at 60 °C for a duration of 6 h. In addition, separately copolymerization of monomer **16** with maleic

acid **8** (APS-initiated) and SO₂ **24** (AIBN-initiated) afforded pure alternate copolymers **22** and **25**, each containing bis-zwitterionic motifs, in high yields. Both polymers were insoluble in salt-free water while they were soluble in the presence of various salts like NaCl, NaBr, NaI, CaCl₂, and HCl.

Furthermore, the two polymers were found to have a similar point of zero charge “pHPZC” value of 2.4, implying that the polymers will have cationic and anionic character below and above the pH 2.4, respectively. The two copolymers **22** and **25** were found to be water-soluble outside the pH-windows of 0.81-4.46 and 1.49-3.35, respectively. On either side of the pH-windows, the polymers remain soluble because of decreasing zwitterionic motifs and increasing participation of cationic or anionic groups in the pH-responsive equilibria. The ‘apparent’ pK_a of two cationic centers involving NH⁺ in **25** was determined to be 5.18 and 9.92.

The copolymer with Maleic acid **22** was proved to be a powerful antiscalant, where at a concentration of 2.5 ppm, it avoided formation CaSO₄(s) from its super-saturated solution for over 180 min with 99% inhibition ability, while at a meagre concentration of 1.5 ppm, the percent scale inhibitions were found to be 99 and 98% for over 30 and 50 min, respectively. As noticed, the copolymer **22** demonstrated superior antiscalant activities as compared to homopolymer PBZs **17** and SO₂-copolymer **25**. Interestingly, the two copolymers were turned out to be very good inhibitors of mild steel corrosion in 1 M HCl at 60 °C . At a concentration of 20 ppm in the presence of 200 ppm KI, the copolymer with Maleic acid **22** imparted synergistic 98% inhibition of mild steel corrosion for a duration of 24 h.

4.2 Future work

The synthesized polymers showed very impressive performance in real applications like water treatment as scale inhibitors as well as mild steel corrosion inhibitors. There are some scopes for the future study to be taken into account as follows:

- The synthesized polymers could be tested as Flocculants.
- These polymers can be applied for the separation techniques such as in protein separation.
- Inspired by the antimicrobial activity of similar zwitterionic Gemini-materials such polymers could be tested as antifouling agents.
- Newly novel resins could be synthesized representing another important family of cross-linked polyzwitterionic/anionic resins with important applications in both academia and industry.

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LIST OF PUBLICATIONS

1. **Aldahdooh, M.K.**, Ali, S.A., Synthesis and application of a poly(bis-zwitterion) containing chelating motifs of N-(2-aminoethyl)iminodiacetic acid, European Polymer Journal (2020)
doi: <https://doi.org/10.1016/j.eurpolymj.2020.110071> .
2. Ibrahim Y. Yaagoob, **Mohammed K. Aldahdooh**, Ali A. Al-Taq, Hasan A. Al-Muallem, Mohammad A. J. Mazumder, and Shaikh A. Ali*(**2020**)” Synthesis of stimuli-responsive ionic cyclopolymers in search of phosphate-free antiscalants” **accepted in the journal of applied polymer science.**
3. **Mohammed K. Aldahdooh**, Shaikh A.Ali (2020) “Synthesis and application of alternate cyclopolymers of b-diallylaminoethyliminodiacetic acid with maleic acid and sulfur dioxide ” **Manuscript is submitted.**
4. Nurudeen A. Odewunmi, Mohammad A. J. Mazumder, **Mohammed K. Aldahdooh**, Shaikh A.Ali (**2020**) “N1 ,N1 ,N12 ,N12 -Tetramethyl-N1 ,N12 -dioctyldodecane-1,12-diaminium bromide: Its synthesis and application in inhibition of mild steel corrosion in 15% HCl ” **Manuscript in preparation.**

Honors, Awards, and Distinctions

- Full scholarship for distinguished students, top student in the college of science for all four academic years (B.Sc.), 2011 – 2015, Al Azhar University in Gaza, Palestine.
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