

**SYNTHESIS AND APPLICATION OF POLYMERS  
CONTAINING BIOGENIC MOTIFS OF METHIONINE  
AND  $\beta$ -CYCLODEXTRIN TO MITIGATE TOXIC  
CONTAMINANTS**

BY

**SABRI ABDELKREEM**

A Thesis Presented to the  
DEANSHIP OF GRADUATE STUDIES

**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**CHEMISTRY**

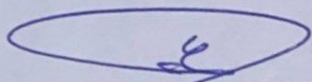
**MAY 2024**

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

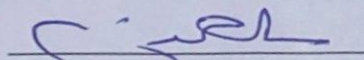
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **SABRI ABDELKREEM** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY**.



Dr. Jameel R. Al-Thagfi

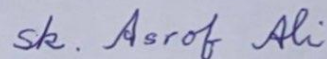
Department Chairman



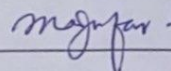
Dr. Suliman Saleh Al-Homidan

Dean of Graduate Studies

\_\_\_\_\_  
Date



Dr. Shaikh Asrof Ali  
(Advisor)



Dr. M. A. Jafar Mazumder  
(Member)



Dr. Hassan Al-Muallem  
(Member)



© SABRI ABDELKREEM

2024

| In loving memory of my dear parents |

## **ACKNOWLEDGMENTS**

Completing this thesis would not have been possible without the support and guidance of my committee members, friends, and family. I am profoundly grateful to Dr. Shaikh Ali for his invaluable mentorship and support throughout my research journey at King Fahd University of Petroleum and Minerals in Saudi Arabia. His extensive knowledge, patience, and inspiring guidance have significantly shaped my academic and personal growth. Dr. Ali was always accessible for discussions, eager to solve problems, and provided practical advice that only comes with experience. His encouragement was crucial, especially during challenging times, and I am deeply appreciative of his role as a mentor in my life.

I would also like to express my gratitude to my committee members, Dr. Mohammad A. Jafar Mazumder and Dr. Hassan Al-Muallem, for their indispensable insights and steadfast support. Their willingness to help and expert advice have greatly enriched my research and broadened my perspectives.

Special thanks are due to Dr. Jameel Al-Thagfi, Chairman of the Chemistry Department, for his leadership and support throughout my academic journey. His guidance has been instrumental in navigating the challenges of research and academic life.

To my siblings, thank you for your unwavering encouragement, understanding, and patience throughout this process. Your support has been my comfort and motivation, helping me navigate through the toughest times with strength and love.

A special thanks goes to my friends, whose companionship and support have been invaluable. You have shared in both my struggles and successes, providing thoughtful advice, laughter, and reminders of the importance of friendship and solidarity.

Finally, I must acknowledge the vital opportunity given to me by King Fahd University of Petroleum and Minerals in Saudi Arabia. Without the chance to study and conduct research here, none of this would have been possible. I am profoundly grateful for the privilege of being part of this esteemed institution.

I am fortunate to have such a supportive circle and am sincerely thankful to everyone who has contributed to my journey. |

# TABLE OF CONTENTS

|                                                                  |      |
|------------------------------------------------------------------|------|
| ACKNOWLEDGMENTS                                                  | III  |
| TABLE OF CONTENTS                                                | V    |
| LIST OF TABLES                                                   | VIII |
| LIST OF FIGURES                                                  | IX   |
| ABSTRACT                                                         | XI   |
| ملخص الرسالة                                                     | XII  |
| 1 CHAPTER 1 INTRODUCTION                                         | 1    |
| 1. $\beta$ -Cyclodextrin and Environmental Remediation           | 1    |
| 2. Challenge and Present State of the Problem:                   | 3    |
| 3. Objectives:                                                   | 4    |
| CHAPTER 2 LITERATURE REVIEW                                      | 5    |
| 2.1 Removal of Priority Toxic Metal Ions like Pb(II) and Hg(II): | 5    |
| 2.2 Polymers Containing $\beta$ -Cyclodextrin Pendants.          | 5    |
| 2.3 Butler's Cyclopolymerization Protocol                        | 7    |
| 2.4 Corrosion Inhibition                                         | 10   |
| CHAPTER 3 EXPERIMENTAL                                           | 13   |
| 3.1 Materials                                                    | 13   |
| 3.2 Physical Methods                                             | 13   |
| 3.3 Synthesis of Zwitterionic Monomer 3                          | 14   |
| 3.4 Cyclopolymerization of Zwitterionic Monomer 3                | 15   |

|                                                                                           |           |
|-------------------------------------------------------------------------------------------|-----------|
| <b>3.4.1 Procedure A:</b>                                                                 | <b>15</b> |
| <b>3.4.2 Procedure B:</b>                                                                 | <b>15</b> |
| <b>3.4.3 Procedure C:</b>                                                                 | <b>16</b> |
| <b>3.5 Copolymerization of Zwitterionic Monomer 3 and Glycine-Based Monomer 14</b>        | <b>16</b> |
| <b>3.6. Copolymerization of Zwitterionic Monomer 3 and Maleic acid 4</b>                  | <b>17</b> |
| <b>3.6.1 Procedure A:</b>                                                                 | <b>17</b> |
| <b>3.6.2 Procedure B:</b>                                                                 | <b>17</b> |
| <b>3.6.3 Procedure C:</b>                                                                 | <b>18</b> |
| <b>3.7 Copolymerization of Zwitterionic Monomer 3 and Aspartic Acid Monomer 17</b>        | <b>18</b> |
| <b>3.7.1 Procedure A:</b>                                                                 | <b>18</b> |
| <b>3.7.2 Procedure B:</b>                                                                 | <b>19</b> |
| <b>3.8 Synthesis of <math>\beta</math>-Cyclodextrin-Based Monomer 4</b>                   | <b>19</b> |
| <b>3.9 Copolymerization of Zwitterionic Monomer 3 and CD Monomer 4</b>                    | <b>19</b> |
| <b>3.10 Terpolymerization of Zwitterionic Monomer 3, CD Monomer 4, and Cross-Linker 5</b> | <b>20</b> |
| <b>3.11 Corrosion Inhibition Study</b>                                                    | <b>20</b> |
| <b>3.12 Assessment of Poisonous Metal ion Removal Efficiency:</b>                         | <b>21</b> |
| <b>3.13 Removal of Organic Micropollutants:</b>                                           | <b>22</b> |
| <b>CHAPTER 4 RESULTS AND DISCUSSION</b>                                                   | <b>23</b> |
| <b>4.1 Synthesis of Monomers, Polymers, and Cross-linked Resins</b>                       | <b>23</b> |
| <b>4.2 Solution properties of the synthesized polymers:</b>                               | <b>51</b> |
| <b>4.3 Mild steel corrosion inhibition by the synthesized polymers in 15% HCl</b>         | <b>53</b> |
| <b>4.4. Adsorption isotherms</b>                                                          | <b>59</b> |

|                                                                   |           |
|-------------------------------------------------------------------|-----------|
| <b>4.5 Removal of Organic Micropollutants: Adsorption Studies</b> | <b>66</b> |
| <b>Conclusion:</b>                                                | <b>68</b> |
| <b>REFERENCES</b>                                                 | <b>69</b> |
| <b>RESUME</b>                                                     | <b>85</b> |

## LIST OF TABLES

|                                                                                             |    |
|---------------------------------------------------------------------------------------------|----|
| Table 1. Polymerization of monomers $M_1$ (3), and $M_2$ (4, 8, 14, 17).                    | 52 |
| Table 2. Inhibition efficiency (IE) ( $\eta\%$ ) of compound 3, 13, 15, 16, and 18.         | 55 |
| Table 3. Adsorption of metal ions Pb (II) and Hg(II) by resin 24 at 25 °C                   | 60 |
| Table 4. Langmuir Freundlich and Temkin isotherm model constants for Hg<br>(II) and Pb(II). | 63 |

## LIST OF FIGURES

|                                                                                                                                                                                               |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1. Truncated Structure of $\beta$ -Cyclodextrin .                                                                                                                                      | 6  |
| Figure 2 . Different types of ionic polymers-based on charge types on the polymer chain                                                                                                       | 10 |
| Figure 3. Intra group, intra-, and interchain Zwitterionic interactions in a polyzwitterion.                                                                                                  | 10 |
| Figure 4 FTIR spectrum of monomer 3.                                                                                                                                                          | 24 |
| Figure 5 $^1\text{H}$ NMR spectrum of monomer 3 in $\text{D}_2\text{O}$ .                                                                                                                     | 25 |
| Figure 6 (a) $^{13}\text{C}$ NMR spectrum of monomer 3 in $\text{D}_2\text{O}$ ; (b) DEPT C-135 NMR spectrum of monomer 3 in $\text{D}_2\text{O}$ .                                           | 26 |
| Figure 7. FTIR spectrum of 13.                                                                                                                                                                | 28 |
| Figure 8. $^1\text{H}$ NMR spectrum of 13 in $\text{D}_2\text{O}$ .                                                                                                                           | 29 |
| Figure 9. $^{13}\text{C}$ NMR spectrum of 13 in $\text{D}_2\text{O}$ .                                                                                                                        | 29 |
| Figure 10. FTIR spectrum of 15.                                                                                                                                                               | 31 |
| Figure 11. $^1\text{H}$ NMR spectrum of (a) 13; (b) cyclopolymer bearing glycine residues; (c) 15 in $\text{D}_2\text{O}$ .                                                                   | 32 |
| Figure 12. $^{13}\text{C}$ NMR spectrum of (a) 13; (b) cyclopolymer bearing glycine residues; (c) 15 in $\text{D}_2\text{O}$ . 13 in $\text{D}_2\text{O}$ .                                   | 33 |
| Figure 13. FTIR spectrum of 16.                                                                                                                                                               | 35 |
| Figure 14. $^1\text{H}$ NMR spectrum of (a) 13 and (b) 16 in $\text{D}_2\text{O}$ .                                                                                                           | 36 |
| Figure 15. $^{13}\text{C}$ NMR spectrum of (a) 13 and (b) 16 in $\text{D}_2\text{O}$ .                                                                                                        | 37 |
| Figure 16. FTIR spectrum of 18.                                                                                                                                                               | 39 |
| Figure 17. $^1\text{H}$ NMR spectrum of (a) 13; (b) cyclopolymer bearing aspartic acid residues; (c) 18 in $\text{D}_2\text{O}$ .                                                             | 40 |
| Figure 18. $^{13}\text{C}$ NMR spectrum of (a) 13; (b) cyclopolymer bearing aspartic acid residues; (c) 18 in $\text{D}_2\text{O}$ .                                                          | 41 |
| Figure 19. $^1\text{H}$ NMR spectra of (a) $\beta$ -Cyclodextrin (2) in $\text{DMSO-d}_6$ , (b) 2 in $\text{D}_2\text{O}$ , (c) 20 in $\text{DMSO-d}_6$ , and (d) 4 in $\text{D}_2\text{O}$ . | 44 |
| Figure 20. $^{13}\text{C}$ NMR spectra of (a) $\beta$ -Cyclodextrin (2) in $\text{DMSO-d}_6$ , (b) 2 in $\text{D}_2\text{O}$ , (c) 20 in $\text{DMSO-d}_6$ , (d) 4 in $\text{D}_2\text{O}$ .  | 45 |
| Figure 21. FTIR spectrum of 18.                                                                                                                                                               | 47 |

|                                                                                                                                                                                     |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 22. $^1\text{H}$ NMR spectrum of (a) 13 and (b) cyclopolymer 23 in $\text{D}_2\text{O}$ .                                                                                    | 48 |
| Figure 23. FTIR spectrum of resin 24.                                                                                                                                               | 51 |
| Figure 24. (a) Temkin, (b) Langmuir, (c) Frumkin, and (d) Freundlich adsorption isotherms of 18 in 15% HCl at 30 °C.                                                                | 58 |
| Figure 25 Interaction of sulfur lone pair and cationic nitrogens on halide assisted adsorption on metal surface.                                                                    | 58 |
| Figure 26. Equilibrium adsorption capacity ( $\theta_e$ ) versus initial concentration ( $C_o$ ) plots at 298 K for the adsorption of metal ions on resin 24.                       | 61 |
| Figure 27. (a) Temkin for Hg (II), (b) Freundlich for Hg (II), (c) Temkin for Pb(II), and (d) Freundlich for Pb (II) isotherms of the adsorption of metal ions on resin 24 at 298K. | 61 |
| Figure 28. FTIR spectra of (a) Pristine resin 24, (b) Resin loaded with Hg (II), and (c) Resin loaded with Pb (II).                                                                 | 64 |
| Figure 29. SEM and EDX analysis for resin 24 (a) unloaded, (b) loaded with Hg(II), (c) and loaded with Pb(II).                                                                      | 65 |
| Figure 30. UV spectra of organic analytes with known concentrations and adsorption sample                                                                                           | 67 |

## ABSTRACT

Full Name : [Sabri Saghieron Alshiekh Abdelkreem]

Thesis Title : [Synthesis and Application of Polymers Containing Biogenic Motifs of Methionine and  $\beta$ -Cyclodextrin to Mitigate Toxic Contaminants]

Major Field : [Chemistry]

Date of Degree : [May 2024]

Various amino acid-based diallylamine salt monomers with the general formula  $(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)_2\text{NH}^+\text{CH}(\text{R})\text{CO}_2^-$  have been synthesized, including methionine, glycine, and aspartic acid-based monomers (monomers **3**, **14**, and **17**) where R represents  $(\text{CH}_2)_2\text{SMe}$ , H, and  $\text{CH}_2\text{CO}_2\text{H}$ , respectively. Additionally, a  $\beta$ -cyclodextrin (CD) based monomer  $(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)_2\text{NH}^+\text{CH}_2\text{R}, \text{Cl}^-$  (**4**), where R is the CD residue, and a cross-linker  $(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)_2\text{NH}^+(\text{CH}_2)_6\text{NH}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2, 2\text{Cl}^-$  (**5**) were developed. Cyclopolymerization of monomer **3** yielded homopolymer **13**, while its copolymerization with monomers **14**, maleic acid (**8**), **17**, and **4** produced copolymers **15**, **16**, **18**, and **23**, respectively. Terpolymerization involving monomers **3**, **4**, and **5** resulted in a cross-linked resin **24**. Monomer **3** and polymers **13**, **15**, **16**, and **18** were evaluated as corrosion inhibitors for mild steel in 15% HCl at temperatures of 30°C, 45°C, and 60°C. The polymers generally showed higher inhibition efficiency than the monomer, with copolymer **18** performing the best, achieving impressive inhibition efficiencies (IEs) even at concentrations as low as 1-5 ppm. The addition of potassium iodide (KI) further enhanced the IEs. Resin **24** has been effectively used to capture organic micropollutants and priority metal ions such as Hg (II) and Pb (II).

## ملخص الرسالة

الاسم الكامل: صبري صغبيرون الشيخ عبدالكريم

عنوان الرسالة: تصنيع البوليمرات التي تحتوي على زخارف حيوية من الميثيونين و بيتا-سيكلوديكسترين و تطبيقها للتخفيف من الملوثات السامة.

التخصص: الكيمياء

تاريخ الدرجة العلمية: مايو/2024

تم تصنيع العديد من مونومرات ملح الدايليل المبنية على الأحماض الأمينية ، بما في ذلك الميثايونين والجلاليسين والمونومرات القائمة على حمض الأسبارتيك. بالإضافة إلى ذلك تم إنتاج مونومر قائم على بيتا-سايلوديكسترين، وأنتجت البلمرة الحلقية للمونومر 3 البوليمر المتجانس 13 ، في حين أن البلمرة الثنائية المشتركة للميثايونين مع المونومرات 14 وحمض المالبك (8) و حمض الأسبارتيك (17) و جلايسين (14) أنتجت البوليمرات الثنائية غير المتجانسة 15 و 16 و 18 و 23 على التوالي. و نتج عن البلمرة الثلاثية التي تتضمن المونومرات 3 و 4 و 5 راتنج متصالب 24.

تم دراسة المونومر 3 والبوليمرات 13 و 15 و 16 و 18 كمثبطات للتآكل الفولاذي في وسط حمضي 15% حمض الهيدروكلوريك عند درجات حرارة مختلفة ( 30 و 45 و 60 درجة مئوية). و أظهرت البوليمرات عموما كفاءة تثبيط أعلى من المونومر. وحقق البوليمر 18 كفاءات تثبيط (IEs) ممتازة، حتى عند تراكيز منخفضة تصل إلى (1-5ppm). وأدت إضافة يوديد البوتاسيوم (KI) إلى زيادة تعزيز IEs.

وقد استخدم البوليمر 24 لازالة الملوثات العضوية الدقيقة وأيونات الفلزات الثقيلة مثل الزئبق (II) والرصاص

# CHAPTER 1

## INTRODUCTION

### 1. $\beta$ -Cyclodextrin and Environmental Remediation

Recycling wastewater that contains organic and toxic materials is critical due to the potential detrimental effects on human health and the environment.<sup>1</sup> This issue represents a significant challenge as it necessitates compliance with stringent health-based regulations<sup>2,3</sup>

The remediation of industrial effluents is crucial in mitigating water pollution and protecting ecological health. These effluents often contain harmful chemicals with limited biodegradability. As a result, various effective strategies have been developed and optimized to address this issue, including adsorption,<sup>4</sup> precipitation,<sup>5</sup> dialysis,<sup>6</sup> ion exchange,<sup>7</sup> reverse osmosis,<sup>8</sup> and extraction.<sup>9</sup> The main goal of these techniques is to remove metallic impurities from water sources, rendering the water safe for consumption and other uses.

Among these methods, adsorption is widely used due to its efficiency in removing pollutants from wastewater using various solid adsorbents.<sup>10-14</sup> Understanding the physicochemical sorption pathways has significantly enhanced the development of sorbent materials.<sup>15-16</sup>

Factors such as hydrophobic interactions, dispersion forces, and mild dipolar interactions between the adsorbent and the pollutants play a crucial role in the adsorption process.<sup>17</sup>

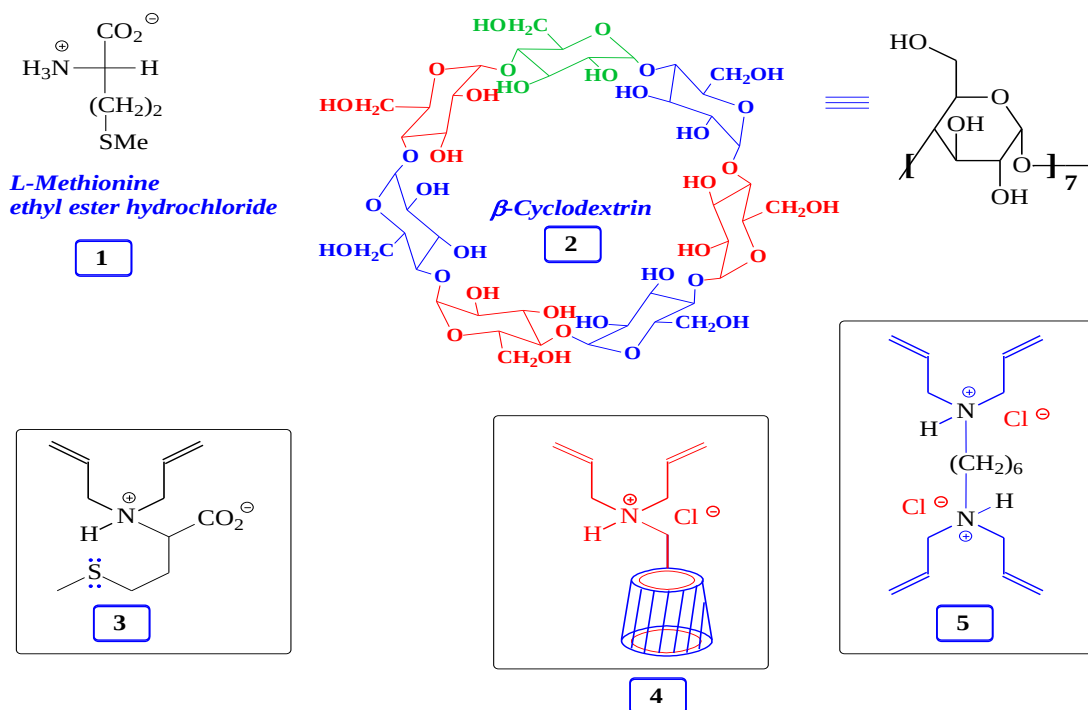
The adsorption process, though effective at eliminating metals and various organic pollutants non-selectively, presents significant challenges in metal recovery and reuse. This highlights a critical need for innovative methodologies specifically aimed at the targeted removal of organic contaminants and heavy metals from aqueous sources. However, these methodologies come with their own set of limitations and drawbacks, necessitating the development of new technologies.

This research thesis focuses on synthesizing pH-responsive resins incorporating biogenic amino acid methionine and  $\beta$ -cyclodextrin residues, using monomers **3**, **4**, and **5** to create reusable materials (Scheme 1).  $\beta$ -Cyclodextrin ( $\beta$ -CD) consists of seven glucopyranose units linked by  $\alpha$ -1,4 glycosidic bonds and has a cyclic oligosaccharide structure resembling a truncated cone, with its apex replaced by a plane parallel to the base (Scheme 1).<sup>18</sup> Produced via enzymatic degradation of starch,  $\beta$ -CD features an inner lipophilic cavity approximately 0.60-0.65 nm in diameter, surrounded by a hydrophilic exterior.<sup>19</sup>

The copolymerization of biogenic amino acid methionine with monomers **14**, maleic acid (**8**), **17**, and **4** produced copolymers **15**, **16**, **18**, and **23**, respectively. Polymers **13**, **15**, **16**, and **18** were evaluated as corrosion inhibitors for mild steel in 15% HCl at temperatures of 30°C, 45°C, and 60°C.

$\beta$ -CD's broad availability and versatility make it valuable in various applications, including drug delivery, pharmaceuticals, biosensors, tissue engineering, and water

treatment.<sup>20</sup> Its structure allows for the formation of intramolecular hydrogen bonds between secondary OH groups, contributing to its relatively poor water solubility.<sup>21-22</sup> Notably, each glucopyranose unit in  $\beta$ -CD is densely packed with two secondary OH groups, whereas the primary OH group at the C-6 position is less sterically hindered.



Scheme 1.  $\beta$ -Cyclodextrin and the monomers

## 2. Challenge and Present State of the Problem:

There is a lack of literature documenting the synthesis of polymeric materials incorporating both amino acid methionine and  $\beta$ -cyclodextrin motifs through the utilization of Butler's cyclopolymerization technique.

Methionine having a sulfide group and amino carboxylate chelating motifs is suitable for trapping  $\text{Pb}^{2+}/\text{Hg}^{2+}$ , while cyclodextrin is expected to capture organic contaminants.

Our proposed research is expected to pave the way for simultaneous removal of both organic and inorganic contaminants.

### 3. Objectives:

The main goal of the proposed project is to conduct the synthesis of a range of copolymers that incorporate methionine and  $\beta$ -cyclodextrin motifs, together with a cross-linked resin, utilizing Butler's cyclopolymerization process. These copolymers are intended to be used in the remediation of both organic and inorganic pollutants, the specific objectives for the study are as follows:

- Synthesis of methionine-based zwitterionic diallylamine salt monomer.
- Synthesis of  $\beta$ -cyclodextrin-based diallylamine salt monomer.
- Polymerization of methionine-based monomer and its copolymerization with the  $\beta$ -cyclodextrin-based monomer.
- Polymerization of methionine-based and  $\beta$ -cyclodextrin-based monomers in the presence of a cross-linker to produce cross-linked resin.
- Copolymerization of zwitterionic monomer **3** with glycine-based monomer **14**, maleic acid **4** and aspartic acid monomer **17**.
- Physical and chemical characterization of the synthesized compounds
- Application of  $\beta$ -cyclodextrin and methionine-based resin polymers for simultaneous trapping of  $\text{Pb}^{2+}/\text{Hg}^{2+}$  priority metal contaminants and some organic contaminants,
- Application of polymers **13**, **15**, **16**, and **18** in mild steel corrosion inhibitors

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Removal of Priority Toxic Metal Ions like Pb(II) and Hg(II):

For drinking water, the concentration of mercury Hg(II) approaching zero is preferable. However, the Environmental Protection Agency (EPA) has set a regulatory limit at 0.002 mg/L (2 ppb).<sup>23</sup> The challenge of removing mercury at these exceedingly low concentrations remains significant. In the case of lead (Pb), the Chinese standard specifies a permissible limit of 0.01 mg/L in drinking water,<sup>24</sup> while the U.S. EPA aims for concentrations as close to zero as possible.<sup>25</sup>

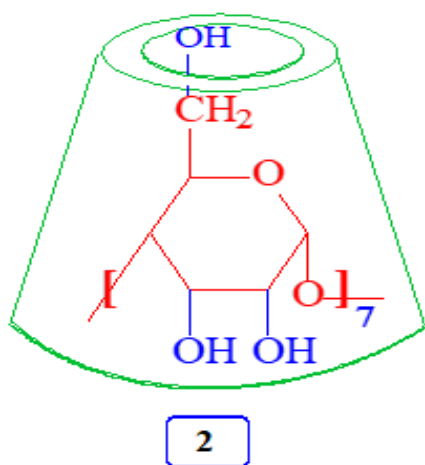
While numerous studies have reported on the adsorptive removal of Hg(II) at higher concentrations,<sup>26-28</sup> research focused on its removal at lower concentrations of Hg(II) and Pb(II) is limited. Our laboratory has developed various resins that have been successfully used to remove organic dyes and priority metal ions from water.<sup>29-34</sup>

#### 2.2 Polymers Containing $\beta$ -Cyclodextrin Pendants.

Cyclodextrin has been found safe by Food and Drug Administration (FDA).<sup>35</sup> Various hydrophobic drugs form inclusion compounds, which upon penetration to body tissues release biologically active compounds.<sup>36,37</sup>

The larger opening of  $\beta$ -cyclodextrin exposes the secondary hydroxyl groups, while its smaller opening exposes primary hydroxyl groups to the hydrophilic solvents (Scheme 2). The water-solubility and insolubility in ordinary organic solvents of cyclodextrin or its complexes can be attributed to the hydrophilic character of their exterior.  $\beta$ -Cyclodextrins

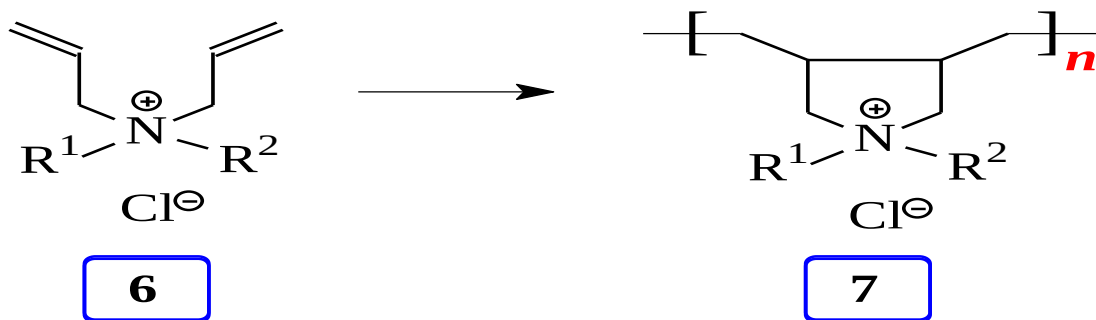
exhibit poor solubility in water, with a solubility of 18.5 g/L. The hydrophobic cholesterol molecule seeks safety within the core of the cyclodextrin.<sup>38</sup> Cyclodextrin-based polymers have been used to encapsulate and remove micropollutants from water by means of adsorption.<sup>39,40</sup>



**Figure 1.** Truncated Structure of  $\beta$ -Cyclodextrin .

## 2.3 Butler's Cyclopolymerization Protocol

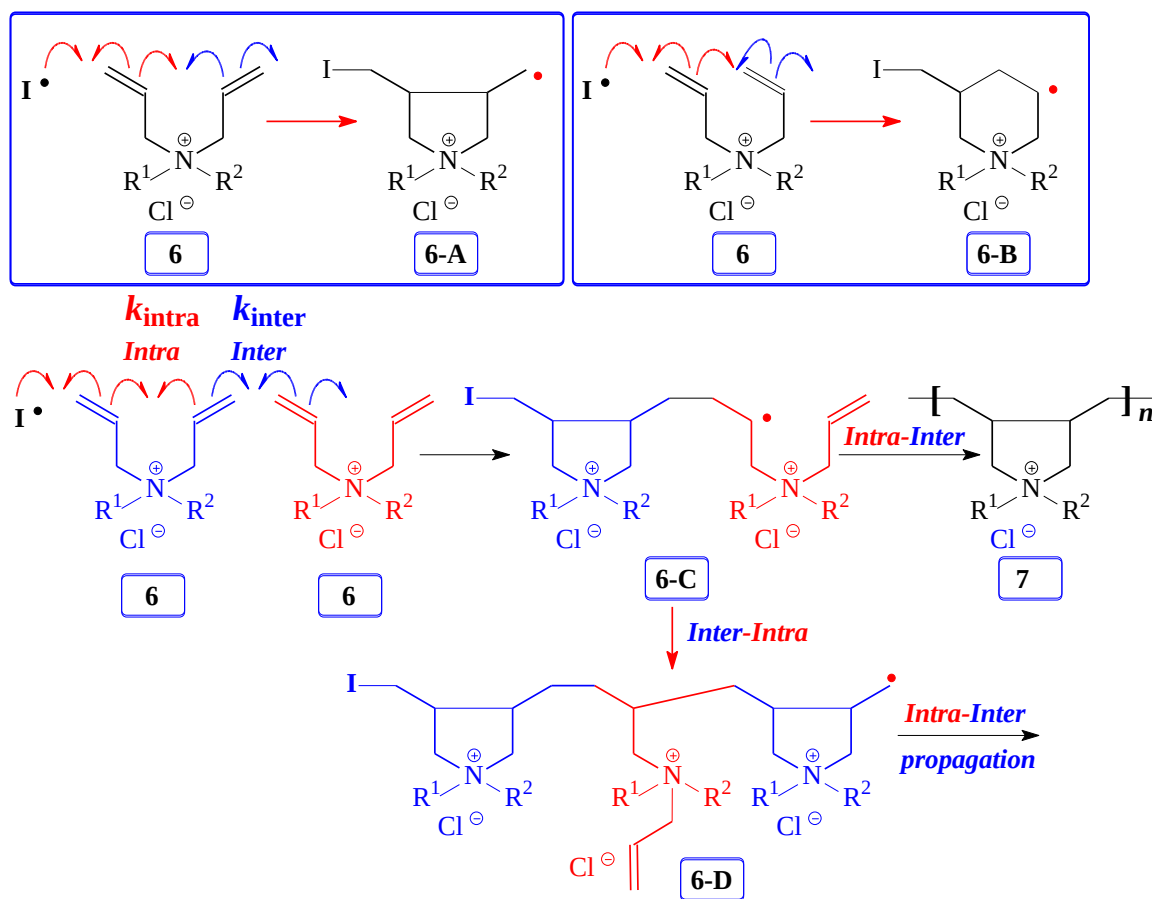
Free radical addition polymerization of *N,N*-diallyl quaternary ammonium salts **6**, known as Butler's cyclopolymerization protocol, led to numerous syntheses of industrially important polyelectrolytes **7** (Scheme 3).<sup>41-44</sup>



**Scheme 2.** Cyclopolymerization of diallylamine salts.

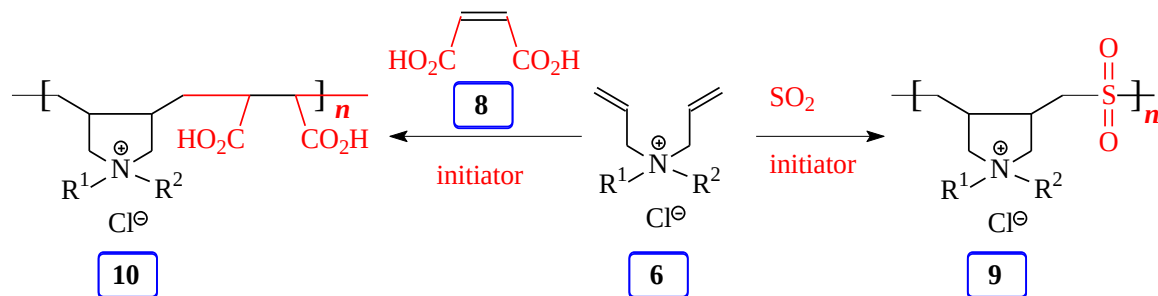
The initiator radical predominantly forms the less stable primary radical **6-A** over the more stable secondary radical **6-B** (Scheme 3).<sup>45-49</sup> Due to the significantly faster intra-molecular chain propagation ( $k_{\text{intra}}$ ) compared to inter-molecular chain propagation ( $k_{\text{inter}}$ ), the formation of polymer **7** via pathway **6-C** is favored. However, a less favored inter-intra molecular pathway may result in up to 3% of pendant double bonds remaining within the polymer chains of **7**, leading to the formation of **6-D**.<sup>50-54</sup>

In polymer **7**, the cis/trans ratio of the 3,4-substituents in the five-membered rings is observed to be between 3-6:1 (Scheme 3).<sup>52,55,56</sup>



**Scheme 3.** Intra-intermolecular chain propagation in Butler cyclopolymerization.

When diallyl amine salts **6** are copolymerized with sulfur dioxide<sup>57</sup> or maleic acid (MA) **8**<sup>58,59</sup> the result is the formation of alternate copolymers **9** and **10**. This is due to the nearly zero reactivity ratios (i.e.,  $r^1 \approx 0$ ,  $r^2 \approx 0$ ) of the monomeric pairs, which are illustrated in (Scheme 4).<sup>58</sup>

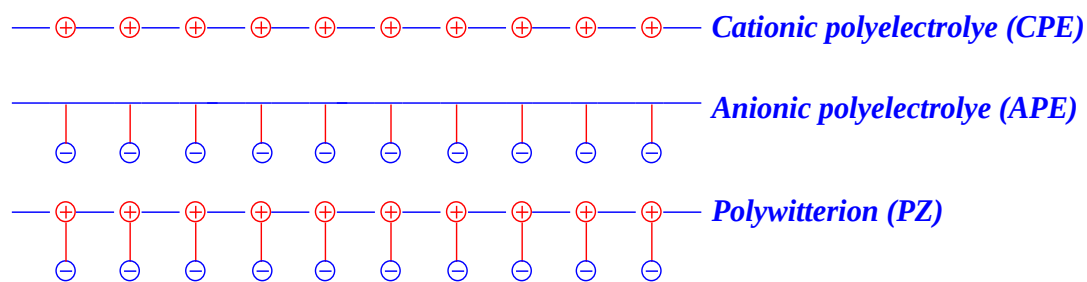


**Scheme 4.** Alternate cyclopolymerization of diallylamine salts with SO<sub>2</sub> and maleic acid.

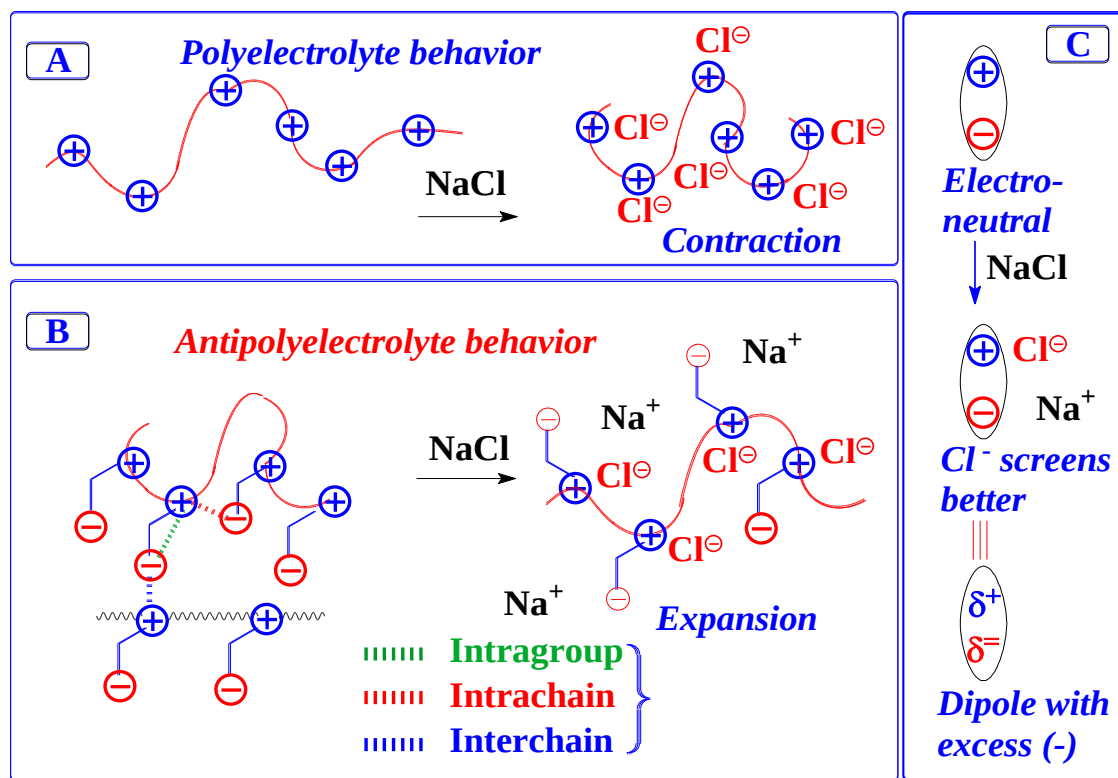
Polymer chains that bear cationic, anionic, and zwitterionic charges are referred to as cationic polyelectrolytes (CPE), anionic polyelectrolytes, and polyzwitterions (PZs), respectively. CPE and anionic polyelectrolytes exhibit polyelectrolyte effects, enhancing solution conductivity and reducing viscosity due to charge repulsion, which is moderated by salts like NaCl. Conversely, PZs display antipolyelectrolyte behaviors, where adding salts like NaCl increases solution viscosity due to reduced charge repulsion<sup>60</sup>. In these systems, the ions (Na<sup>+</sup> or Cl<sup>-</sup>) neutralize opposing charges on the polymer chains, thus diminishing repulsions among like charges and reducing the hydrodynamic volume and, consequently, the viscosity (Figure 2).

Unlike polyelectrolytes (PEs), water-insoluble polyzwitterions (PZs) typically form collapsed coil or globular structures in salt-free solutions due to intragroup, inter-, and intra-chain zwitterionic interactions, creating a three-dimensional ionic network (Figure 3).<sup>61</sup> However, the addition of salts such as NaCl induces a transition from globular to coil conformations by disrupting these zwitterionic interactions, neutralizing the polymer's ionic network and enhancing water solubility.<sup>62,63</sup>

This process is facilitated as Na<sup>+</sup> and Cl<sup>-</sup> ions bind to the polymer's positive (N<sup>+</sup>) and negative centers respectively, reducing internal charge repulsions and increasing both hydrodynamic volume and viscosity.<sup>64,65</sup>



**Figure 2 .** Different types of ionic polymers-based on charge types on the polymer chain.



**Figure 3.** Intra group, intra-, and interchain Zwitterionic interactions in a polyzwitterion.

## 2.4 Corrosion Inhibition

Mild steel, which is both affordable and widely used due to its low carbon content (up to 0.3%), boasts appropriate mechanical properties for extensive use in the oil and gas

sectors.<sup>66-68</sup> However, its extensive exposure to acidic environments in various industrial settings significantly increases its susceptibility to damage.<sup>69</sup> Organic corrosion inhibitors containing heteroatoms like N, O, S, and P, possess lone electron pairs that can safeguard metal surfaces against acid corrosion by creating coordinate bonds with vacant d orbitals on the metal.<sup>70</sup> These inhibitors typically disrupt the electrochemical processes that occur on metal surfaces, effectively reducing or preventing corrosion.<sup>71</sup>

Amino acids are valued for their biodegradability and compatibility with biological systems, and they have shown promising results as corrosion inhibitors in harsh environments.<sup>72-74</sup> Specifically, alanine and glycine have been tested for their effectiveness in preventing corrosion of mild steel in 0.1 M HCl, where they demonstrated inhibition efficiencies of 80% and 78.9%, respectively, at concentrations of 10 mM.<sup>75</sup> Further studies on alanine, cysteine, and S-methyl cysteine have indicated their potential in protecting iron from corrosion in 1.0 M HCl, with maximum reported efficiencies of 77.3%, 86%, and 94.2% respectively at 5.0 mM.<sup>76</sup> Additionally, methionine, which is non-toxic and easily available, has been researched for its corrosion inhibition capabilities in 0.1 M HCl at 25 ppm, achieving a maximum efficiency of 47%.<sup>77</sup>

In recent years, polymers have attracted attention as corrosion inhibitors.<sup>77,78</sup> With their expansive surface area and numerous anchoring sites, these materials are effective in bonding with metal ions or adhering to metal surfaces. The formation of polymer-metal complexes acts as a barrier, protecting the metal surface and thus preserving the active sites from corrosive environments.<sup>79</sup>

The presence of pH-responsive elements such as nitrogen (N), oxygen (O), and sulfur (S), along with multiple anchoring sites in the polymer chain, allows for an in-depth

examination and comparison of the effectiveness of sulfide functional motifs in preventing corrosion of mild steel in 15% HCl. This concentration of HCl is commonly used for pickling.<sup>80, 81</sup> Larger molecules are expected to cover a greater surface area, potentially offering superior protection against corrosion compared to smaller molecules.<sup>82-84</sup>

The oil and gas industries frequently utilize highly corrosive acidic solutions such as 15% HCl and 20% H<sub>2</sub>SO<sub>4</sub> to enhance productivity by breaking down the rocky substratum.

These acids, however, can severely corrode associated metal pipelines, causing substantial economic losses and safety risks.<sup>85-87</sup> According to a recent NACE report, corrosion costs the global economy over US \$2.5 trillion each year.<sup>88</sup>

Synergism is a strategy that has been employed to improve the effectiveness of corrosion inhibitors. This concept is based on the principle that the combined effect of a compound is greater than the sum of its individual effects. The synergistic inhibitive impact of iodide ions, for instance, has been well-documented.<sup>89,90</sup>

## CHAPTER 3

# EXPERIMENTAL

### 3.1 Materials

Azoisobutyronitrile (AIBN) (crystallized from chloroform-ethanol) and imidazole were purchased from Fluka Chemie AG.  $\beta$ -Cyclodextrin ( $\beta$ -CD), p-toluenesulfonyl chloride, diallylamine, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPD), ammonium persulfate (APS), and dimethylsulfoxide (DMSO) ( $\geq 99.5\%$ ) were purchased from Sigma-Aldrich. Membranes with molecular weight cut-off (MWCO) values of 3500 and 6000-8000 were obtained from Spectra/Por (Spectrum Laboratories, Inc.) and used for dialysis against distilled water. Monomers N, N-diallylaspartic acid hydrochloride (15),<sup>91</sup> and diallylammonioethanoate (10)<sup>92</sup> were synthesized as described. Tosyl imidazole (2) was prepared as described.<sup>94</sup> in a 90% yield (mp 78-79 °C, lit.<sup>93</sup> 78.0-79.0 °C). The cross-linker was synthesized as described.<sup>94</sup>

### 3.2 Physical Methods

FTIR spectra were recorded using a Perkin Elmer instrument (Series II Model 2400). Elemental analysis was conducted on a Perkin Elmer (16F PC) spectrometer. For elemental analysis, samples were dried in vacuo at 60°C for 6 hours. Thermogravimetric analysis (TGA) was performed using an SDT Q600 analyzer from TA Instruments, operated under a nitrogen flow. NMR spectra were obtained with a JEOL 600 MHz spectrometer at operational frequencies of 600.00 MHz for  $^1\text{H}$  and 125.00 MHz for  $^{13}\text{C}$ , using the signal of

HOD protons at  $\delta$  4.65 and the  $^{13}\text{C}$  dioxane signal at  $\delta$  67.4 ppm as internal standards. Viscosity measurements were conducted using an Ubbelohde viscometer (Constant = 0.005 cSt/s) under a nitrogen atmosphere at a precisely controlled temperature of  $30.0 \pm 0.1^\circ\text{C}$ , maintained by a CT72/P water bath from SI Analytics, Germany. Viscosity was measured at least three times to ensure an average error of less than 0.2%.  $\text{CO}_2$ -free distilled water was utilized for all viscosity measurements.

### 3.3 Synthesis of Zwitterionic Monomer 3

The methionine diallyl derivative, referred to as compound **12**, was synthesized from L-methionine ethyl ester hydrochloride (compound **11**) using established methods.<sup>29,95</sup> Initially, a heterogeneous mixture comprising (18.02 grams, 70 mmol) of monomer precursor **12**, 45 mL of methanol, 20 mL of water, and 3.12 g, (78 mmol) of sodium hydroxide was stirred at  $55^\circ\text{C}$  for five hours. Post solvent evaporation, the remaining mixture was diluted with water, neutralized with 37% HCl (37%) (7.68 g; 78 mmol), and freeze-dried to separate a mixture of the zwitterionic monomer **3** and sodium chloride. The mixture was further processed by triturating with 100 mL of acetone to remove insoluble NaCl (4.3 g, 73.6 mmol) through filtration. The clear filtrate was then evaporated to secure monomer **3** (15.4 g, 96%) as a colorless, viscous liquid, which crystallized on cooling in the refrigerator.

Elemental analysis of  $\text{C}_{11}\text{H}_{19}\text{NO}_2\text{S}$  found: C, 57.2; H, 8.5; N, 6.0; S, 13.7; requires C, 57.61; H, 8.35; N, 6.11; S, 13.98%;  $\nu_{\text{max}}$ . (Neat) 3080, 2979, 2917, 2834, 2283, 1613, 1456, 1425, 1357, 1338, 1215, 1150, 1121, 1081, 1063, 1015, 993, 951, 920, 894, 823, 775, 761, 719, 694, 667, 629, and  $575\text{ cm}^{-1}$ ;  $\delta_{\text{H}}$  ( $\text{D}_2\text{O}$ ) 1.98 (3H, s), 2.06 (1H, m), 2.45 (1H, m), 2.57 (1H, ddd,  $J$  5.4, 7.8, 13.2 Hz), 3.65 (2H, m), 3.75 (1H, m), 5.47 (4H, m), 5.81 (2H, m),

(residual H in D<sub>2</sub>O at 4.65 ppm);  $\delta_C$  (D<sub>2</sub>O)(2 °C): 15.06 (1C, SCH<sub>3</sub>), 27.09 (1C, CH<sub>2</sub>CH<sub>2</sub>S), 30.50 (1 C, CH<sub>2</sub>CH<sub>2</sub>S), [53.31 (1C, NCH<sub>2</sub>), 55.33 (1C, NCH<sub>2</sub>): (diastereotopic)], 65.72 (1C, NCH), [126.35 (1C, CH=CH<sub>2</sub>), 126.89 (1C, CH=CH<sub>2</sub>), 127.28 (1C, CH=CH<sub>2</sub>), 127.33 173.30 (1C, CO<sub>2</sub>): diastereotopic], (67.4, dioxane). The DEPT-135 NMR analysis was used for the <sup>13</sup>C assignments.

### 3.4 Cyclopolymerization of Zwitterionic Monomer 3

#### 3.4.1 Procedure A:

A mixture containing (1.15 g, 5 mmol ) of monomer **3**, (50 mg, 5 mmol) of AMPD, and 0.49 g of water was purged with nitrogen gas and agitated in a sealed flask at 80 °C for 24 hours, resulting in a monomer-to-water mass ratio of 70:30. This thick mixture was subjected to dialysis against distilled water using a 3500 MWCO dialysis tube for 24 hours, then freeze-dried to yield 520 mg (40% yield) of homopolymer **13** as a white solid.  $\nu_{\max}$ . (Neat) 3591, 2917, 2853, 1729, 1617, 1449, 1381, 1347, 1227, 1162, 993, 956, 920, 873, 792, 648, and 548 cm<sup>-1</sup>. Elemental analysis of C<sub>11</sub>H<sub>19</sub>NO<sub>2</sub>S found: C, 57.4; H, 8.6; N, 6.2; S, 13.8; requires C, 57.61; H, 8.35; N, 6.11; S, 13.98%.

#### 3.4.2 Procedure B:

A mixture containing monomer **3** (1.15 g, 5 mmol), NaCl (86 mg, 1.47 mmol), and AMPD (50 mg) in water (0.49 g) was degassed with nitrogen and stirred in a sealed flask at 80 °C for 24 hours. The NaCl concentration reached 3.0 M. The ratio of monomer to water by weight was established at 70:30. After dialysis against distilled water using a 3500 MWCO dialysis tube for 24 hours, the mixture was freeze-dried, resulting in homopolymer **13** as a white solid weighing 509 mg, achieving a 44% yield.

Repeating the polymerization process with an increased amount of AMPD (100 mg) while maintaining the same proportions of other reactants resulted in a polymer yield of 659 mg (57%).

### **3.4.3 Procedure C:**

A mixture of monomer **3** (1.15 g, 5 mmol), AMPD (50 mg), and 37% concentrated HCl (493 mg, 5 mmol) in water (0.180 g) was degassed with nitrogen and stirred in a sealed flask at 80°C for 24 hours. The weight ratio of monomer to water was adjusted to 70:30. After the mixture thickened, it was dialyzed against distilled water using a 3500 MWCO dialysis tube for 24 hours and subsequently freeze-dried to yield homopolymer **13** as a white solid (819 mg, 71% yield).

## **3.5 Copolymerization of Zwitterionic Monomer 3 and Glycine-Based Monomer 14**

A solution of monomer **3** (1.15 g, 5 mmol), monomer **14** (0.776 g, 5 mmol), NaCl (61 mg, 1.04 mmol), and AMPD (100 mg) in water (1.037 g) was purged with N<sub>2</sub> and stirred in a closed flask at 80 °C for 24 h. The concentration of NaCl became 1.0 M. Monomer/water weight ratio becomes 65:35. The thickened mixture upon dialysis against distilled water using dialysis tube of 3500 MWCO for 24 h was freeze-dried to afford the copolymer **15** as a white solid (1.3 g, 67%).  $\nu_{\text{max}}$ . (Neat) 3389, 2930, 2858, 2359, 1615, 1453, 1383, 1295, 1169, 1061, 911, 776, and 649 cm<sup>-1</sup>. Elemental analysis of copolymer having monomer/monomer incorporation of 50:50: found: C, 59.0; H, 8.5; N, 7.1; S, 8.1; requires C, 59.34; H, 8.39; N, 7.29; S, 8.34%.

## 3.6. Copolymerization of Zwitterionic Monomer **3** and Maleic acid **4**

### 3.6.1 Procedure A:

In a reaction mixture, monomer **3** (1.15 g, 5 mmol), maleic acid **8** (0.696 g, 6 mmol), NaCl (110 mg, 1.88 mmol), and AMPD (75 mg) were dissolved in water (1.23 g). This mixture was degassed with nitrogen and stirred at 80 °C in a sealed flask for 24 hours, achieving a NaCl concentration of 1.5 M. The weight ratio of monomers to water was set at 70:30. After thickening, the mixture was treated with K<sub>2</sub>CO<sub>3</sub> to maintain solubility, followed by dialysis for 2 hours against 0.5 M HCl to keep the polymer water-soluble, and then further dialyzed against distilled water for 24 hours using a 3500 MWCO dialysis tube. The polymer adhered to the wall of the dialysis tube. Freeze-drying the entire mixture yielded copolymer **16** as a white solid (1.29 g, 75%).  $\nu_{\text{max}}$ . (Neat) 3468, 2971, 2921, 2524, 2359, 1722, 1607, 1445, 1392, 1177, 956, 808, and 648 cm<sup>-1</sup>. Elemental analysis of copolymer having monomer/monomer incorporation of 50:50: found: C, 51.8; H, 6.9; N, 3.9; S, 9.1; requires C, 52.16; H, 6.71; N, 4.06; S, 9.28%.

### 3.6.2 Procedure B:

In a reaction setup, monomer **3** (1.15 g, 5 mmol), maleic acid **8** (0.838 g, 7.2 mmol), 37% concentrated HCl (542 mg, 5.5 mmol), and AMPD (75 mg) were combined in water (0.94 g). This mixture was then purged with nitrogen and continuously stirred at 80 °C within a sealed flask for 24 hours. The monomers to water weight ratio was adjusted to 63:37. Following the same cleanup procedure as in procedure A, the resulting mixture yielded copolymer **16** as a white solid, with a total weight of 0.54 g, representing a 31% yield.

### 3.6.3 Procedure C:

A reaction mixture containing monomer **3** (1.15 g, 5 mmol), maleic acid **8** (0.838 g, 7.2 mmol), 37% concentrated HCl (542 mg, 5.5 mmol), and AMPD (50 mg) was prepared in water (0.96 g). This solution was purged with nitrogen and agitated in a sealed flask at 80 °C for 24 hours. The ratio of monomers to water by weight was established at 63:37. Following the same cleanup procedure as outlined in procedure A, this process resulted in the formation of copolymer **16**, which was isolated as a white solid weighing 0.69 g, corresponding to a 40% yield.

## 3.7 Copolymerization of Zwitterionic Monomer **3** and Aspartic Acid Monomer **17**

### 3.7.1 Procedure A:

A mixture was prepared with monomer **3** (1.15 g, 5 mmol), monomer **17** (1.25 g, 5 mmol), 37% concentrated HCl (493 mg, 5 mmol), and AMPD (125 mg) in water (1.3 g). This solution was purged with nitrogen and agitated in a sealed flask at 80°C for 36 hours. The ratio of monomers to water by weight was 60:40. After thickening, the mixture was dialyzed against distilled water using a dialysis tube of 3500 MWCO for 24 hours. The polymer, which settled at the bottom of the dialysis tube as a jelly-like liquid, was subsequently freeze-dried, yielding the copolymer **18** as a white solid (1.21 g, 55%).  $v_{\max}$ . (Neat) 3413, 2928, 2522, 2359, 1713, 1614, 1451, 1378, 1181, 958, 864, 772, 668, and 591  $\text{cm}^{-1}$ . Elemental analysis of copolymer having monomer/monomer incorporation of 50:50: found: C, 56.7; H, 7.9; N, 6.3; S, 7.0; requires C, 56.99; H, 7.74; N, 6.33; S, 7.24%.

### 3.7.2 Procedure B:

A mixture of monomer **3** (1.15 g, 5 mmol), monomer **17** (1.25 g, 5 mmol), 37% concentrated HCl (493 mg, 5 mmol), and AMPD (125 mg) was dissolved in water (1.02 g). This solution was nitrogen-purged and stirred in a sealed flask at 80°C for 36 hours. The monomers to water weight ratio was adjusted to 65:35. Following this, the thickened mixture underwent dialysis against distilled water for 24 hours using a 3500 MWCO dialysis tube. The polymer, which settled as a jelly-like liquid at the bottom of the tube, was freeze-dried to yield copolymer **18** as a white solid, achieving a final weight of 1.68 g, which corresponds to a 72% yield.

### 3.8 Synthesis of $\beta$ -Cyclodextrin-Based Monomer **4**

$\beta$ -Cyclodextrin **2**, when selectively tosylated,<sup>94</sup> leads to intermediate **20**. This intermediate, upon reaction with diallylamine **21** and subsequent treatment with HCl, results in the formation of monomer **4**.<sup>95,96</sup>

### 3.9 Copolymerization of Zwitterionic Monomer **3** and CD Monomer **4**

A solution of monomer **3** (0.575 g, 2.5 mmol), monomer **4** (0.782 g, 0.625 mmol), NaCl (62 mg, 1.06 mmol), and AMPD (90 mg) was combined in water (0.708 g). This mixture was purged with nitrogen and stirred in a sealed flask at 75 °C for 48 hours. The ratio of monomers to water was 65:35, and the concentration of NaCl adjusted to 1.5 M. After heating, the thickened mixture underwent dialysis against distilled water using a 3500 MWCO dialysis tube for 24 hours. Finally, the homogeneous solution was freeze-dried to yield the copolymer **23** as a white solid, achieving a 76% yield (1.04 g).  $\nu_{\text{max}}$ . (Neat) 3331, 2919, 1729, 1620, 1444, 1366, 1154, 1081, 1031, 999, 943, 849, 754, 704, 649, and 587

cm<sup>-1</sup>. Elemental analysis of copolymer having monomer/monomer incorporation of 80:20: found: C, 50.6; H, 7.4; N, 3.3; S, 5.6; requires C, 50.97; H, 7.25; N, 3.23; S, 5.92%.

### **3.10 Terpolymerization of Zwitterionic Monomer 3, CD Monomer 4, and Cross-Linker 5**

A solution of monomer **3** (2.29 g, 10 mmol), monomer **4** (3.13 g, 2.5 mmol), cross-linker **5** (0.769 g, 2.2 mmol), NaCl (291 mg, 4.86 mmol), and AMPD (300 mg) was combined in water (3.32 g). This mixture was purged with nitrogen and stirred in a sealed flask at 75 °C. The monomers to water ratio was set at 65:35, and the NaCl concentration was adjusted to 1.5 M. Within 1 hour, the mixture thickened into a solid resin. After 3 hours, an additional 0.5 g of water was added, and the mixture continued to stir at 75 °C for a total of 36 hours. The solidified resin **24** was then immersed in water for 24 hours, with periodic water changes. Finally, resin **24** was washed with acetone, filtered, and dried under vacuum at 60 °C until a constant weight was achieved, yielding a white solid of 4.80 g (78% yield).  $\nu_{\text{max}}$ . (Neat) 3353, 2921, 2859, 2579, 1703, 1615, 1451, 1359, 1225, 1153, 1080, 1030, 999, 937, 845, 752, 653, and 580 cm<sup>-1</sup>. Elemental analysis of terpolymer having monomer/monomer/cross-linker incorporation of 68:17:15 found: C, 52.8; H, 7.8; N, 3.9; S, 5.3; requires C, 52.32; H, 7.57; N, 3.83; S, 5.18%.

### **3.11 Corrosion Inhibition Study**

Mild steel samples were sourced from Chrome Contracting Ltd in Riyadh, Saudi Arabia, with a chemical composition (wt.%) including carbon (0.21%), silicon (0.29%), phosphorus (0.06%), manganese (0.49%), sulfur (0.05%), copper (0.06%), and the remainder being iron. The steel specimens measured 2.96×3.01×0.78 cm<sup>3</sup> and were used for weight loss experiments. Before each test, the coupons were polished using emery paper

(grades 800-1200), then cleaned with deionized water and acetone. A 15% hydrochloric acid solution was prepared by diluting concentrated HCl (37%) for use as the corrosive medium. Inhibitor solutions were also prepared in this 15% HCl medium. The weight loss experiments were conducted in 250 mL Wheaton bottles containing 200 mL of the 15% HCl and varying concentrations of inhibitors over a 6-hour immersion. After immersion, the steel samples were washed, treated with acetone, and air-dried. Each experiment was replicated three times to confirm the consistency of the weight loss results, which were averaged and reported with standard deviations included in Table 1.

The inhibition efficiency (% IE) was calculated as follows <sup>97,98</sup>

$$\%IE = \frac{W_0 - W_{inh}}{W_0} \times 100 \quad EQ (1)$$

here,  $W_{inh}$  and  $W_0$  indicate the weight losses recorded when different concentrations of polymers are tested and when no polymers are used, respectively.

### 3.12 Assessment of Poisonous Metal ion Removal Efficiency:

To assess the resin's ability to remove toxic metals<sup>99,100</sup> and organic pollutants<sup>9</sup>, established procedures from existing literature<sup>40</sup> will be followed. Specifically, isotherm construction will involve batch experiments as follows: 50 mg of resin **24** is combined with aqueous solutions of Hg (II) or Pb (II) at concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 ppm (each 18 mL) and maintained at pH 5.0. These mixtures are stirred at 300 rpm for **24** hours at 298 K. After stirring, the solutions are filtered and the concentrations of Hg (II) or Pb (II) in the filtrates are measured using ICP-MS to determine the amount of metal ions absorbed by the resin. The percent removal of Hg (II) or Pb (II) at equilibrium is calculated by the following equation:

$$\% Removal = \frac{C_o - C_e}{C_o} \times 100 \quad \text{EQ (2)}$$

Adsorption capacities were calculated using the Eqs. (2) and (3):

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad \text{EQ (3)}$$

Describing  $C_o$  and  $C_e$  as the initial and equilibrium concentrations of Hg (II) in ( $\text{mg L}^{-1}$ ), respectively, with  $V$  representing the volume in liters and  $m$  the mass of the polymer in grams, the equilibrium adsorption capacity ( $q_e$ ,  $\text{mg g}^{-1}$ ) was calculated using Equation (3). Variability in adsorption data from duplicate experiments ranged between 1-3%.

### 3.13 Removal of Organic Micropollutants:

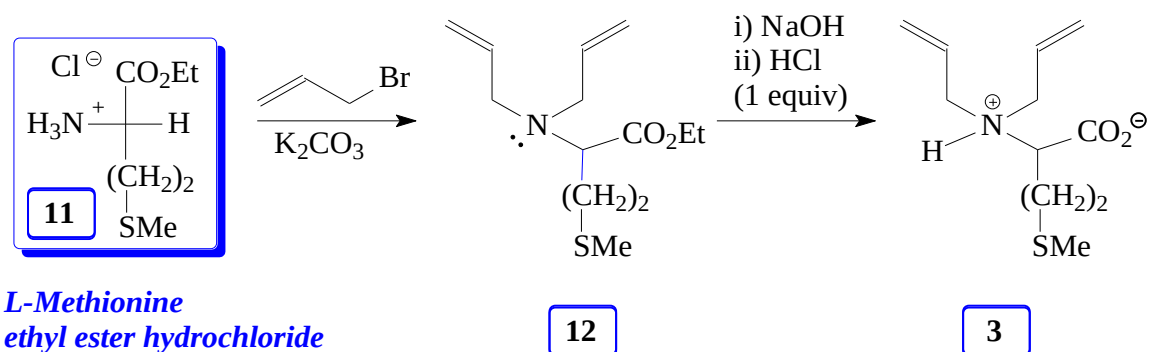
Stock solutions of Bisphenol A (BPA) were prepared at concentrations of 1 mM and 0.1 mM. Heterogeneous mixtures containing polymer 15 (50 mg and 5 mg, with 20 mol% CD residues) and 9 mL of each BPA solution were prepared separately. These mixtures were stirred at 300 rpm for 3 hours. After centrifugation, the supernatants were analyzed using a UV-Vis Spectrophotometer (Genesys 10S, Thermo Scientific). Calibration curves for each analyte concentration were plotted, and the unknown concentrations of the analytes post-adsorption were calculated using the slope equations.

## CHAPTER 4

### RESULTS AND DISCUSSION

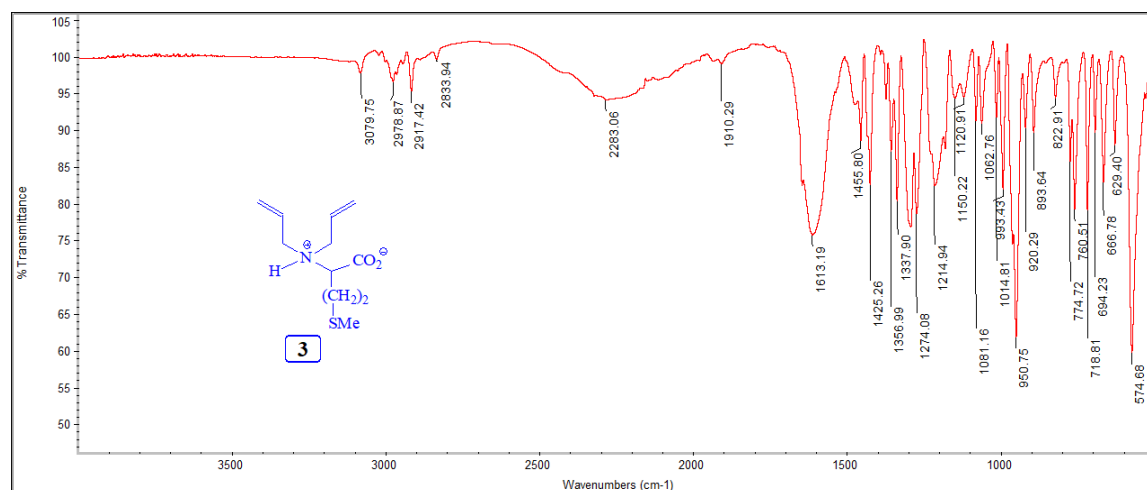
#### 4.1 Synthesis of Monomers, Polymers, and Cross-linked Resins

The synthesis of monomer **3** from amino acid methionine ethyl ester hydrochloride **11** is outlined in Scheme 5. Treatment with allyl bromide followed by ester hydrolysis led to the zwitterionic monomer.<sup>29,96</sup>



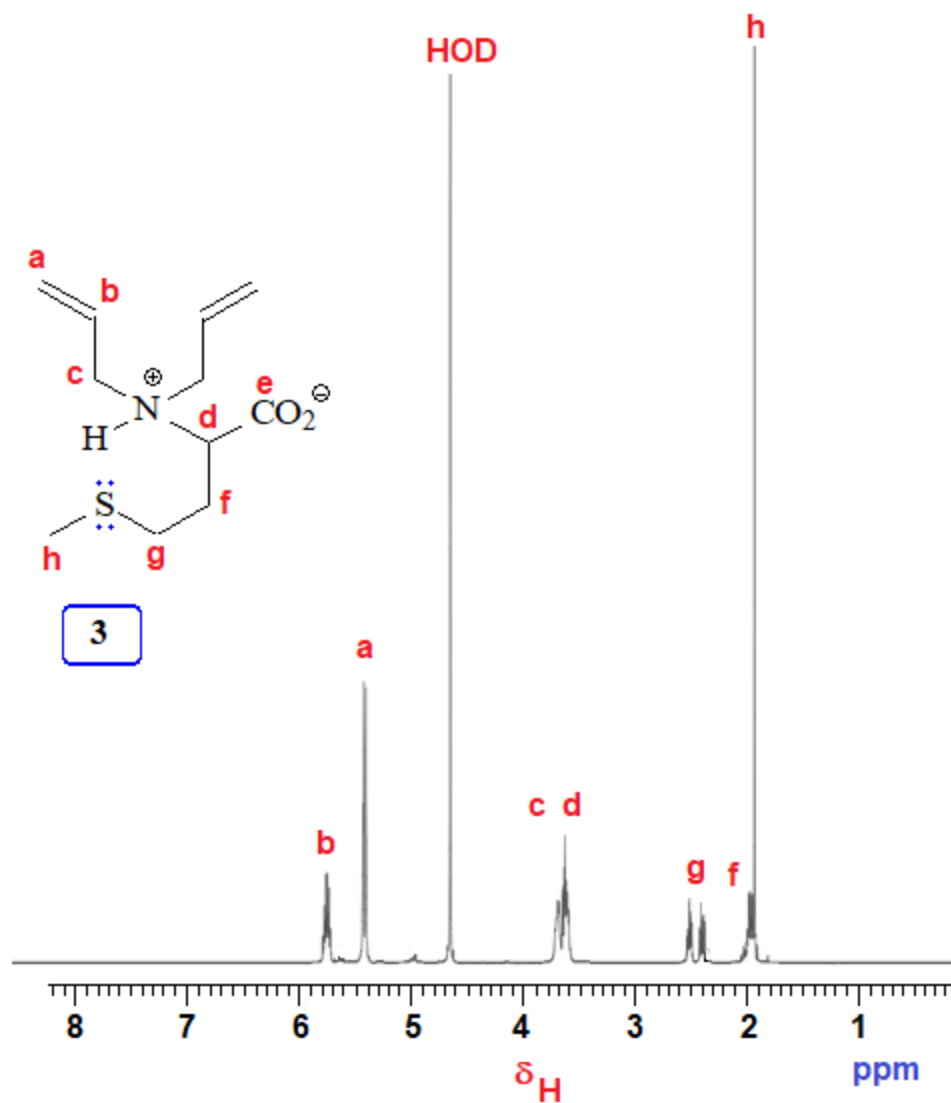
**Scheme 5.** Synthesis of methionine-based monomer.

Figures 4, 5, and 6 show the FTIR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra, respectively. The symmetric stretching of  $\text{COO}^-$  in the dipolar form of **3** was observed at a frequency of  $1425\text{ cm}^{-1}$ , while its equivalent antisymmetric stretching was observed at  $1613\text{ cm}^{-1}$  (Figure 4). The stretching vibrations of the carbon-sulfur bonds were detected at wavenumbers of  $629$  and  $761\text{ cm}^{-1}$ . The absorption peaks correspond to those seen for basic amino acids.<sup>101,102</sup>



**Figure 4** FTIR spectrum of monomer **3**.

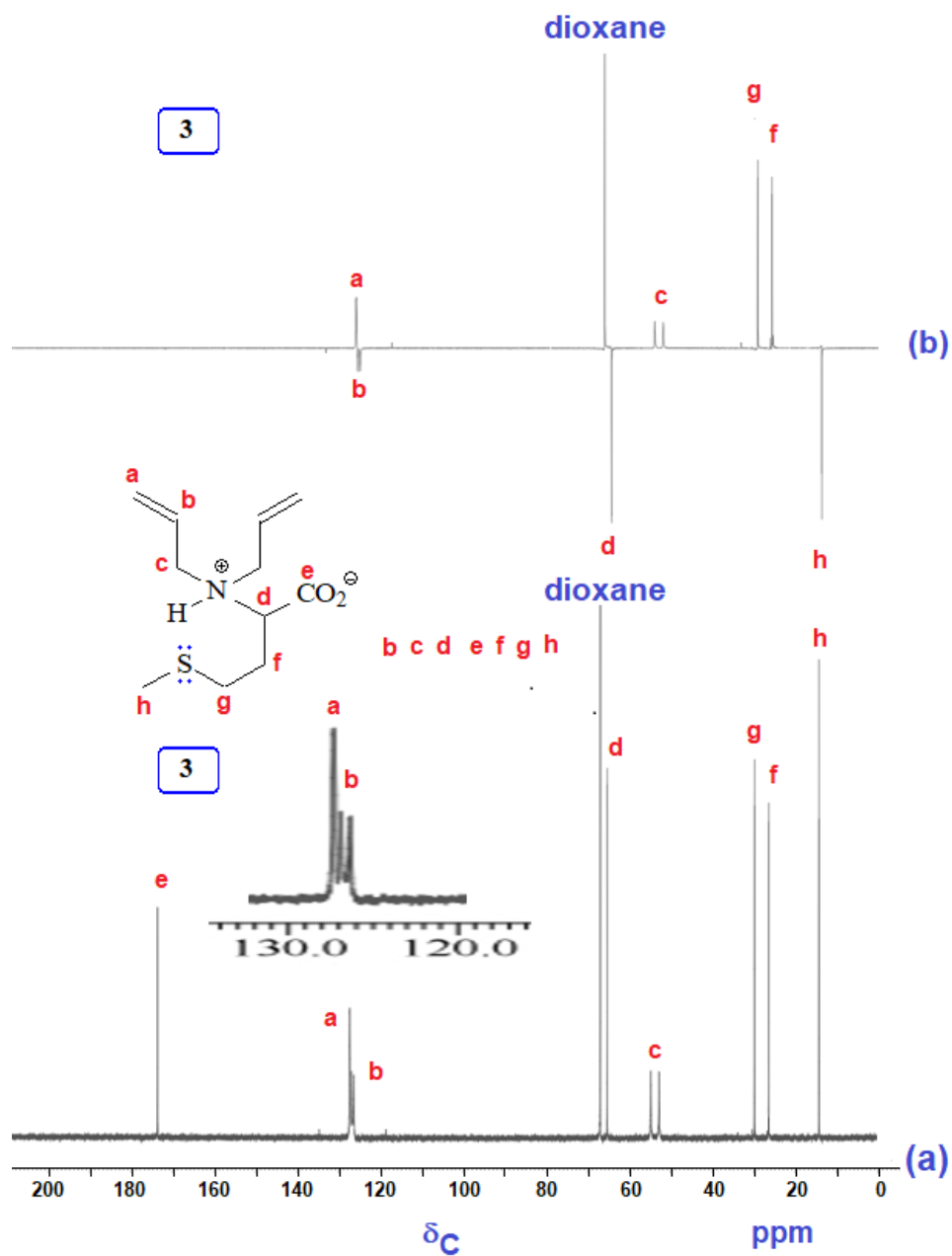
The  $^1\text{H}$  NMR spectrum matched the structure of monomer **3** as shown in (Figure 5). All proton signals were accounted for. The  $\text{CH}_2$  protons, labeled as 'g', showed different chemical shifts due to their diastereotopic nature.



**Figure 5** <sup>1</sup>H NMR spectrum of monomer **3** in D<sub>2</sub>O.

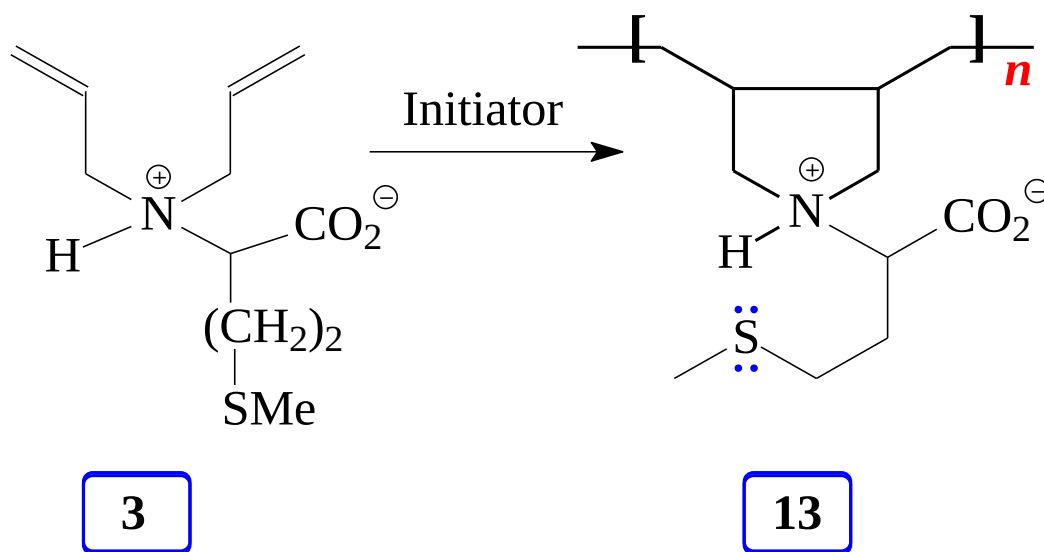
The <sup>13</sup>C NMR spectrum aligns well with the structure of monomer **3** as shown in (Figure 6a), with all carbon signals properly accounted for. The DEPT-135 NMR spectrum supports these assignments, as depicted in (Figure 6b). Notably, the carbon labeled 'b' appears upfield relative to the carbon labeled 'a'. Due to the diastereotopic nature of the

allyl groups, the carbons labeled 'a', 'b', and 'c' each split into two signals of equal intensity. As expected, phase inversion is observed in the carbons 'b' (CH), 'd' (CH), and 'h' (CH<sub>3</sub>).



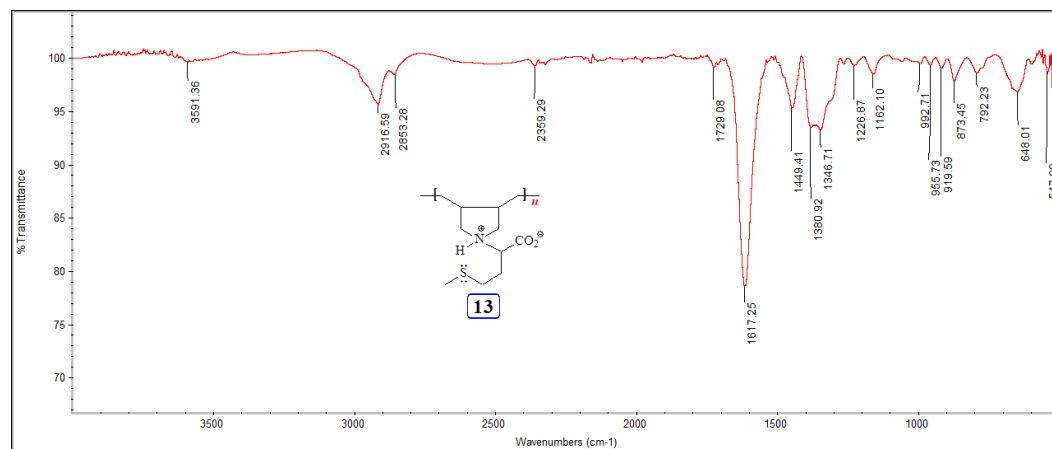
**Figure 6** (a) <sup>13</sup>C NMR spectrum of monomer 3 in D<sub>2</sub>O; (b) DEPT C-135 NMR spectrum of monomer 3 in D<sub>2</sub>O.

An aqueous solution of zwitterionic monomer **3** underwent cyclopolymerization under various conditions in the presence of initiator AMPD at 80 °C to give polymer **13** (Scheme 6). The results are included in Table 1 (*vide infra*). A monomer to water weight ratio of 70:30 was maintained, and the polymerization was carried out in salt-free water (entry 1, Table 1) and in the presence of NaCl (1.47 M; entries 2 and 3) and HCl (1 equiv, entry 4). The presence of HCl improves the yield. The presence of HCl converts zwitterionic monomer **3** to cationic monomer by protonating CO<sub>2</sub><sup>-</sup> to CO<sub>2</sub>H. Cationic repeating units in the growing macroradicals is expanded owing to charge repulsion thereby providing better access to the incoming monomer. The presence of NaCl helps to expand the zwitterionic backbone.



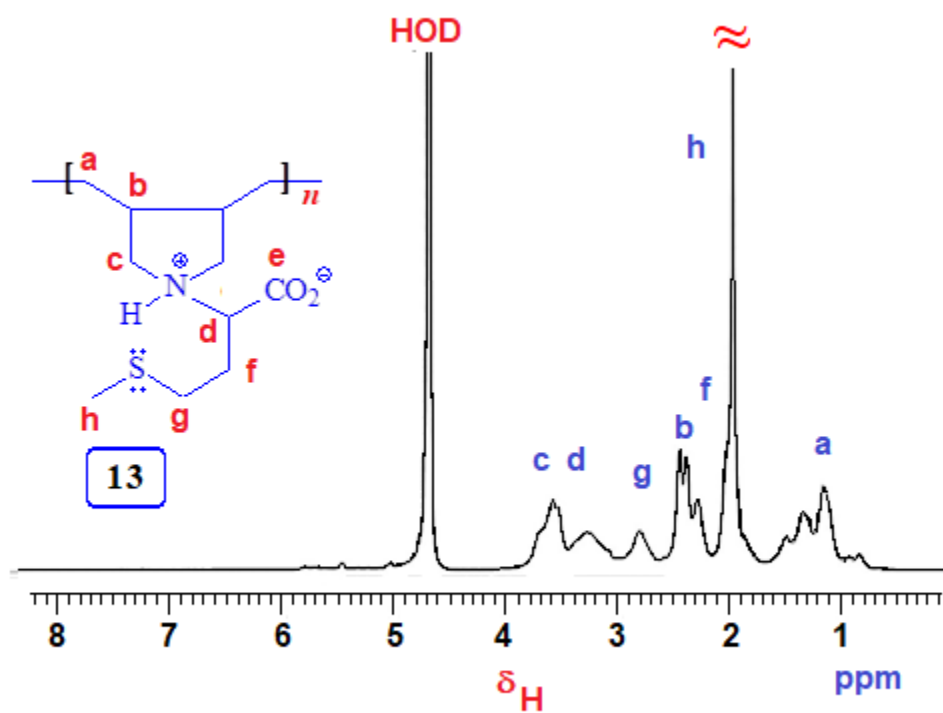
**Scheme 6.** Cyclopolymerization of zwitterionic monomer **3**.

The FTIR, <sup>1</sup>H, and <sup>13</sup>C NMR spectra of polymer **13** are displayed in Figures 7, 8, and 9, respectively. The antisymmetric stretching of COO<sup>-</sup> in the dipolar form of **13** appeared at 1617 cm<sup>-1</sup> (Figure 7).

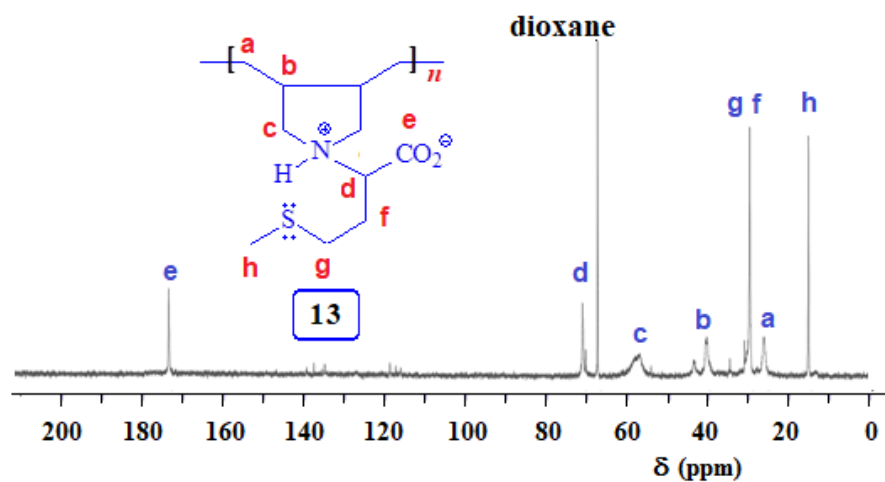


**Figure 7.** FTIR spectrum of **13**.

$^1\text{H}$  (Figure 8) and  $^{13}\text{C}$  (Figure 9) NMR spectra revealed the absence of alkene proton and carbons (cf. Figures 5 and 6), which is consistent with the mechanism of cyclopolymerization protocol.



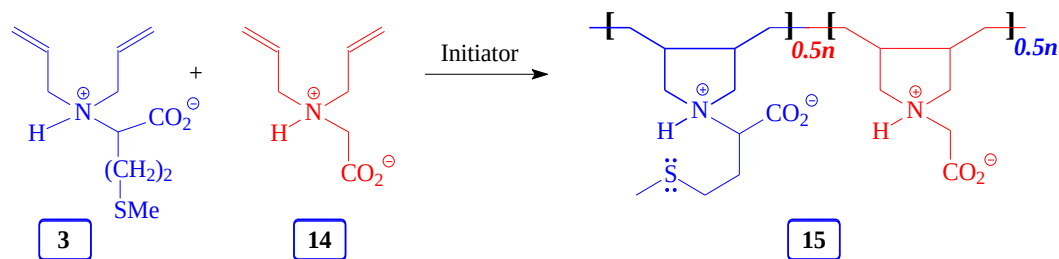
**Figure 8.** <sup>1</sup>H NMR spectrum of **13** in D<sub>2</sub>O.



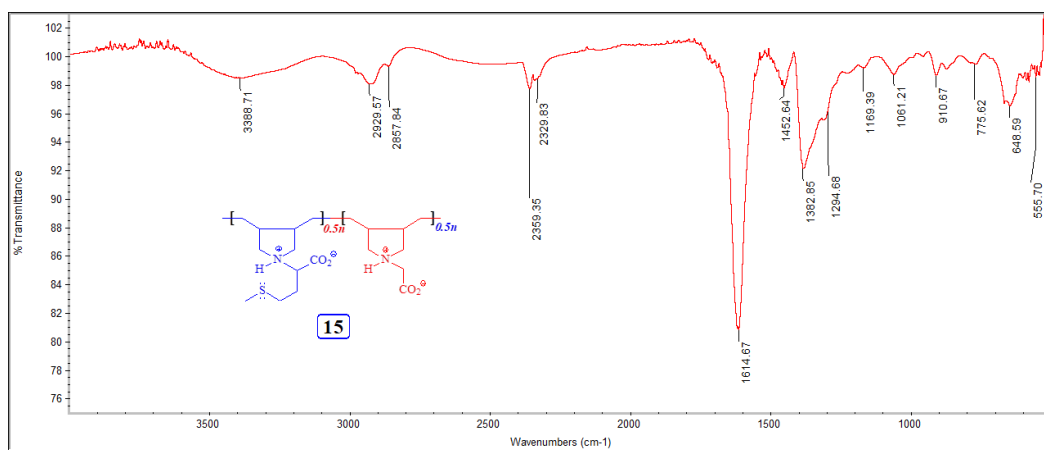
**Figure 9.** <sup>13</sup>C NMR spectrum of **13** in D<sub>2</sub>O.

The copolymerization of zwitterionic monomers **3** and **14** in a 1:1 weight ratio afforded copolymer **15** (Scheme 7). The results are included in Table 1 (entry 5) (*vide infra*). The FTIR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra are displayed in Figures 10, 11, and 12, respectively. The antisymmetric stretching of  $\text{COO}^-$  in the dipolar form of **15** appeared at  $1615\text{ cm}^{-1}$  (Figure 10).

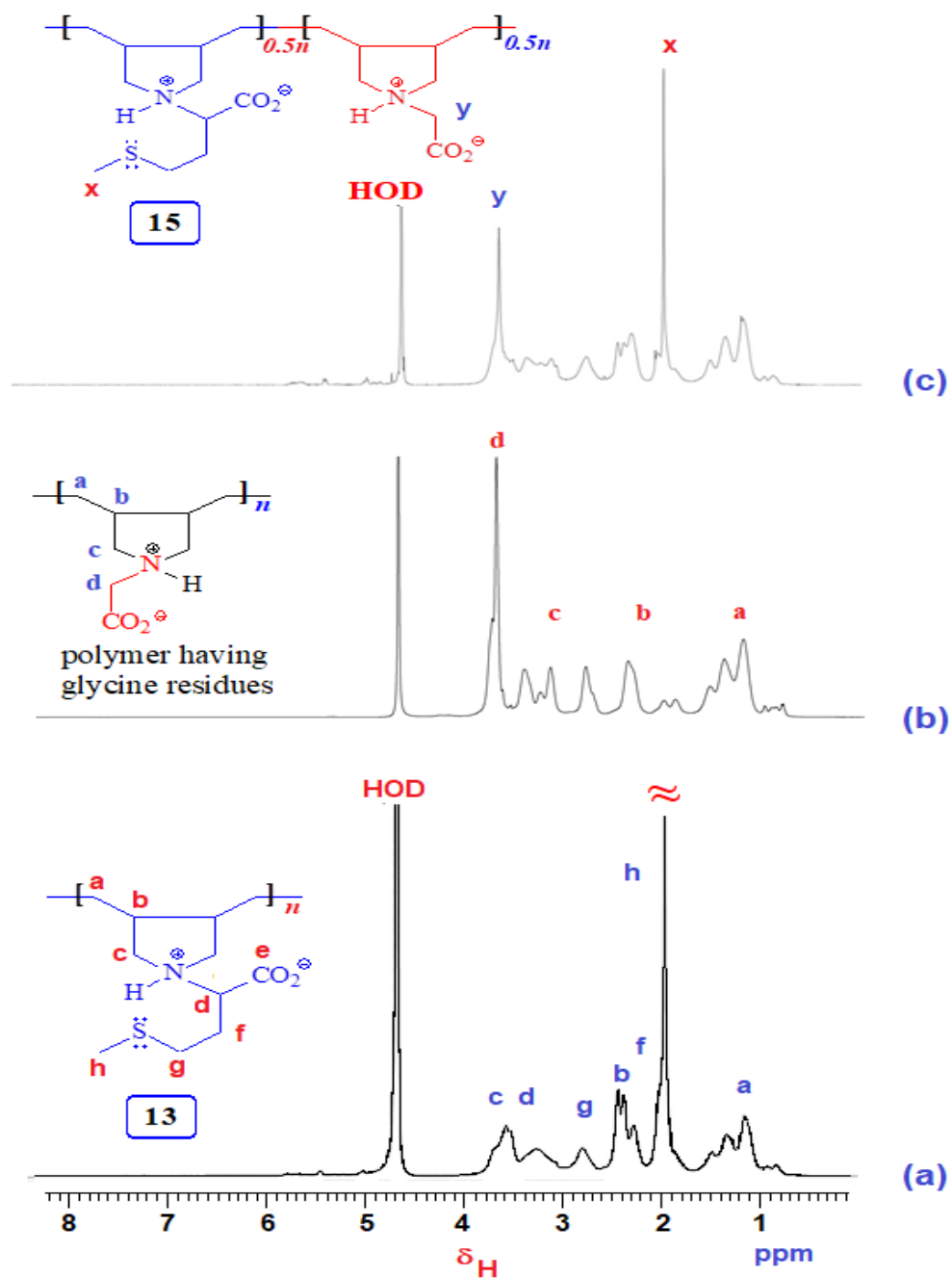
$^1\text{H}$  (Figure 11) and  $^{13}\text{C}$  (Figure 12) NMR spectra revealed the absence of alkene proton and carbons (cf. Figures 5 and 6), which is consistent with the mechanism of cyclopolymerization protocol. The NMR spectra of polymer having residues of glycine are included for the sake of comparison (Figures 11b and 12b).<sup>103</sup>  $^1\text{H}$  NMR spectrum (Figure 11c) easily identifies the protons marked ‘x’ and ‘y’, thereby implying the incorporation of both monomers **3** and **14** into the polymer **15**. Likewise, carbons marked ‘v’, ‘x’, and ‘y’ can be identified in the spectrum of the copolymer **15** (Figure 12c).



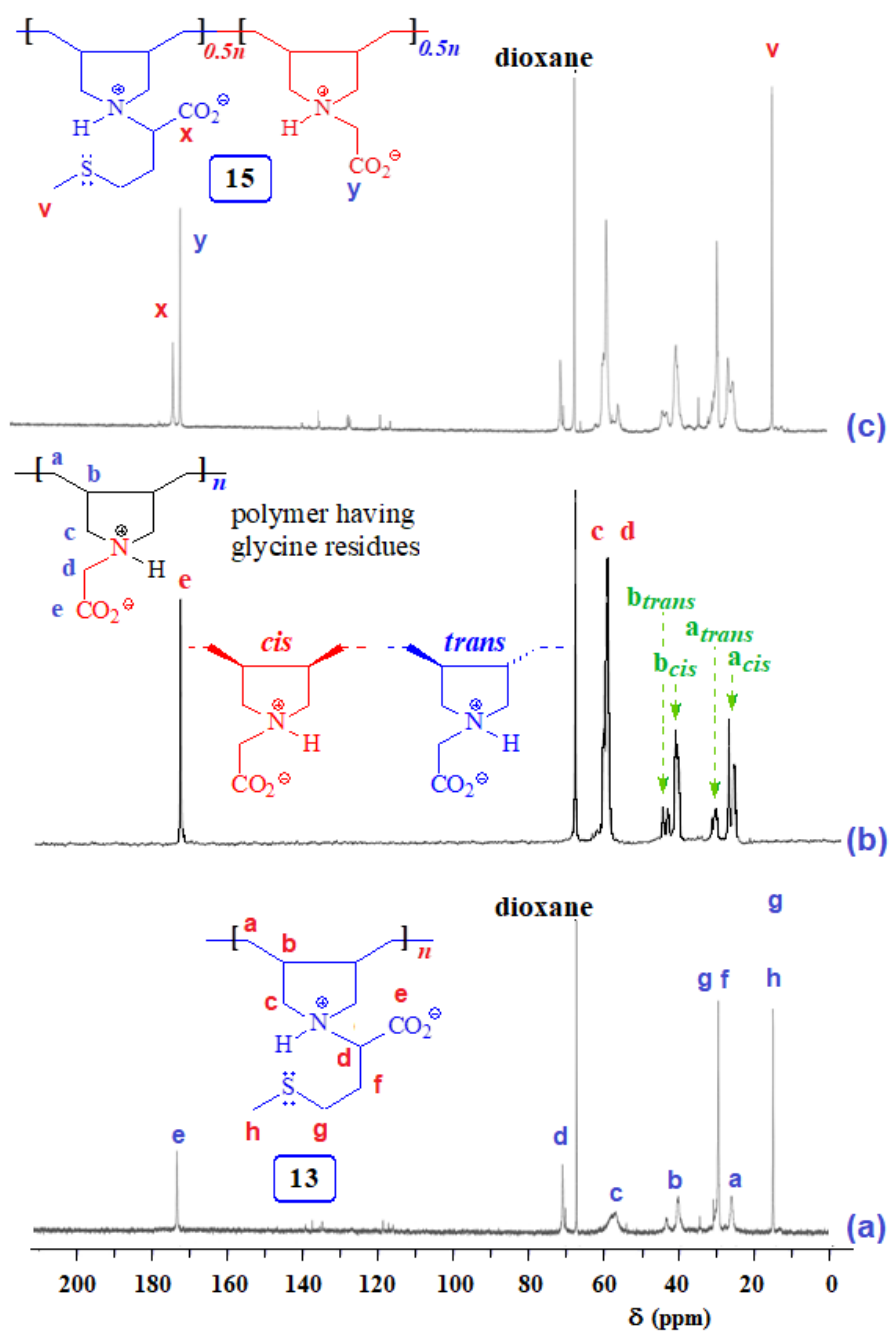
**Scheme 7.** Cyclopolymerization of zwitterionic monomer **3** and glycine-based monomer **14**.



**Figure 10.** FTIR spectrum of **15**.



**Figure 11.**  $^1\text{H}$  NMR spectrum of (a) 13; (b) cyclopolymer bearing glycine residues; (c) 15 in  $\text{D}_2\text{O}$ .

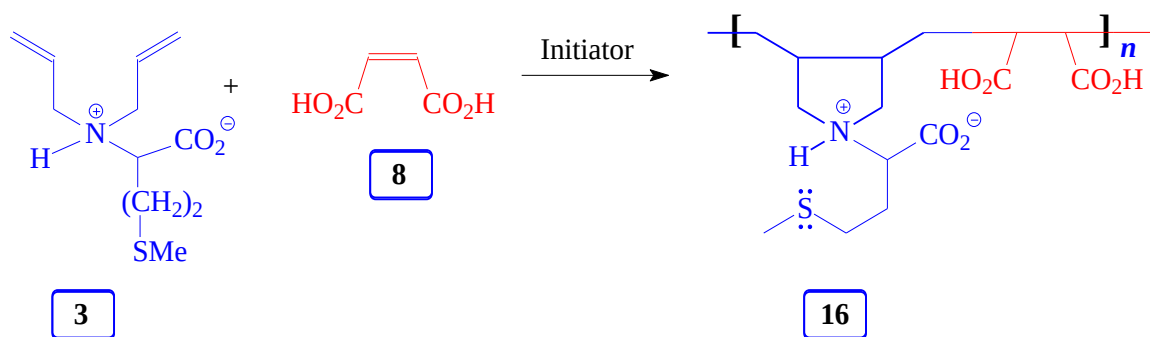


**Figure 12.**  $^{13}\text{C}$  NMR spectrum of (a) **13**; (b) cyclopolymer bearing glycine residues; (c) **15** in  $\text{D}_2\text{O}$ . **13** in  $\text{D}_2\text{O}$ .

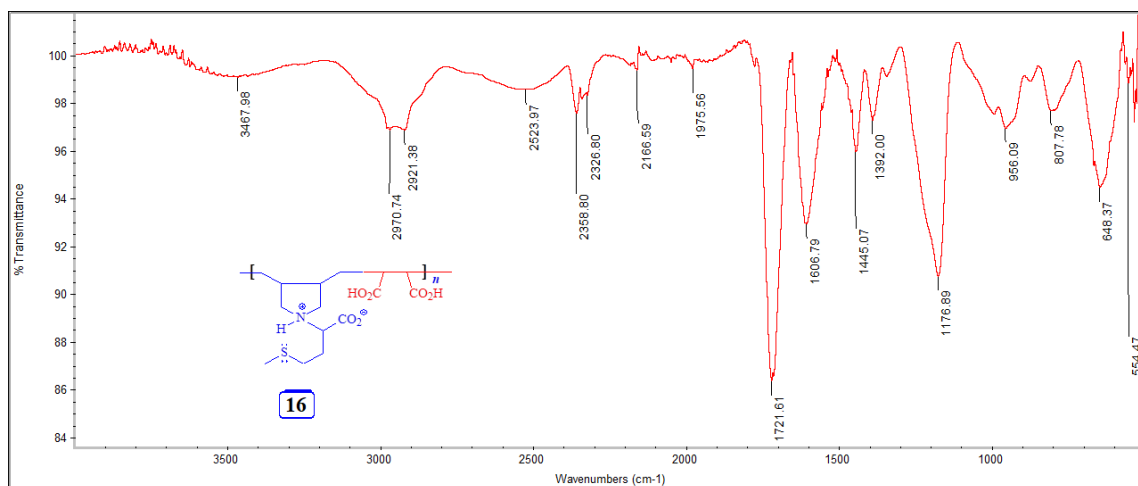
The alternate copolymerization of zwitterionic monomers **3** and maleic acid **8** afforded alternate copolymer **16** (Scheme 8). The results are included in Table 1 (entry 6-8) (*vide infra*). In the presence of NaCl (1.5 M), the polymer yield was improved. The FTIR,  $^1\text{H}$ ,

and  $^{13}\text{C}$  NMR spectra are displayed in Figures 13, 14, and 15, respectively. The antisymmetric stretching of  $\text{COO}^-$  in the dipolar form of **16** appeared at  $1607\text{ cm}^{-1}$ , while the  $\text{C}=\text{O}$  in  $\text{CO}_2\text{H}$  was found to be at  $1722\text{ cm}^{-1}$  (Figure 13).

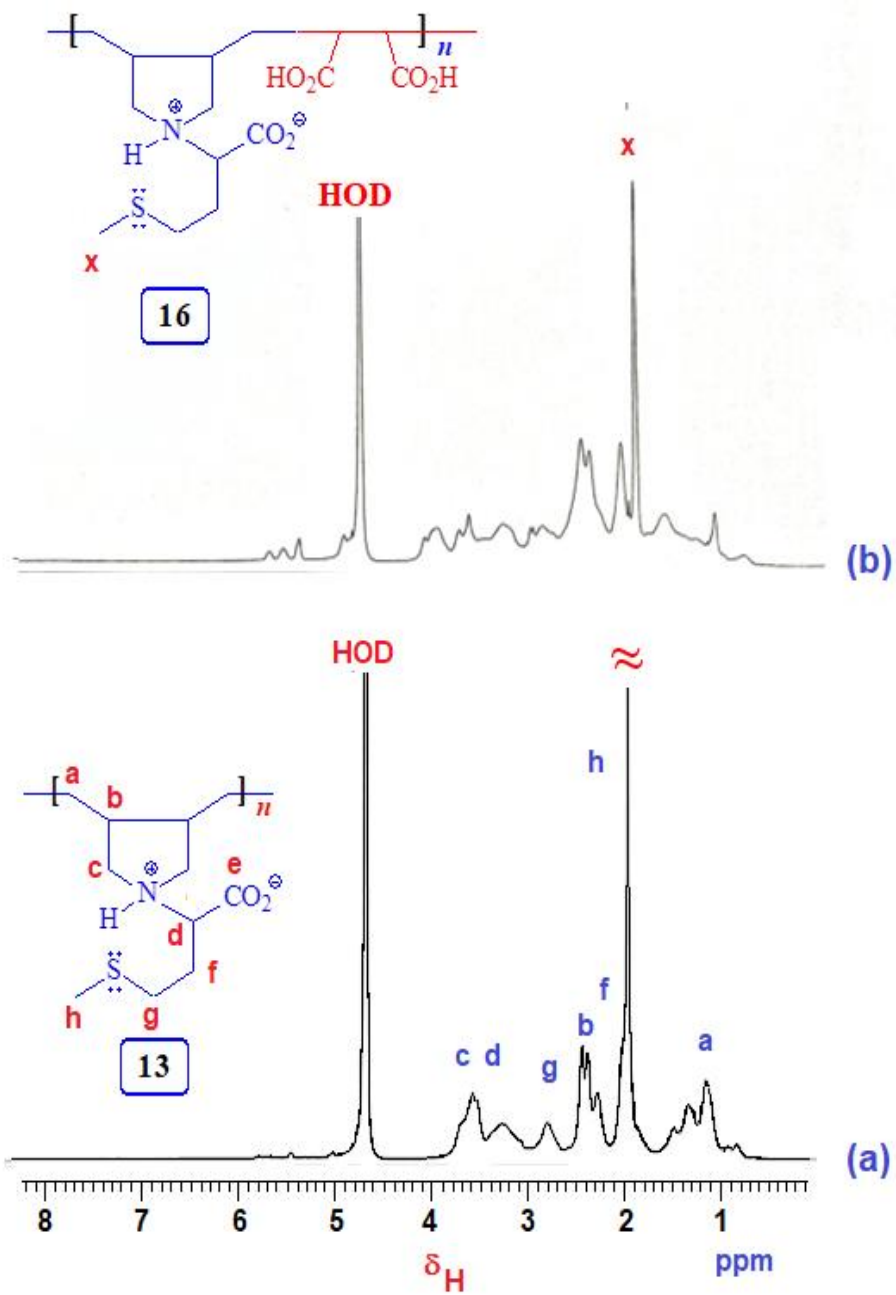
$^1\text{H}$  (Figure 14) and  $^{13}\text{C}$  (Figure 15) NMR spectra revealed the absence of alkene proton and carbons (cf. Figures 5 and 6), which is consistent with the mechanism of cyclopolymerization protocol.  $^{13}\text{C}$  NMR spectrum (Figure 15b) easily identifies several signals for the carbon ( $\text{C}=\text{O}$ ) marked 'y', thereby implying the incorporation of both monomers **3** and **8** into polymer **16**. Note that homopolymer **13** has one signal for the  $\text{C}=\text{O}$  (Figure 15a).



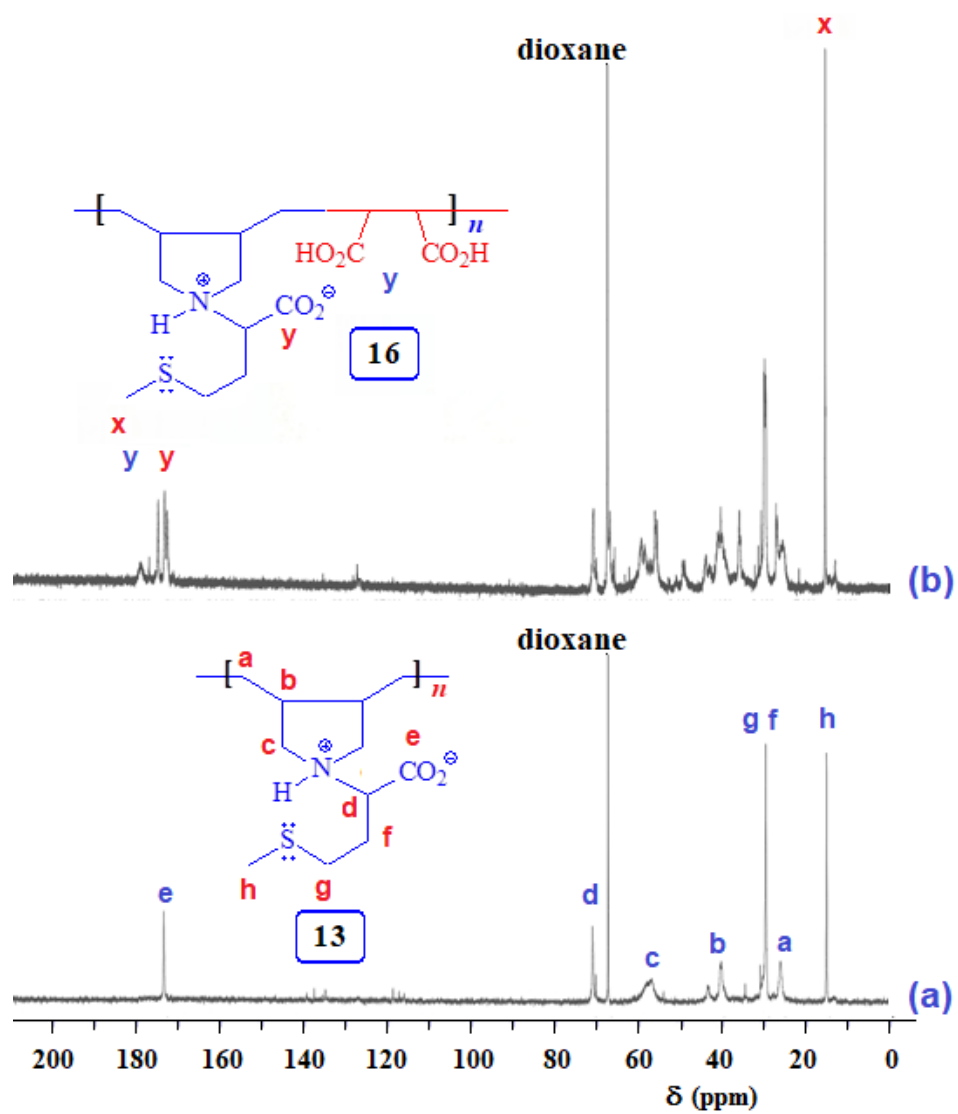
**Scheme 8.** Cyclopolymerization of zwitterionic monomer **3** and maleic acid **8**.



**Figure 13.** FTIR spectrum of **16**.

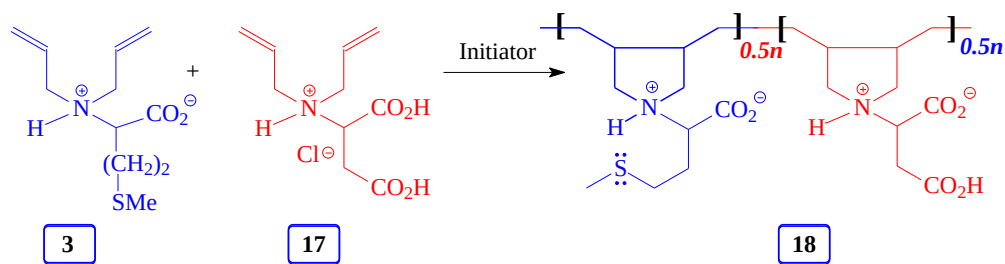


**Figure 14.**  $^1\text{H}$  NMR spectrum of (a) **13** and (b) **16** in  $\text{D}_2\text{O}$ .

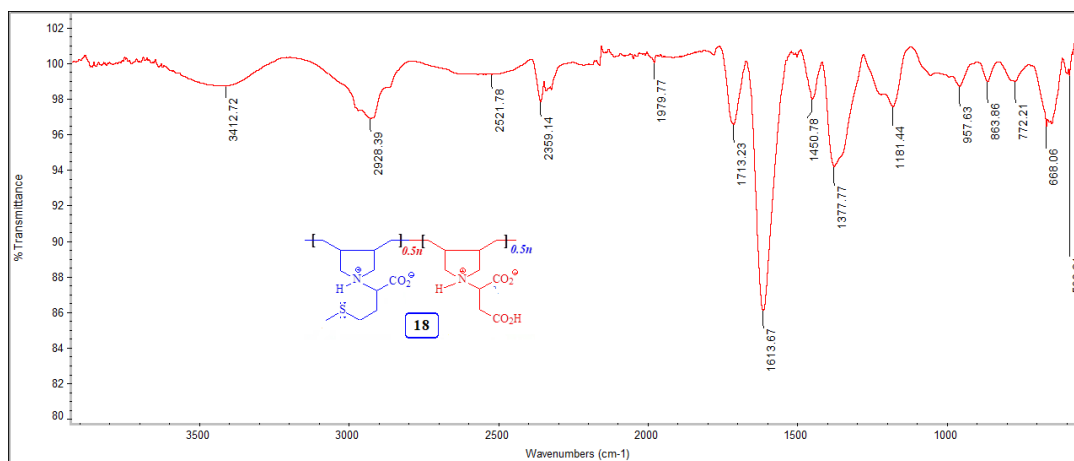


**Figure 15.**  $^{13}\text{C}$  NMR spectrum of (a) **13** and (b) **16** in  $\text{D}_2\text{O}$ .

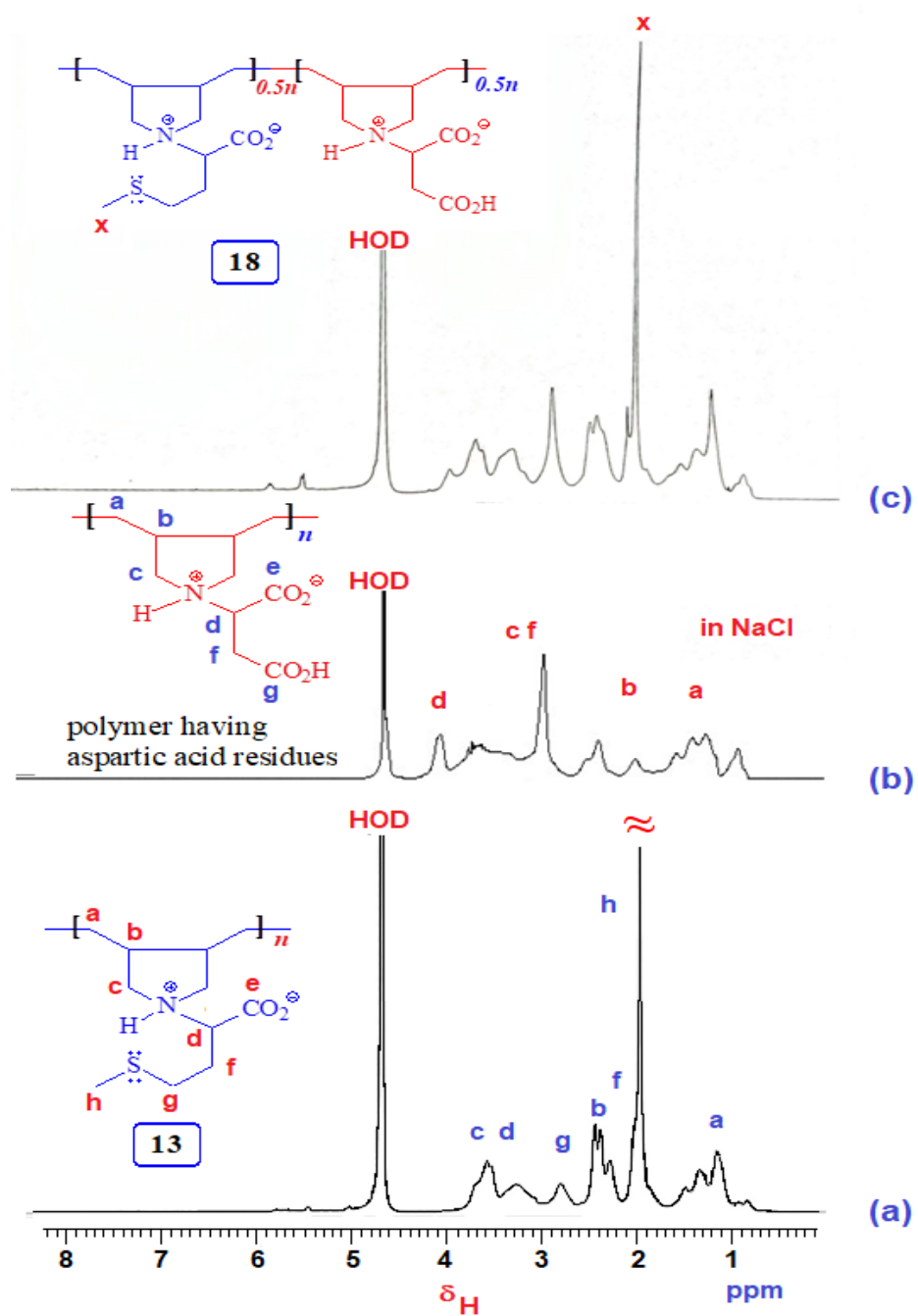
The copolymerization of zwitterionic monomers **3** and **17** in a 1:1 weight ratio afforded copolymer **18** (Scheme 9). The results are included in Table 1 (entries 9 and 10) (*vide infra*). The FTIR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra are displayed in Figures 16, 17, and 18, respectively. The antisymmetric stretching of  $\text{COO}^-$  in the dipolar form of **15** appeared at  $1614\text{ cm}^{-1}$  (Figure 16). The  $\text{C}=\text{O}$  in  $\text{CO}_2\text{H}$  was found to be at  $1713\text{ cm}^{-1}$ .  $^1\text{H}$  (Figure 17) and  $^{13}\text{C}$  (Figure 18) NMR spectra revealed the absence of alkene proton and carbons (cf. Figures 5 and 6), which is consistent with the mechanism of cyclopolymerization protocol. The NMR spectra of polymer having residues of aspartic acid are included for the sake of comparison (Figures 17b and 18b).<sup>91</sup>  $^{13}\text{C}$  NMR spectrum (Figure 18c) easily identifies the carbons marked ‘w’, ‘x’, y, and ‘z’ in the spectrum of the copolymer **18**, thereby implying the incorporation of both monomers **3** and **17** into the polymer **18**.



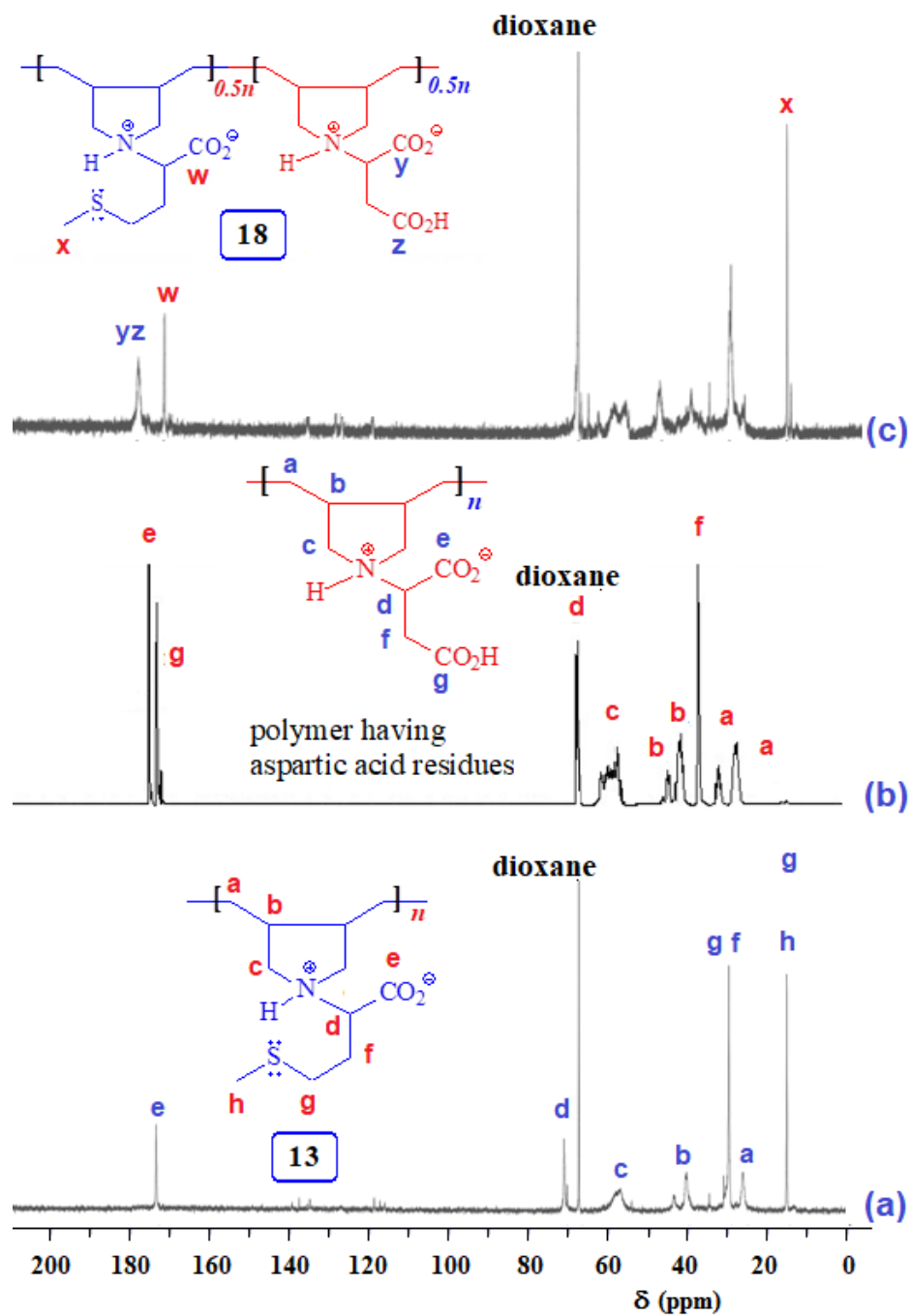
**Scheme 9.** Copolymerization of monomers **3** and **17**.



**Figure 16.** FTIR spectrum of **18**.



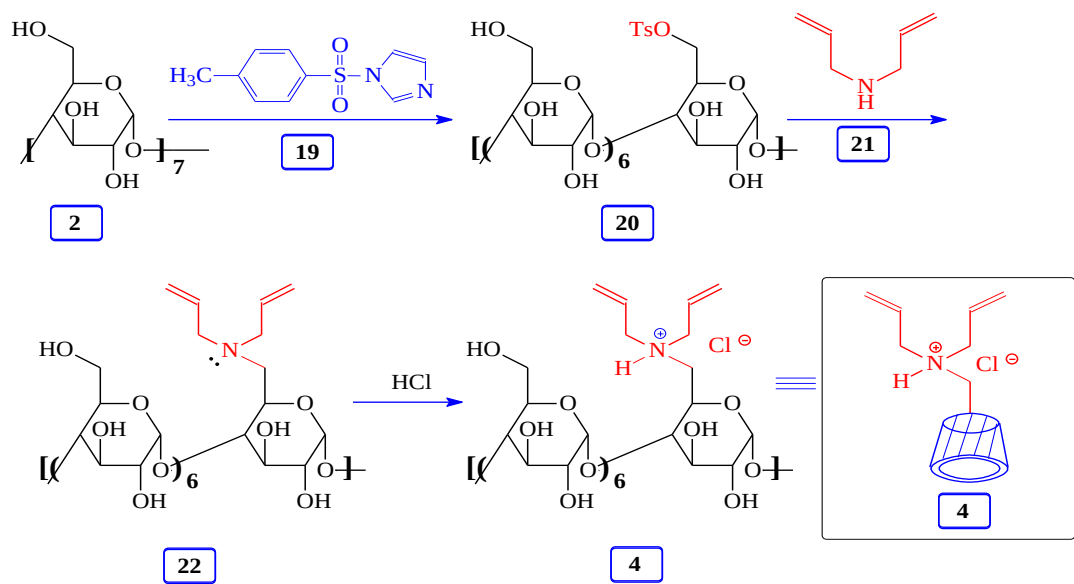
**Figure 17.**  $^1\text{H}$  NMR spectrum of (a) 13; (b) cyclopolymer bearing aspartic acid residues; (c) 18 in  $\text{D}_2\text{O}$ .



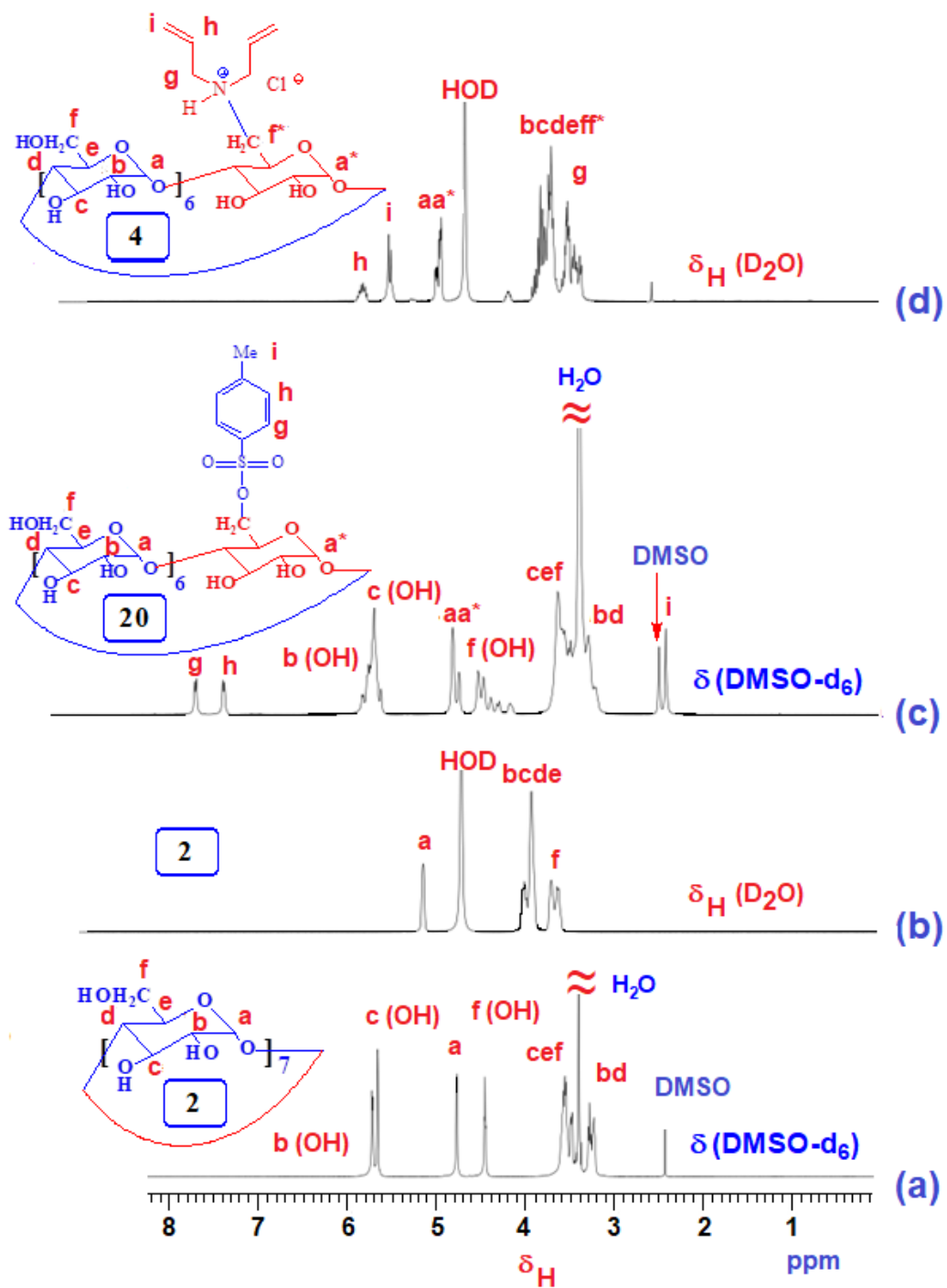
**Figure 18.**  $^{13}\text{C}$  NMR spectrum of (a) 13; (b) cyclopolymer bearing aspartic acid residues; (c) 18 in  $\text{D}_2\text{O}$ .

Scheme 10 outlines the synthesis of monomer **4** having the residue of  $\beta$ -CD as reported.<sup>98</sup> To confirm the structure and integrity of the CD motifs, NMR spectra of **2**, **20**, and **4** were recorded and displayed in Figures 19 and 20. The carbons are marked **a-f** as shown in the structure of **2** (Scheme 1). The proton marked ‘**a**’ at C1 appeared at  $\delta$ 4.8 ppm in all the spectra, while alkene protons marked ‘**h**’ and ‘**i**’ of **4** are displayed around  $\delta$ 5.5 ppm as expected (Figure 19 d). Note that the spectra in D<sub>2</sub>O are simpler than in DMSO-d<sub>6</sub>, because in the latter solvent the OH signals appear at different chemical shifts (cf. Figure 19a vs. 19b).

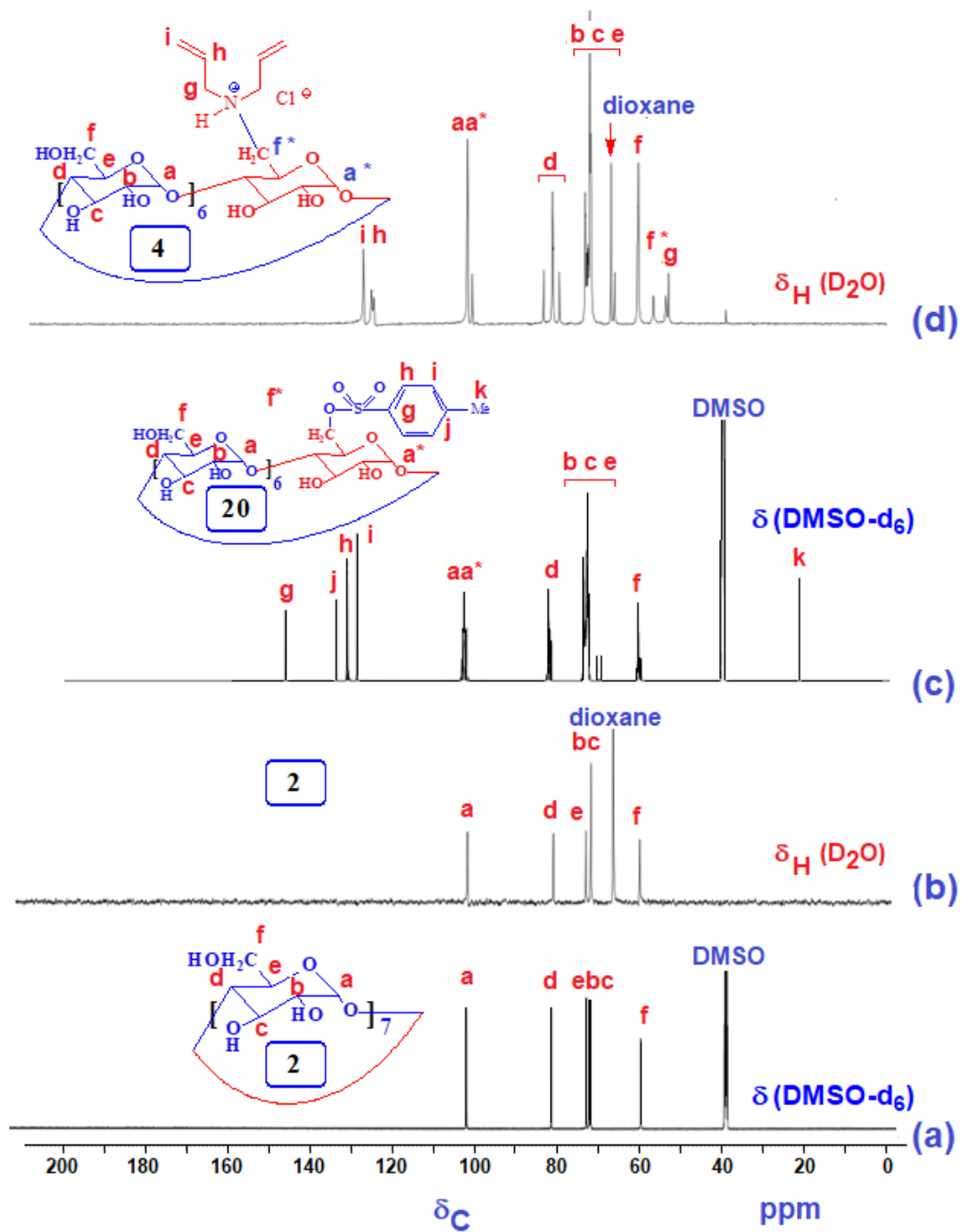
<sup>13</sup>C NMR spectra of  $\beta$ -CD **2** display six signals in DMSO-d<sub>6</sub> confirming the equivalent nature of all the seven cyclic skeletons (Figure 20a, b). However, in the tosyl **20** and diallylamine salt **4**, the cyclic rings become nonequivalent and as such display more signals (Figure 20d). The alkene carbons marked ‘**h**’ and ‘**i**’ of **4** appeared in their expected chemical shifts (Figure 20d). Note each alkene carbon around 127 ppm is split into a doublet of equal intensity because of their diastereotopic nature (Figure 20d). Knowledge of the chemical shifts of the protons and carbons marked ‘**a/a\***’ would indeed help the spectral characterization of the cyclopolymerization products (*vide infra*).



**Scheme 10.** Synthesis  $\beta$ -cyclodextrin-based monomer **4**.



**Figure 19.**  $^1\text{H}$  NMR spectra of (a)  $\beta$ -Cyclodextrin (**2**) in  $\text{DMSO-d}_6$ , (b) **2** in  $\text{D}_2\text{O}$ , (c) **20** in  $\text{DMSO-d}_6$ , and (d) **4** in  $\text{D}_2\text{O}$ .

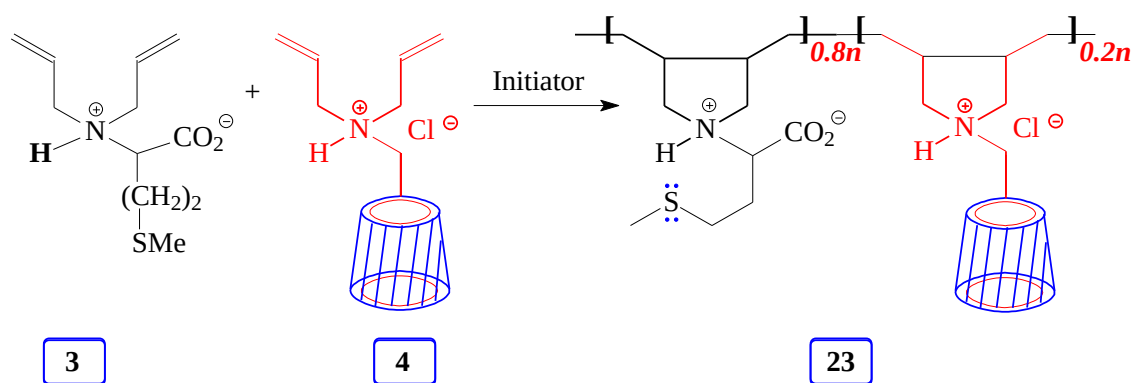


**Figure 20.**  $^{13}\text{C}$  NMR spectra of (a)  $\beta$ -Cyclodextrin (**2**) in  $\text{DMSO-d}_6$ , (b) **2** in  $\text{D}_2\text{O}$ , (c) **20** in  $\text{DMSO-d}_6$ , (d) **4** in  $\text{D}_2\text{O}$ .

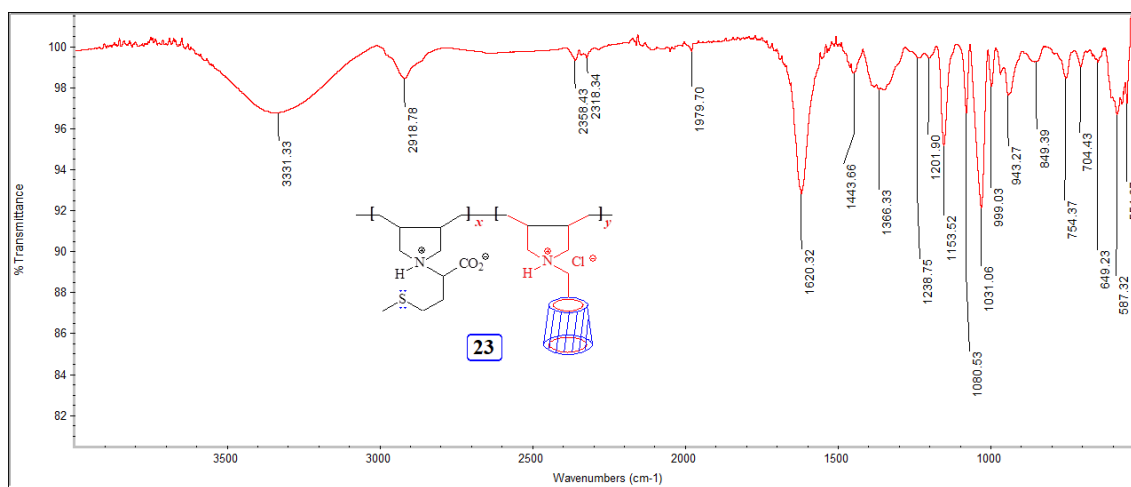
The copolymerization of monomers **3** and **4** afforded copolymer in excellent yield (Table 1, entry 11) (*vide infra*).

The antisymmetric stretching of  $\text{COO}^-$  in the dipolar form of **23** appeared at  $1620\text{ cm}^{-1}$  (Figure 21). Absorption at  $3331\text{ cm}^{-1}$  indicates the presence of OH groups.

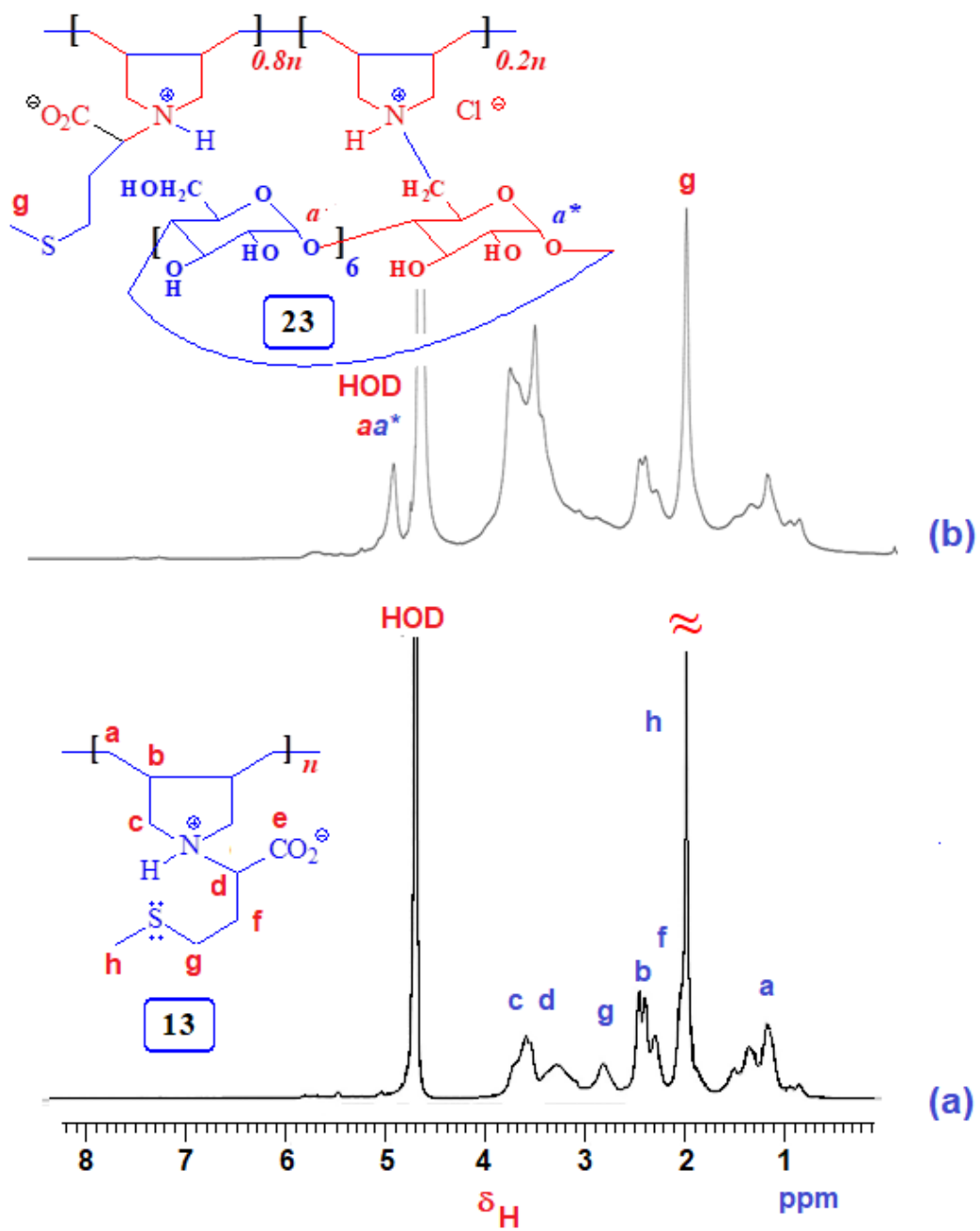
NMR spectral analyses of **23** can decipher the incorporation of  $\beta$ -CD-derived monomer **3** into the polymer **23**. Figure 22 reveals the  $^1\text{H}$  spectra of copolymer **23**, while the corresponding  $^{13}\text{C}$  spectra are displayed in Figures 23. Note the signals of the alkene Hs and Cs marked ‘a’ and ‘b’ of **4** (Figures 19d and 20d) disappeared in the spectra of copolymer **23** (Figures 22b and 23b), thereby implying the successful cyclopolymerization leading to five-membered ring embedded polymer backbone. The chemical shifts of the acetal H and C marked a/a\* of monomer **4** and polymers **23** appeared at  $\delta 55\text{ ppm}$  (Figure 22b) and  $100\text{ ppm}$  (Figure 23b), thereby ensuring the incorporation of cyclodextrin residues into the polymer backbone.



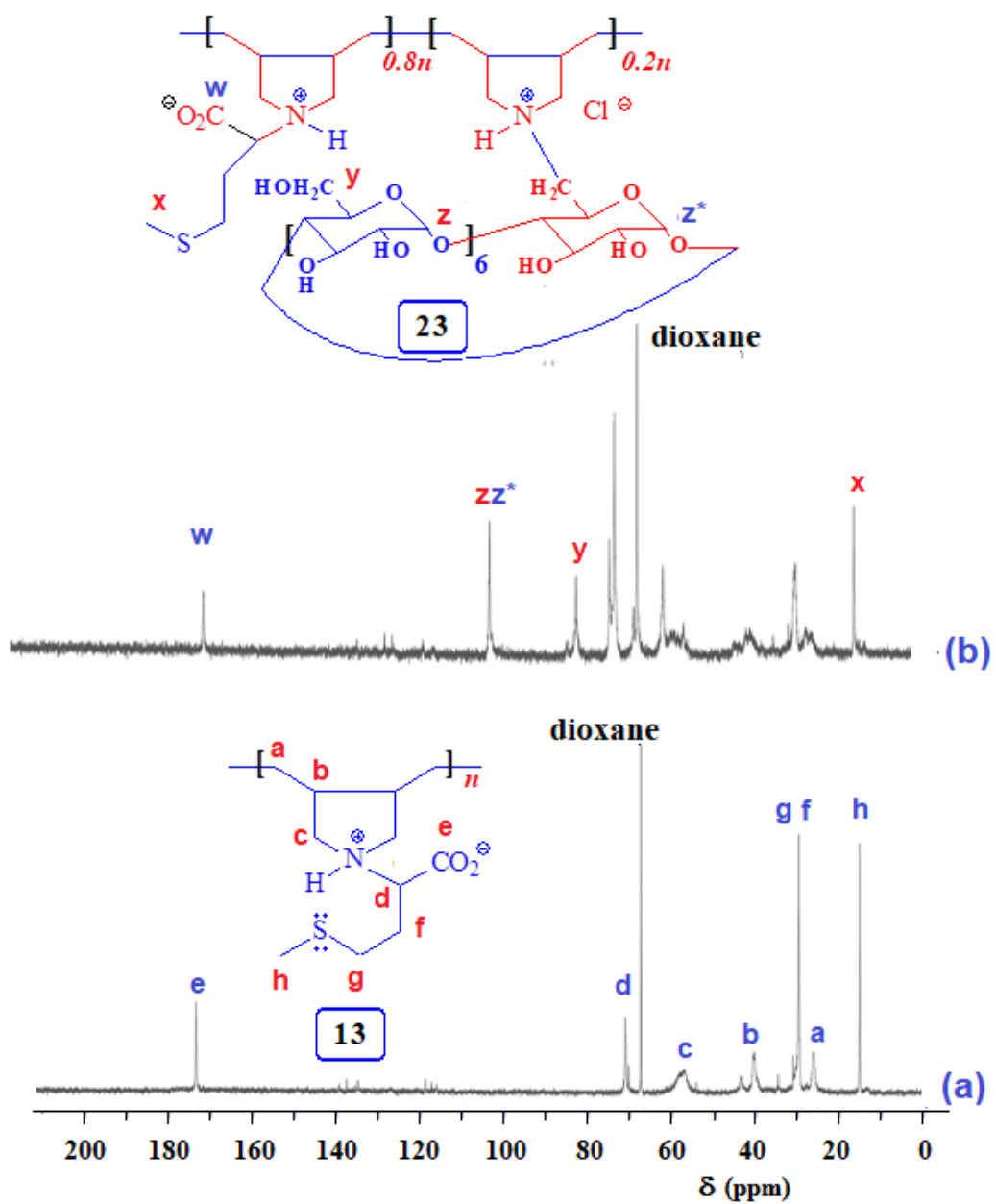
**Scheme 11.** Copolymerization of monomers **3** and **4**.



**Figure 21.** FTIR spectrum of 18.

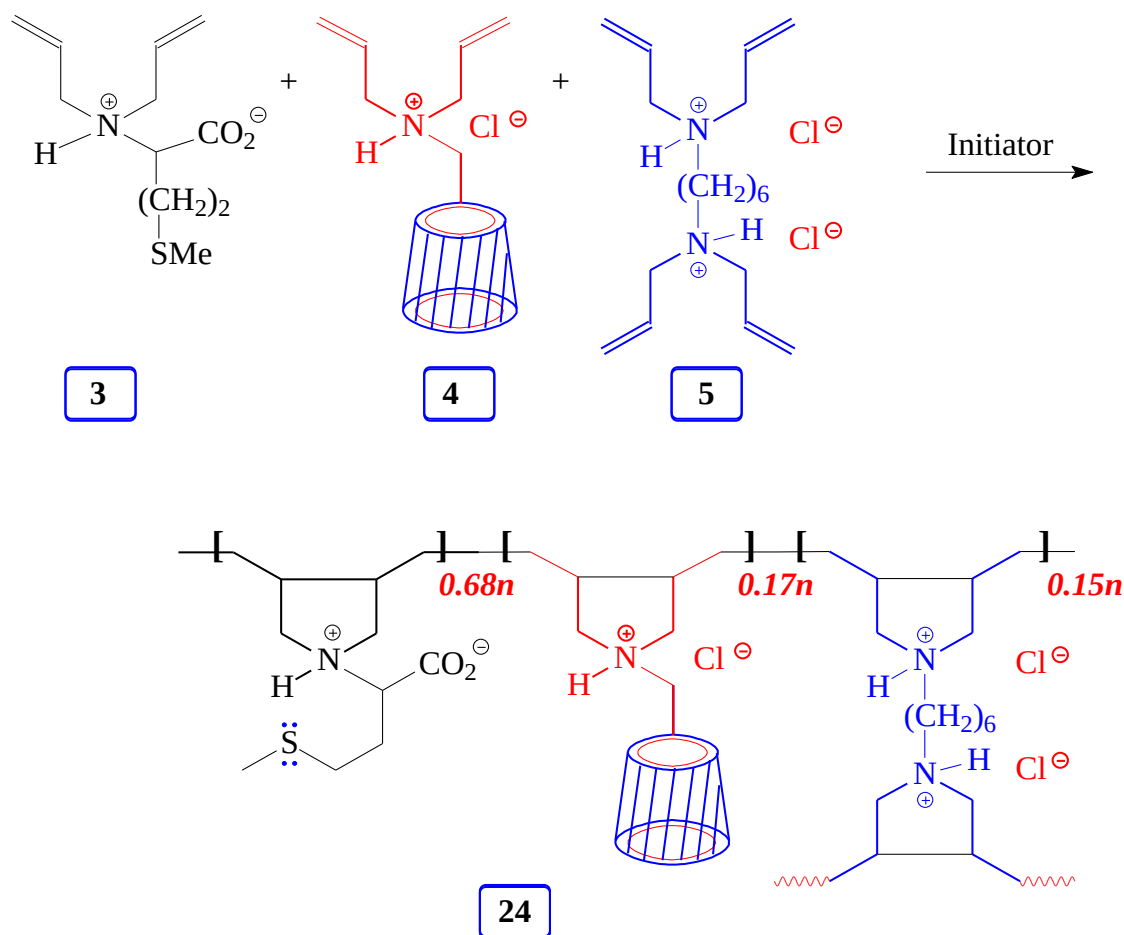


**Figure 22.**  $^1\text{H}$  NMR spectrum of (a) **13** and (b) cyclopolymer **23** in  $\text{D}_2\text{O}$ .

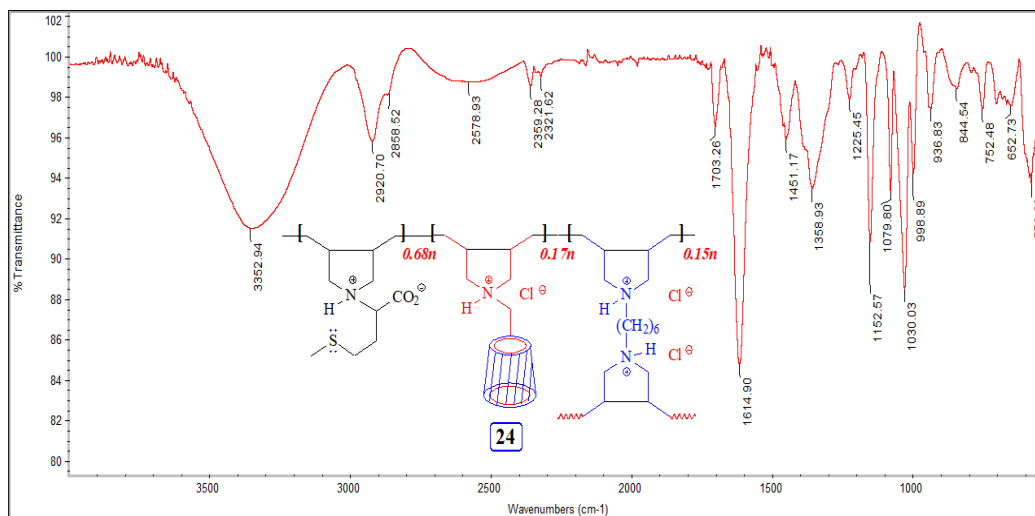


**Figure 23.**  $^{13}\text{C}$  NMR spectrum of (a) **13** and (b) cyclopolymer **18** in  $\text{D}_2\text{O}$ .

Finally, resin **24** was synthesized in excellent yield via terpolymerization of monomers **3**, **4**, and cross-linker **5** in a mole ratio 68:17:15 (Scheme 12). The FTIR spectrum is displayed in Figure 24. The antisymmetric stretching of  $\text{COO}^-$  in the dipolar form of **24** appeared at  $1615\text{ cm}^{-1}$  (Figure 24). Absorption at  $3353\text{ cm}^{-1}$  indicates the presence of OH groups. Minor absorption at  $1703\text{ cm}^{-1}$  indicates the presence of  $\text{CO}_2\text{H}$  form via proton transfer from monomer **5**.



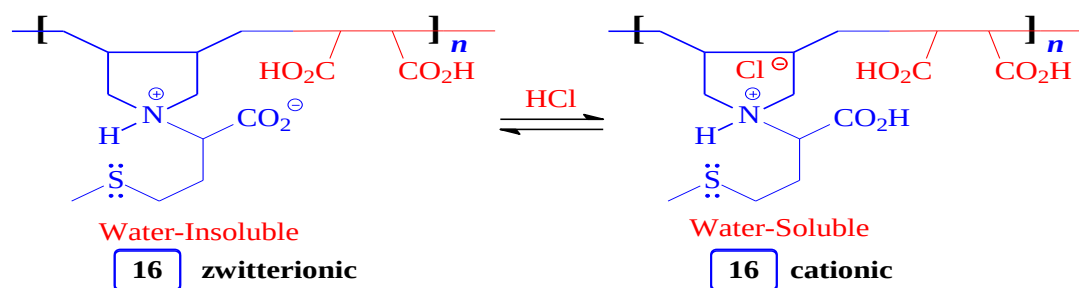
**Scheme 12.** Synthesis of cross-linked resin **24**.



**Figure 23.** FTIR spectrum of resin **24**.

## 4.2 Solution properties of the synthesized polymers:

The outcomes of the cyclopolymerization are presented in [Table 1](#). The final column in the table displays the values of the intrinsic viscosities. Aqueous solutions containing 1 weight percent of homopolymer **13**, as well as copolymers **15** and **18**, were determined to be soluble in water without the presence of salt. Nevertheless, a solution containing a 7 wt% of **18** resulted in a turbid mixture that became transparent after the addition of a small amount of NaCl. Copolymer **16** was determined to be insoluble in water, but soluble in the presence of 0.099 M HCl due to the transformation of its zwitterionic form into the cationic backbone ([Scheme 13](#)). The solubility of the substance was found to be limited when the hydrochloric acid concentration reached 0.047 M. Copolymer **16** remained insoluble even in the presence of even 5 M NaCl. Copolymer **23** bearing CD residues was water-soluble, but surprisingly addition of NaCl (5 mg) to a 1 wt% solution gave immediate precipitation, which remained insoluble even after making the mixture up to 5 M NaCl. At this stage we cannot rationalize this solubility behavior.



**Scheme 13.** pH-dependent solubility of copolymer **16**.

Table 1. shows the Polymerization of monomers  $M_1$  (3),  $M_2$  (4, 8, 14, 17) at 80 °C for 24 h.

**Table 1.** Polymerization of monomers  $M_1$  (3), and  $M_2$ .

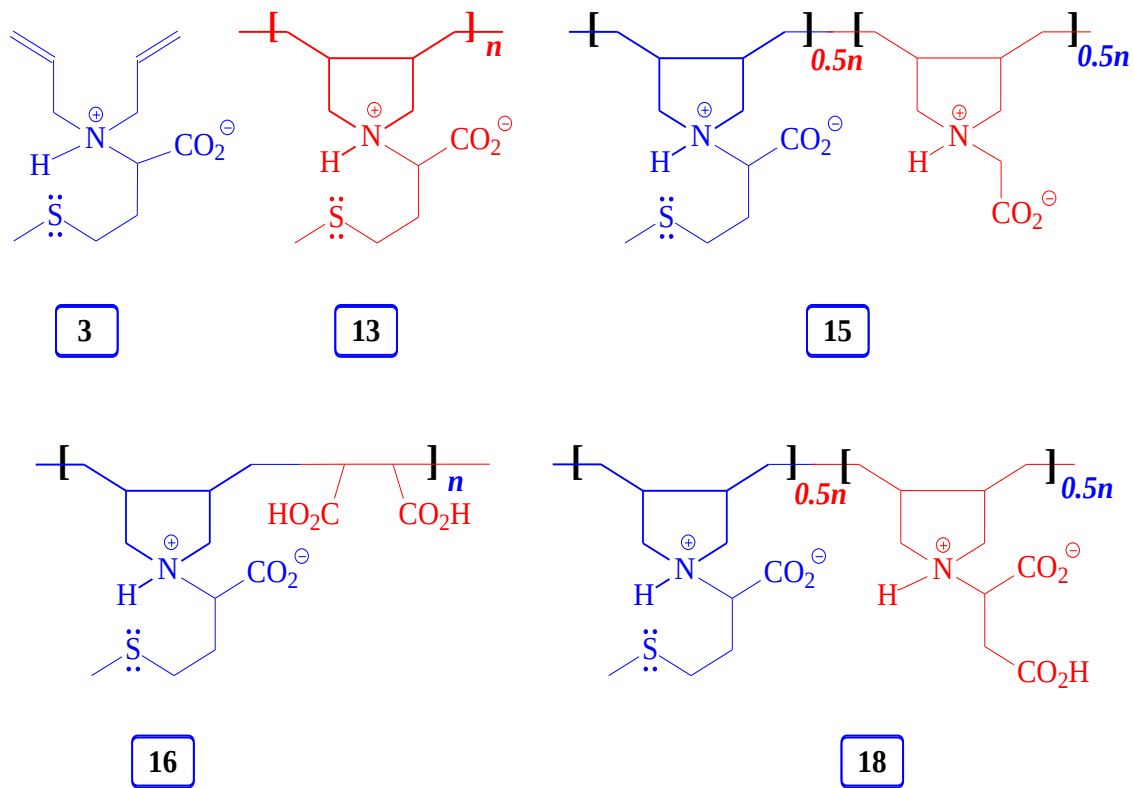
| Entry           | $M_1$<br>(mmol) | $M_2$<br>(mmol)    | Water<br>(%) | HCl<br>(mmol) | NaCl<br>(M) | Initiator<br>AMPD<br>(mg) | Yield <sup>b</sup><br>Polymer<br>(%) | $M_1/M_2$<br>feed | $M_1/M_2$<br>polymer | Intrinsic<br>Viscosity <sup>c</sup><br>(dL g <sup>-1</sup> ) |
|-----------------|-----------------|--------------------|--------------|---------------|-------------|---------------------------|--------------------------------------|-------------------|----------------------|--------------------------------------------------------------|
| 1               | 5               | –                  | 30           | –             | –           | 50                        | <b>13</b> (40)                       | 100:0             | 100:0                | 0.0654 <sup>d</sup>                                          |
| 2               | 5               | –                  | 30           | –             | 1.47        | 50                        | <b>13</b> (44)                       | 100:0             | 100:0                | 0.0793 <sup>d</sup>                                          |
| 3               | 5               | –                  | 30           | –             | 1.47        | 100                       | <b>13</b> (57)                       | 100:0             | 100:0                | 0.174 <sup>d</sup>                                           |
| 4               | 5               | –                  | 30           | 5             | –           | 50                        | <b>13</b> (71)                       | 100:0             | 100:0                | 0.0824 <sup>d</sup><br>0.0874<br>0.0895 <sup>f</sup>         |
| 5               | 5               | <b>14</b> (5)      | 35           | –             | 1           | 100                       | <b>15</b> (67)                       | 50:50             | 50:50                | 0.115 <sup>e</sup>                                           |
| 6               | 5               | <b>8</b> (5)       | 30           | –             | 1.5         | 75                        | <b>16</b> (75)                       | 50:50             | 50:50                | 0.0672 <sup>g</sup>                                          |
| 7               | 5               | <b>8</b> (5)       | 37           | 5.5           | –           | 75                        | <b>16</b> (31)                       | 50:50             | 50:50                | 0.0443 <sup>g</sup>                                          |
| 8               | 5               | <b>8</b> (5)       | 37           | 5.5           | –           | 50                        | <b>16</b> (31)                       | 50:50             | 50:50                | 0.0307 <sup>g</sup>                                          |
| 9               | 5               | <b>17</b> (5)      | 40           | 5             | –           | 125                       | <b>18</b> (55)                       | 50:50             | 50:50                | 0.0342 <sup>e</sup>                                          |
| 10              | 5               | <b>17</b> (5)      | 35           | 5             | –           | 125                       | <b>18</b> (72)                       | 50:50             | 50:50                | 0.0303 <sup>e</sup>                                          |
| 11 <sup>a</sup> | 2.5             | <b>4</b><br>(0.62) | 35           | –             | 1.5         | 90                        | <b>23</b> (76)                       | 80:20             | 80:20                | 0.0033 <sup>e,h</sup>                                        |

<sup>a</sup>Entry 11 Run at 75 C for 48 h; <sup>b</sup>yields are written under parentheses.  
<sup>c</sup>Viscosity of 1-0.25% at 30 °C using Ubelohde viscometer; <sup>d</sup> salt-free water; <sup>e</sup>0.1 NaCl; <sup>f</sup>0.5 N NaCl; <sup>g</sup>0.1 HCl; at concentrations of 1, 0.5, and 0.25 wt% in salt-free water, the reduced viscosities became 0.098, 0.1116, and 0.122 dl g<sup>-1</sup>, respectively, thereby showing polyelectrolyte behavior.

### **4.3 Mild steel corrosion inhibition by the synthesized polymers in 15% HCl**

The weight loss method was initially employed to investigate the efficacy of synthetic polymers in protecting against mild steel corrosion in a 15% hydrochloric acid solution due to its straightforwardness and dependability. The weight-loss measurements were conducted on the monomer and polymers indicated below. The standard deviation of the average percent inhibition efficiency ranges from 0.4% to 1.1%. If the coupons have different masses, the weight reductions were determined using a method that compares the weight loss relative to the initial mass. <sup>104</sup>

Each test was performed in triplicate, and the values for inhibitory efficiency (IE) ( $\eta\%$ ) and standard deviation (SD) have been recorded in [Table 2](#).



**Scheme 12.** Monomer **3** and Polymer **13**, **15**, **16** and **18** as Corrosion Inhibitors.

Table 2.illustrate the Inhibition efficiency (IE) ( $\eta\%$ ) imparted by 3, 13, 15, 16, and 18 to arrest corrosion of mild steel in 15% HCl for an immersion time of 6 h.

| <b>Table 2.</b> Inhibition efficiency (IE) ( $\eta\%$ ) of compound 3, 13, 15, 16, and 18. |           |              |          |                             |                 |
|--------------------------------------------------------------------------------------------|-----------|--------------|----------|-----------------------------|-----------------|
| Entry                                                                                      | Inhibitor | Sample (ppm) | KI (ppm) | Temp ( $^{\circ}\text{C}$ ) | IE ( $\eta\%$ ) |
| 1                                                                                          | <b>18</b> | 0.25         | -        | 30                          | $11.2 \pm 1.5$  |
| 2                                                                                          |           | 0.25         | -        | 30                          | $42.0 \pm 1.6$  |
| 3                                                                                          |           | 0.75         | -        | 30                          | $61.9 \pm 1.7$  |
| 4                                                                                          |           | 1.0          | -        | 30                          | $69.2 \pm 1.1$  |
| 5                                                                                          |           | 2.0          | -        | 30                          | $85.2 \pm 0.9$  |
| 6                                                                                          |           | 3.0          | -        | 30                          | $85.9 \pm 0.8$  |
| 7                                                                                          |           | 5.0          | -        | 30                          | $87.1 \pm 0.7$  |
| 8                                                                                          |           | 5.0          | -        | 45                          | $80.5 \pm 1.1$  |
| 9                                                                                          |           | 5.0          | -        | 60                          | $73.8 \pm 1.0$  |
| 10                                                                                         |           | 25           | -        | 30                          | $90.1 \pm 0.7$  |
| 11                                                                                         |           | 50           | -        | 30                          | $89.7 \pm 0.6$  |
| 12                                                                                         |           | 100          | -        | 30                          | $90.2 \pm 0.5$  |
| 13                                                                                         |           | -            | 400      | 30                          | $41.1 \pm 2.1$  |
| 14                                                                                         |           | 5            | 400      | 30                          | $89.9 \pm 0.7$  |
| 15                                                                                         |           | -            | 400      | 60                          | $18.3 \pm 2.5$  |
| 16                                                                                         |           | 5            | 400      | 60 <sup>a</sup>             | $94.5 \pm 0.4$  |
| 17                                                                                         | <b>3</b>  | 100          | -        | 30                          | $61.8 \pm 2.3$  |
| 18                                                                                         | <b>13</b> | 100          | -        | 30                          | $82.8 \pm 1.4$  |
| 19                                                                                         | <b>15</b> | 100          | -        | 30                          | $85.7 \pm 1.2$  |
| 20                                                                                         | <b>16</b> | 100          | -        | 30                          | $88.3 \pm 1.5$  |
| <sup>a</sup> 3h                                                                            |           |              |          |                             |                 |

The achieved  $\eta\%$  values for concentrations of 100 ppm of **3**, **13**, **15**, **16**, and **18** were 61.8, 82.8, 85.7, 88.3, and 90.2%, respectively. The synthesized polymers outperformed monomer **3** due to their larger surface area and increased number of adsorption sites. Out of the various polymers, **18** had superior performance and was selected for additional analysis. As seen by the Table, the inhibitory effect (IE) rises proportionally with higher concentrations of the inhibitor. However, it reaches a plateau after reaching 3 ppm of **18**, which confirms that the surface covering is complete. The results are quite satisfying as a low concentration of 2 ppm yielded an efficiency of 85.2% at a temperature of 30 °C (Table entry 5). IEs were determined to be 87.1%, 80.2%, and 73.8% at temperatures of 30, 45, and 60 °C correspondingly, when the concentration of polymer **18** was 5 ppm (entries 7-9). The inhibitor efficiency (IE) drops as the temperature increases, indicating that more inhibitors are released from the metal surface at higher temperatures.

The surface coverage ( $\theta$ ) values, ranging from 0.25 to 2.0 ppm, were fitted into various isotherm models given below. The corresponding linear plots may be seen in (Figure 25). The symbol "C" represents the concentration of a substance in units of moles per liter ( $\text{mol L}^{-1}$ ), whereas " $K_{\text{ads}}$ " represents the equilibrium constant for adsorption. The concentration of the solution is determined by calculating the molar mass of the repeating unit, which is made up of methionine and aspartic acid, and expressing it in moles per liter ( $\text{mol L}^{-1}$ ). The  $R^2$  values demonstrate a strong match of the data to the Langmuir isotherm, as shown in (Figure 25b). The value of  $K_{\text{ads}}$  was determined to be 1438970 based on the slope. The free energy of adsorption ( $\Delta G_{\text{ads}}$ ), determined using Equation (11) with a molar concentration of water in solution of 55.5, was observed to be  $-50.4 \text{ kJ mol}^{-1}$ . The factor 55.5 is derived from the adsorption of an inhibitor (Inh) at a metal/aqueous interface.<sup>105</sup> This adsorption

can occur through the displacement of adsorbed water molecules (Equation (9)) and/or the consecutive adsorption of  $\text{Cl}^-$  and cationic inhibitor ( $\text{Inh}^+$ ) (Equation (10)) on the metal surface, followed by the entrainment of water coverage (Figure 26).<sup>106</sup> The adsorption process is anticipated to entail the interaction between the lone pair on sulfur (S) and the unoccupied 3d orbital of the metal.

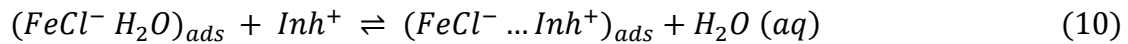
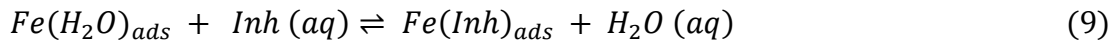
$$\text{Temkin:} \quad K_{ads} C = e^{f\theta} \quad (4)$$

$$\text{Langmuir:} \quad \frac{\theta}{1 - \theta} = K_{ads} C \quad (5)$$

$$\text{Frumkin [106]:} \quad K_{ads} = \frac{\theta}{1 - \theta} e^{-2a\theta} \quad (6)$$

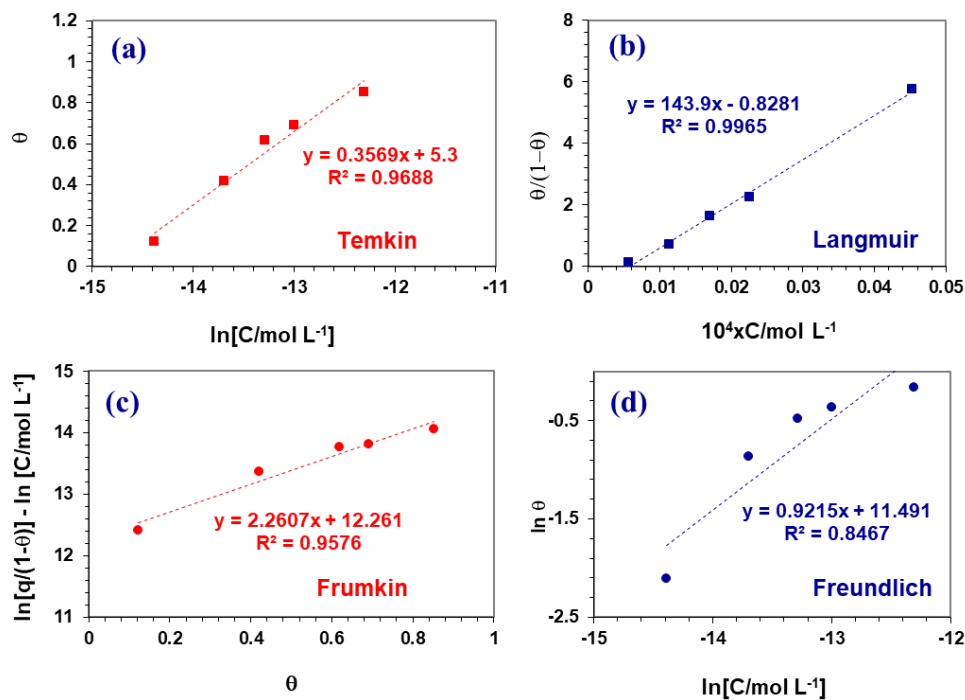
$$\text{Freundlich [107]:} \quad \theta = K_{ads} C^n \quad (7)$$

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G_{ads}^0}{RT}} \quad (8)$$

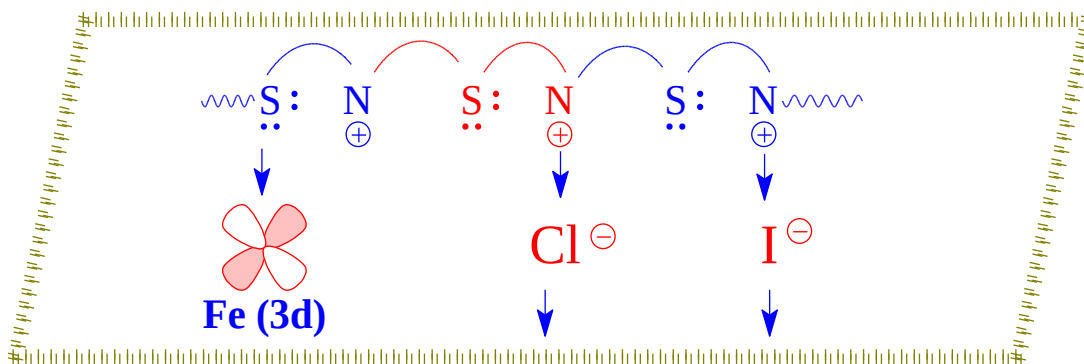


The value of  $\Delta G$ , which is  $-50.4 \text{ kJ mol}^{-1}$ , can be attributed to the dominance of chemisorption. If the  $\Delta G_{ads}$   $G_{oads}$  value is less negative than  $-20 \text{ kJ mol}^{-1}$ , it is assigned to physisorption on the metal surface<sup>108,109</sup>.

Physisorption refers to the adsorption of cationic motifs of the polymer on the layer of  $\text{Cl}^-$  ions that cover the Fe-surface. On the other hand, the interaction of carboxyl motifs with the d-orbitals of iron or accumulated  $\text{Fe}^{2+}$  on the anodic sites leads to the formation of a coordinate kind of bond.



**Figure 24.** (a) Temkin, (b) Langmuir, (c) Frumkin, and (d) Freundlich adsorption isotherms of 18 in 15% HCl at 30 °C.



**Figure 25** Interaction of sulfur lone pair and cationic nitrogens on halide assisted adsorption on metal surface.

The addition of halide ions, particularly  $I^-$ , in conjunction with inhibitor molecules, is recognized to enhance the effectiveness of inhibition.<sup>108-110</sup> Various inhibition tests were conducted at a temperature of 30 °C using KI (400 ppm), polymer **18** (5 ppm), and a

combination of polymer **18** (5 ppm) and KI (400 ppm). The resulting inhibition efficiencies (IEs) were 41.1%, 87.1%, and 89.9% respectively. Similarly, at a temperature of 60 °C, the IEs were determined to be 18.3%, 73.8%, and 94.5% respectively. The synergism parameter  $S_0$  is computed using Equation (11) <sup>110</sup>.

$$S_{\theta} = \frac{1 - (\theta_1 + \theta_2 - \theta_1\theta_2)}{1 - \theta_{1+2}} \quad (11)$$

The variables  $\theta_1$  and  $\theta_2$  represent the degree of surface coverages, which are equivalent to fractional inhibition efficiency ( $\eta\%/100$ ) of **18** and KI, respectively.  $\theta_{1+2}$  refers to the degree of surface coverage of the mixture of polymer **18** + KI. Typically, when  $S_0$  is greater than 1 or less than 1, it indicates cooperative co-adsorption (meaning a synergistic effect) or competitive co-adsorption (meaning an antagonistic effect) <sup>110-112</sup>, respectively. The  $S_0$  value was determined to be 1.38 and 2.48 at 30 and 60 °C, respectively. This indicates that the combination of the polymer **18** and KI exhibits a synergistic effect in reducing the corrosion of mild steel.

#### 4.4. Adsorption isotherms

Figure 27 illustrates how the equilibrium adsorption capacity ( $\theta_e$ ) correlates with the initial Hg (II) concentration  $C_o$  using a set amount of resin **24** at 298 K. The values of ( $\theta_e$ ) increase linearly with increasing concentrations, as documented in (Table 3). Understanding the interaction between  $\theta_e$  and the equilibrium concentration  $C_e$  is facilitated by adsorption isotherm models. These models are crucial for elucidating the underlying adsorption mechanisms<sup>29</sup>. In this study, four significant isotherm models, as outlined in Equations (12)-(14), are evaluated to describe these relationships.

$$\text{Langmuir isotherm model: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (12)$$

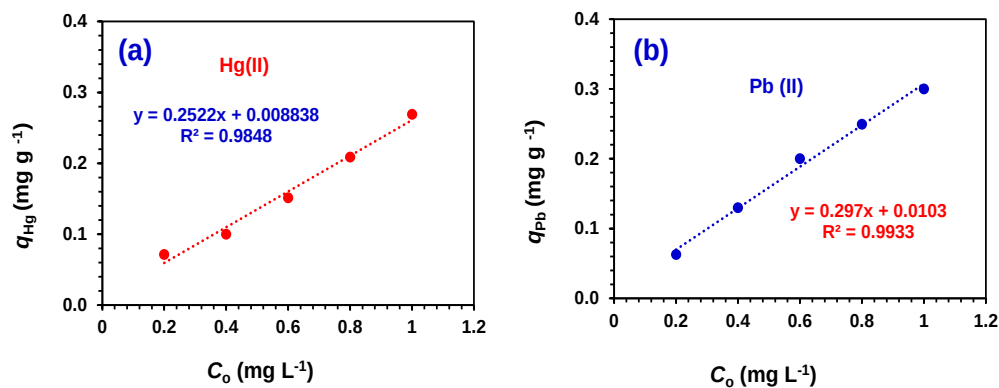
$$\text{Freundlich isotherm model: } \log q_e = \log k_f + \frac{1}{n} \log C_e \quad (13)$$

$$\text{Temkin isotherm model: } q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e = B \ln A + B \ln C_e \quad (14)$$

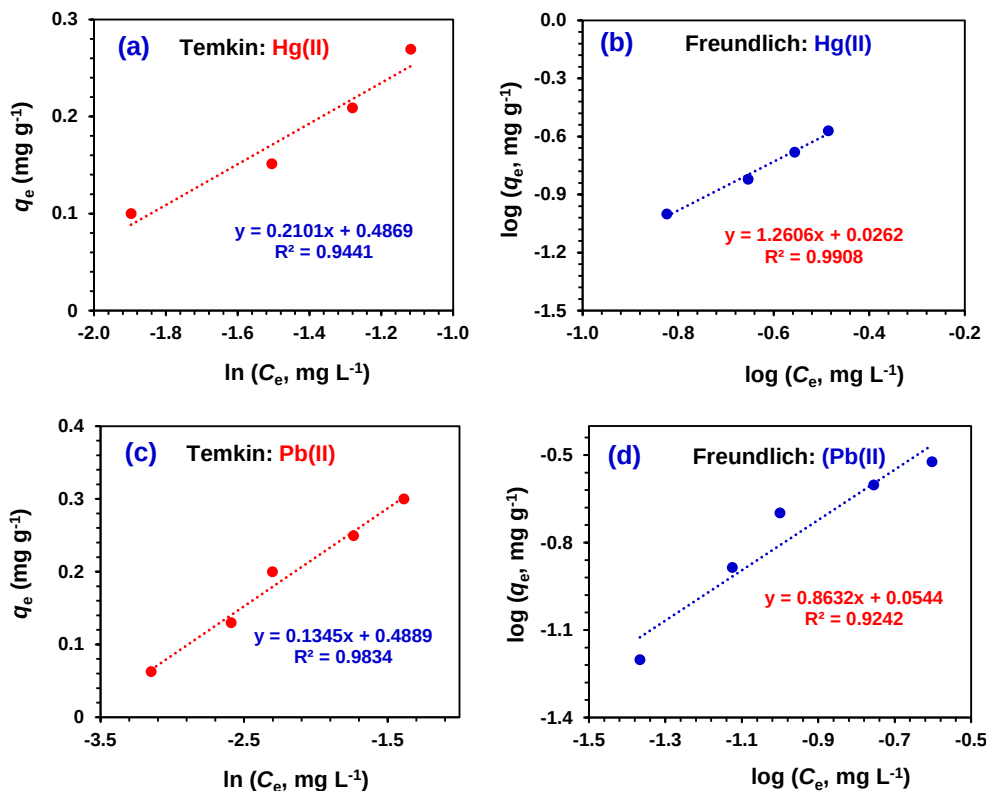
Table 3 describes the adsorption data along with % metal ion removal.

| <b>Table 3.</b> Adsorption of metal ions Pb (II) and Hg(II) by resin <b>24</b> at 25 °C |                                         |                                         |                                         |                 |
|-----------------------------------------------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------|
| MeHg ( ion                                                                              | C <sub>o</sub><br>(mg L <sup>-1</sup> ) | C <sub>e</sub><br>(mg L <sup>-1</sup> ) | θ <sub>e</sub><br>(mg L <sup>-1</sup> ) | % Metal removal |
| Hg (II)                                                                                 | 0.2                                     | 0.02138                                 | 0.071448                                | 89.3            |
|                                                                                         | 0.4                                     | 0.15                                    | 0.1                                     | 62.5            |
|                                                                                         | 0.6                                     | 0.222                                   | 0.1512                                  | 63.0            |
|                                                                                         | 0.8                                     | 0.278                                   | 0.2088                                  | 65.3            |
|                                                                                         | 1.0                                     | 0.327                                   | 0.2692                                  | 67.3            |
| Pb (II)                                                                                 | 0.2                                     | 0.043                                   | 0.0628                                  | 78.5            |
|                                                                                         | 0.4                                     | 0.075                                   | 0.131                                   | 81.3            |
|                                                                                         | 0.6                                     | 0.1                                     | 0.201                                   | 83.3            |
|                                                                                         | 0.8                                     | 0.176                                   | 0.2496                                  | 78.1            |
|                                                                                         | 1.0                                     | 0.25                                    | 0.302                                   | 75.2            |

The extracted parameters from the relevant linear plots ([Figure 26](#)) are given in [Table 4](#).



**Figure 26.** Equilibrium adsorption capacity ( $\theta_e$ ) versus initial concentration ( $C_0$ ) plots at 298 K for the adsorption of metal ions on resin **24**.



**Figure 27.** (a) Temkin for Hg (II), (b) Freundlich for Hg (II), (c) Temkin for Pb(II), and (d) Freundlich for Pb (II) isotherms of the adsorption of metal ions on resin **24** at 298K.

Out of the three isotherms analyzed, the Langmuir model did not accurately match the data, whereas the Temkin and Freundlich isotherms showed a stronger association, as

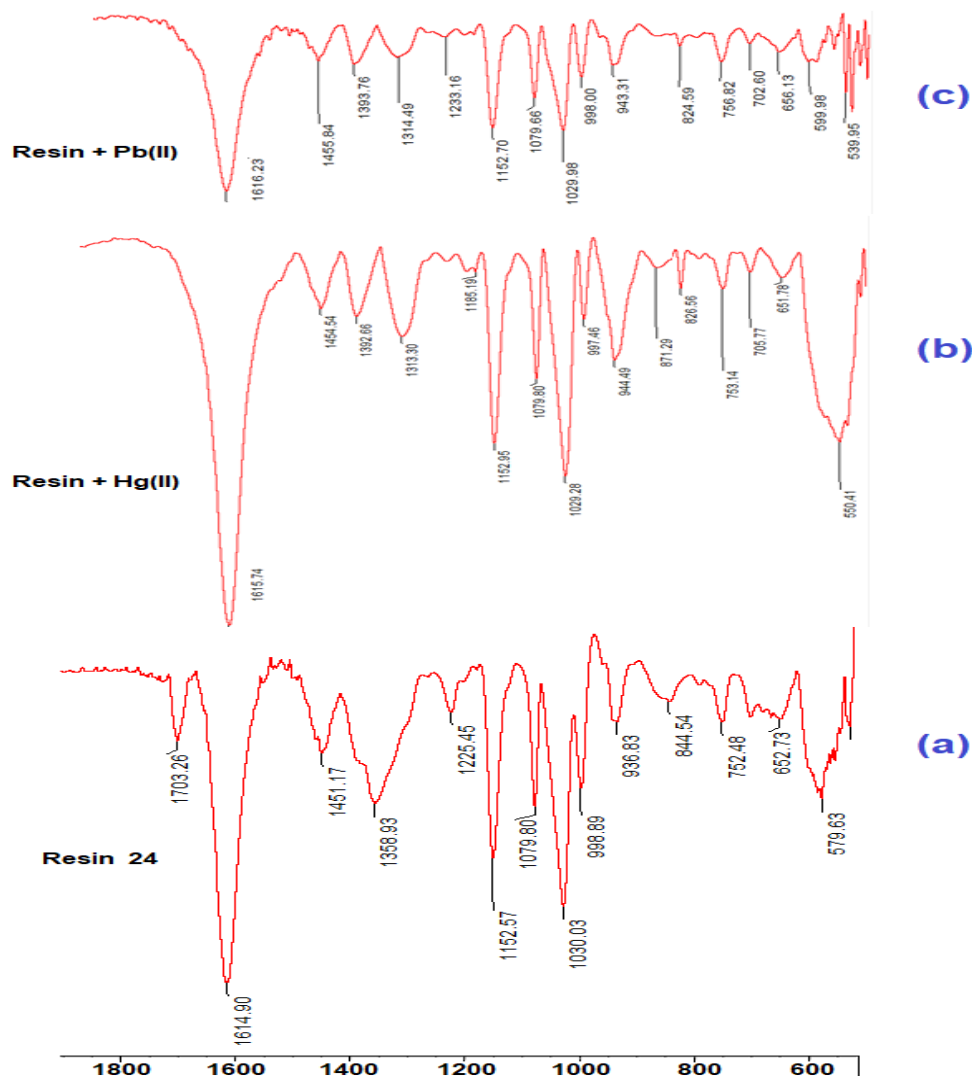
evidenced by the  $R^2$  values (Figure 28). The Freundlich isotherm model [Eq. (10)], applicable to heterogeneous adsorption systems with non-uniform energy distribution, produced linear plots from which the Freundlich constants  $k_f$  and  $n$  were obtained (Table 3).

The Temkin figure, shown in (Figure 27 a,c), allows for the calculation of the equilibrium binding constant  $A$  and the heat of adsorption  $B$  using  $E_0$ . (11), where  $B$  is computed as  $(RT/b)$ . This model suggests that there is a negative correlation between the heat of adsorption and the extent to which the surface is covered with metal ions<sup>39</sup>. The parameters obtained from this plot are presented in (Table 4).

Table 4 describes the adsorption Langmuir Freundlich and Temkin isotherm model constants for Hg (II) and Pb(II) adsorption at 298 K on resin 24.

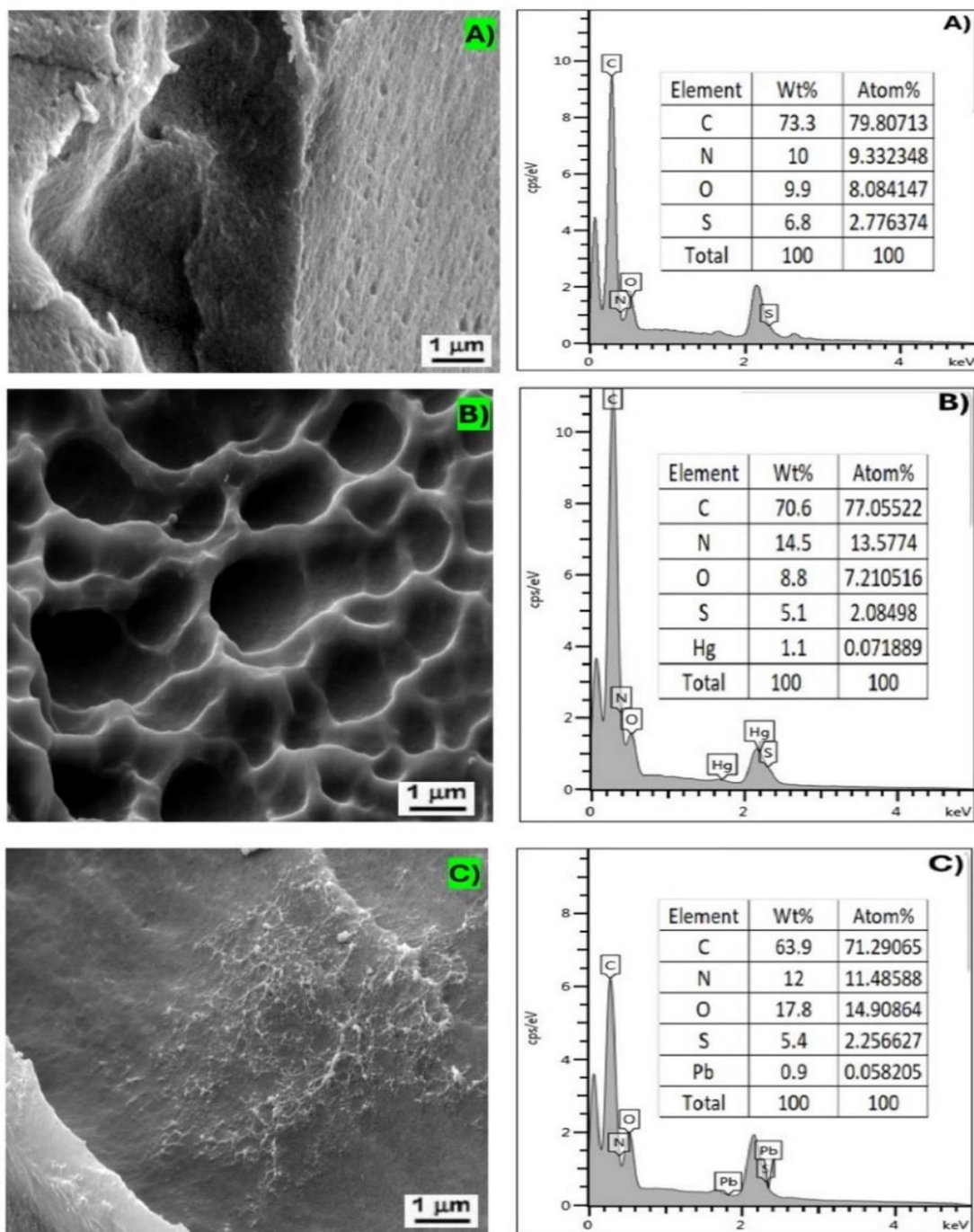
| <b>Table 4</b> Langmuir Freundlich and Temkin isotherm model constants for Hg (II) and Pb(II). |                                  |                |
|------------------------------------------------------------------------------------------------|----------------------------------|----------------|
| Hg (II): Temkin isotherm model                                                                 |                                  |                |
| A(L g <sup>-1</sup> )                                                                          | B(J mol <sup>-1</sup> )          | R <sup>2</sup> |
| 10                                                                                             | 0.2101                           | 0.9441         |
| Hg (II): Freundlich isotherm model                                                             |                                  |                |
| <i>n</i>                                                                                       | $k_f(mg^{1-1/n} g^{-1} L^{1/n})$ | R <sup>2</sup> |
| 0.793                                                                                          | 1.062                            | 0.9908         |
| Pb (II): Temkin isotherm model                                                                 |                                  |                |
| A(L g <sup>-1</sup> )                                                                          | B(J mol <sup>-1</sup> )          | R <sup>2</sup> |
| 38                                                                                             | 0.1345                           | 0.9834         |
| Pb (II): Freundlich isotherm model                                                             |                                  |                |
| <i>n</i>                                                                                       | $k_f(mg^{1-1/n} g^{-1} L^{1/n})$ | R <sup>2</sup> |
| 1.158                                                                                          | 1.133                            | 0.9242         |

FTIR spectra of (a) Pristine resin **24**, (b) Resin loaded with Hg(II), and (c) Resin loaded with Pb(II) are displayed in Figure 28.



**Figure 28.** FTIR spectra of (a) Pristine resin **24**, (b) Resin loaded with Hg (II), and (c) Resin loaded with Pb (II).

SEM and EDX analysis for resin **24** (a) unloaded, (b) loaded with Hg (II), (c) and loaded with Pb(II) is displayed in Figure 29, which ensures the incorporation of Hg(II) (Figure 29b) and Pb(II) (Figure 29c) onto the resin.



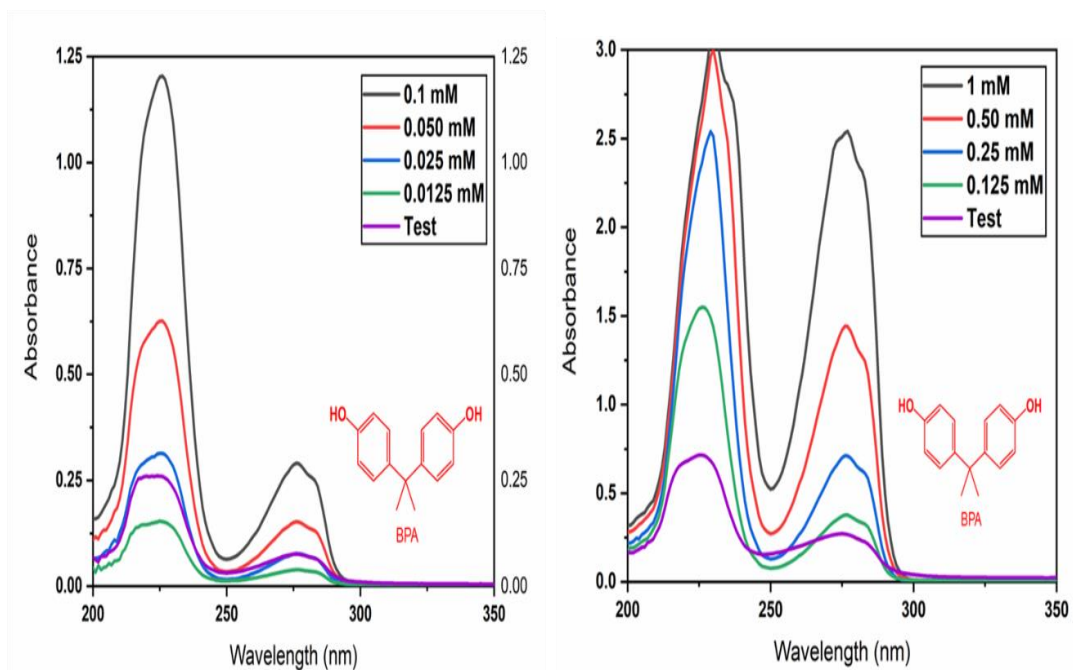
**Figure 29.** SEM and EDX analysis for resin **24** (a) unloaded, (b) loaded with Hg(II), (c) and loaded with Pb(II).

## 4.5 Removal of Organic Micropollutants: Adsorption Studies

The presence of organic micropollutants such as pharmaceuticals and pesticides in water resources due to industrialization posed a serious threat to human health and aquatic ecosystems.<sup>114,115</sup> Insoluble polymers containing motifs of  $\beta$ -cyclodextrin ( $\beta$ -CD), can remove these anthropogenic organic chemicals from contaminated water by adsorption method. The hydrophobic cavity of  $\beta$ -CD formed host-guest complexes with many organic compounds.<sup>115,116</sup> Bisphenol A (BPA), which is endocrine disruptor was used in this study.<sup>117</sup>

The maximum absorption wavelength ( $\lambda_{\text{max}}$ ) for Bisphenol A (BPA) was determined to be 277 nm (Figure 30), which aligns with the characteristic absorption peaks of phenolic compounds in the ultraviolet region. This peak is critical for monitoring the presence of BPA in various environments using UV-Vis spectrophotometry.

The polymer showed a strong ability to remove BPA from water. When the BPA concentration was 1 mM, the polymer removed about 89.45% of it. At a lower concentration of 0.1 mM, it removed about 76.2%. This difference in adsorption efficiency can be attributed to the higher availability of adsorption sites at lower contaminant concentrations.



**Figure 30.** UV spectra of organic analytes with known concentrations and adsorption sample

## Conclusion:

Various amino acid-based diallylamine salt monomers: methionine-based **3**, glycine-based **14**, aspartic acid-based **17** have been synthesized. Likewise, a  $\beta$ -cyclodextrin (CD) based monomer **4** and a cross-linker **5** has been generated. Cyclopolymerization of **3** afforded homopolymer **13**, while copolymerization of **3/14**, **3/maleic acid (8)**, **3/17**, **3/4** pairs gave copolymers **15**, **16**, **18**, and **23**, respectively. Terpolymerization of **3/4/5** led to cross-linked resin **24**.

Monomer **3** and polymers **13**, **15**, **16**, and **18** have been studied as corrosion inhibitors for inhibition of mild steel corrosion in 15% HCl at 30, 45, and 60 °C. Polymers performed better than monomer **3**. Copolymer **18** performed the best; very impressive inhibition efficiencies (IEs) are achieved even in the 1-5 ppm range. The presence of KI further boosts the IEs.

Resin **24** has been used effectively to trap organic micropollutant as well as priority metal ions like Hg (II) and Pb (II).

## References |

1. M. F. Hamoda, Water strategies and potential of water reuse in the south Mediterranean countries, *Desalination* 165 (2004) 31-41  
<https://doi.org/10.1016/j.desal.2004.06.004>.
2. US Bureau of Reclamation and Saudia National Laboratories, *Desalination, and water purification technology roadmap: Water Purification* 2003.  
<https://doi.org/10.2172/809106>.
3. US. -SABC- Public-Private Agreements Upgrade Saudi Water Infrastructure. *U.S.-Saudi Business Brief*. **2010**, 9-10. <https://doi.org/10.1016/j.jenvman.2011.09.023>
4. K. kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Biores. Technol.* 7 (2001) 63-65.  
[https://doi.org/10.1016/S0960-8524\(00\)00072-9](https://doi.org/10.1016/S0960-8524(00)00072-9).
5. W. Wirojanagud, N. Tantemsapya, P. Tantriratna, Precipitation of heavy metals by lime mud waste of pulp and paper mill. *Song. J. Sci. Tech.* 26 (2004) 45-53.  
<https://thaiscience.info/Journals/Article/SONG/10462510.pdf>.
6. K. Dermentzis, A. Davidis, D. Papadopoulou, A.Christoforidis, K.Ouzounis, Copper removal from industrial wastewaters by means of electrostatic shielding driven electrodeionization. *J. Eng. Sci. Technol.* 2 (2009) 131-136.  
<http://dx.doi.org/10.25103/jestr.021.24>.

7. Wojtowicz, A. Stoklosa, Removal of Heavy Metal Ions on Smectite Ion-Exchange Column. J. Env. Studies. 11 (2002) 97-101. <http://www.pjoes.com/Removal-of-Heavy-Metal-Ions-on-Smectite-Ion-Exchange-Column,87428,0,2.html>
8. T. Bakalar, M. Bugel, L. Gajadosova, Heavy metal removal using reverse osmosis. L. Acta Mount. Slov. 14 (2009) 250-253, <https://www.semanticscholar.org/paper/Heavy-metal-removal-using-reverse-osmosis-Gajdo%C5%A1ov%C3%A1.>
9. K. A. Matis, N. K. Lazaridis, A. I. Zouboulis, G. P. Gallios, V. A. Mavrov, Hybrid flotation—microfiltration process for metal ions recovery. J. Membr. Sci. 247 (2005) 29-36. <https://doi.org/10.1016/j.memsci.2004.07.031>.
10. K. Sen Gupta, Environmental separation of heavy metals, CRC Press, New York, (2002). <https://doi.org/10.1201/9781482278941>.
11. Vieira, E. F. S.; Simoni J. D. A.; Airoidi, C, Interaction of cations with SH-modified silica gel: thermochemical study through calorimetric titration and direct extent of reaction determination. J. Mater. Chem. 7 (1997) 2249-2252. <https://doi.org/10.1039/A704286H>.
12. L. Mercier, C. Detellier, Preparation, Characterization, and Applications as Heavy Metals Sorbents of Covalently Grafted Thiol Functionalities on the Interlamellar Surface of Montmorillonite. Environ. Sci. Technol. 29 (1995) 1318– 1323. <https://doi.org/10.1021/cm0112082>.
13. Bibby, L. Mercier. Mercury (II) ion adsorption behavior in thiol-functionalized mesoporous silica microspheres. Chem. Mater. 14 (2002) 1591–1597. <https://doi.org/10.1021/cm0112082>.

14. R. I. Nooney, M. Kalyanaraman, G. Kennedy, E.J. Maginn, Heavy metal remediation using functionalized mesoporous silicas with controlled macrostructure. *J. Langmuir*. 17 (2001) 528–533. <https://doi.org/10.1021/la000720j>
15. R. M Allen-King, P. Grathwohl, W. P. Ball, New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Adv. Water Res.* 25 (2002) 985–1016. [https://doi.org/10.1016/S0309-1708\(02\)00045-3](https://doi.org/10.1016/S0309-1708(02)00045-3).
16. S. E. Bailey, T. J Olin, R. M. Bricka, D. D. Adrian, A review of potentially low-cost sorbents for heavy metals. *Water Res.* 33 (1999) 2469–2479. [https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8).
17. J. J. Pignatello, B. Xing, Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles. *Environ. Sci. Technol.* 30 (1995) 1–11. <https://doi.org/10.1021/es940683g>.
18. Roy, K. Manna, S. Dey, S. Pal, Chemical modification of  $\beta$ -cyclodextrin towards hydrogel formation, *Carbohydrate Polymers* 306 (2023) 12057. <https://doi.org/10.1016/j.carbpol.2023.120576>.
19. Gidwani, A. Vyas, A comprehensive review on cyclodextrin-based carriers for delivery of chemotherapeutic cytotoxic anticancer drugs. *BioMed Research International*, Article ID 198268, 2015. <https://doi.org/10.1155/2015/198268>.
20. J. Wankar, N. G. Kotla, S. Gera, S. Rasala, A. Pandit, Y. A. Rochev. Recent advances in host–guest self-assembled cyclodextrin carriers: Implications for responsive drug

- delivery and biomedical engineering. *Advanced Functional Materials*, 30(44), 2020, Article 1909049. <https://doi.org/10.1002/adfm.201909049>
21. Lade, B., Shanware, A., & Sharma, R. (2021). Effect of  $\beta$ -cyclodextrin stabilized silver nanoparticles on gills, kidney, liver of *Danio rerio*. *Lett. Appl. NanoBioSci.* 11, 2022, 2981-2995. <https://doi.org/10.33263/LIANBS111.29812995>.
  22. K. Manna, P. Patra, A. Roy, R. K. Roy, K. C. Sunka, S. Dhara, N. Patra, S. Pal, Amino acid inspired alginate-based pH sensitive polymeric micelles via reversible addition-fragmentation chain transfer polymerization. *ACS Appl. Polym. Mater.*, 4(6), 2022, 4432–4444. <https://doi.org/10.1021/acsapm.2c00393>.
  23. L. Keith, W. Telliard, ES&T special report: priority pollutants: I-a perspective view, *Environ. Sci. Technol.* 13 (1979) 416–423.  
<https://doi.org/10.1016/j.carbpol.2023.120576>.
  24. Ministry of Health of P. R. China. Standards for drinking water quality. **2006** (GB 5749-2006). <https://doi.org/10.4028/www.scientific.net/AMM.368-370.2034>
  25. U. S. Environmental Protection Agency. National primary drinking water regulations. **2009** (EPA 816-F-09-004). <http://dx.doi.org/10.20431/2454-6224.0304003>.
  26. M.J. Kosnett, The role of chelation in the treatment of arsenic and mercury poisoning. *J. Med. Toxicol.* 9 (2013) 347–54. <https://doi.org/10.1007/s13181-013-0344-5>
  27. C. Shan, Z. Ma, M. Tong, J. Ni, Removal of Hg (II) by poly(1-vinylimidazole)-grafted Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic nanoparticles, *Water Research* 69 (2015) 252-260.  
<https://doi.org/10.1016/j.watres.2014.11.030>
  28. C. Xiong, Y. Li, G. Wang, L. Fang, S. Zhou, C. Yao, Q. Chen, X. Zheng, D. Qi, Y. Fu, Y. Zhu, Selective removal of Hg (II) with polyacrylonitrile-2-amino-1,3,4-

- thiadiazole chelating resin: Batch and column study, Chem. Eng. J. 259 (2015) 257-265. <https://doi.org/10.1016/j.cej.2014.07.114>
29. S. A. Ali, M. A. J. Mazumder, *A new resin embedded with chelating motifs of biogenic methionine for the removal of Hg (II) at ppb levels Journal of Hazardous Materials*, J Hazard Mater, 350 (2018) 169–179.  
<https://doi.org/10.1016/j.jhazmat.2018.02.033>;
30. T. A. Saleh, I. B. Rachman, S. A. Ali, *Tailoring hydrophobic branch in polyzwitterionic resin for simultaneous capturing of Hg (II) and methylene blue with response surface optimization*. Scientific Reports 7, Article number: 4573 (2017).  
<https://doi.org/10.1038/s41598-017-04624-6>.
31. M. A. J. Mazumder, M. T. Alhaffar, S. A. Ali, *Immobilization of two polyelectrolytes leading to a novel hydrogel for high-performance Hg<sup>2+</sup> removal to ppb and sub-ppb levels*.
32. Chemical Engineering Journal, 334 (2018) 1440–1454.  
<https://doi.org/10.1016/j.cej.2017.11.083>
33. Shaikh A. Ali\*, Ibrahim Y. Yaagoob, Mohammad A. J. Mazumder\*, Hasan A. Al-Muallem, *Fast removal of methylene blue and Hg (II) from aqueous solution using a novel super-adsorbent containing residues of glycine and maleic acid*, J Hazard Mater, 369, 2019, 642-654. <https://doi.org/10.1016/j.jhazmat.2019.02.082>
34. Z. A. Jamiu, T. A. Saleh, S. A. Ali, *Synthesis of a unique cross-linked polyzwitterion/anion having aspartic acid residue and its use for Pb<sup>2+</sup> removal from aqueous solution* RSC Adv., 5, 42222-42232 (2015) Used.  
<https://doi.org/10.1039/C5RA05447H>

35. S. A. Mubarak; S. A. Ali, I. Y. Yaagoob; M. A. J. Mazumder, *Design and synthesis of a dual-purpose super-adsorbent containing a high density of chelating motifs for the fast mitigation of methylene blue and Pb (II)*, ACS Omega 2020, 5, 27833–27845, <https://dx.doi.org/10.1021/acsomega.0c02860>
36. K. Uekama, F. Hirayama, T. Irie, Cyclodextrin Drug Carrier Systems. Chemical Reviews, 1998, 98, 2045–2076 <https://doi.org/10.1021/CR970025P>
37. Thomas Wimmer (). "Cyclodextrins". Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH. 2012, ISBN 978-3527306732, [https://doi.org/10.1002/14356007.e08\\_e02](https://doi.org/10.1002/14356007.e08_e02)
38. G. Becket, L. J. Schep, M. Y. Tan, Improvement of the in vitro dissolution of praziquantel by complexation with  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins. International Journal of Pharmaceutics. 1999, 179, 65–71. [https://doi.org/10.1016/S0378-5173\(98\)00382-2](https://doi.org/10.1016/S0378-5173(98)00382-2).
39. S. K. Rodal, G. Skretting, Q. Garred, F. Vilhardt, B. van Deurs; K. Sandvig, Extraction of Cholesterol with Methyl- $\beta$ -Cyclodextrin Perturbs Formation of Clathrin-coated Endocytic Vesicles". Molecular Biology of the Cell. 1999,10, 961–74. <https://doi.org/10.1091/mbc.10.4.961>.
40. D. M. Alzate-Sánchez, Y. Ling, C. Li, B. P. Frank, R. Bleher, D. H. Fairbrother, D. E. Helbling, W. R. Dichtel,  $\beta$ -Cyclodextrin Polymers on Microcrystalline Cellulose as a Granular Media for Organic Micropollutant Removal from Water, ACS Appl. Mater. Interfaces 2019, 11, 8, 8089–8096, <https://doi.org/10.1021/acsami.8b22100>
41. Alsbaiee, A., B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, Rapid removal of organic micropollutants from water by a porous  $\beta$ -cyclodextrin polymer. Nature 529, 190–194 (2016). <https://doi.org/10.1038/nature16185>

42. G. B. Butler, *Cyclopolymerization and cyclopolymerization*, Marcel Dekker: New York, 1992. <https://doi.org/10.1021/ar00083a005>
43. G. B. Butler, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 3451-3461. [https://doi.org/10.1002/1099-0518\(20001001\)38:19%3C3451::AID-POLA10%3E3.0.CO;2-N](https://doi.org/10.1002/1099-0518(20001001)38:19%3C3451::AID-POLA10%3E3.0.CO;2-N)
44. G. B. Butler, F. L. Ingley, *J. Am. Chem. Soc.*, 1951, **73**, 895-896. <https://doi.org/10.1021/ja01147a003>.
45. S. Harada, M. Katayama, *Makromol. Chem.*, 1966, **90**, 177-86. <https://doi.org/10.1002/macp.1966.020900117>
46. S. Harada, K. Arai, *Makromol. Chem.*, 1967, **107**, 64-67. <https://doi.org/10.1002/macp.1967.021070106>
47. S. A. Ali, S. Z. Ahmed, M. I. M. Wazeer, E. Z. Hamad, *Polymer*, 1997;**38**, 3385-3393. [https://doi.org/10.1016/S0032-3861\(96\)00893-2](https://doi.org/10.1016/S0032-3861(96)00893-2)
48. S. Kudaibergenov, W. Jaeger, A. Laschewsky, *Polymeric Betaines: Synthesis, Characterization, and Application*, *Adv. Polym. Sci.*, 2006, **201**, 157-224. [https://doi.org/10.1007/12\\_078](https://doi.org/10.1007/12_078)
49. Laschewsky, *Polymers*, 2014, **6**, 1544-1601. <https://doi.org/10.3390/polym6051544>
50. P. K. Singh, V. K. Singh and M. Singh, *e-Polymers*, 2007, **30**, 1-34. <https://doi.org/10.1515/epoly.2007.7.1.335>
51. G. B. Butler, *Acc. Chem. Res.* **1982**, *15*, 370-378. <https://pubs.acs.org/doi/pdf/10.1021/ar00083a005>
52. D. H. Solomon, D. G. Hawthorne, *J. Macromol. Sci. Part C* **1976**, *15*, 143-164. <https://doi.org/10.1080/15321797608065777>

53. L. C. McCormick, *J. Polym. Sci., Part A, Polym. Chem.* **1996**, 34, 911-912.  
<https://doi.org/10.1021/ma9518520>
54. W. Jaeger, M. Hahn, C. Wandrey, Kinetics of dimethyl diallyl ammonium chloride polymerization, VCH-Verlagsgesellschaft, Weinheim, **1989**, pp. 239–247.
55. W. Jaeger, U. Gohlke, M. Hahn, C. Wandrey, K. Dietrich, *Acta Polym.* **1989**, 40, 161– 170.
56. C. Wandrey, J. Hernandez-Barajas, D. Hunkeler, *Adv. Polym. Sci.* **1999**, 145, 123– 182. [https://doi.org/10.1007/3-540-70733-6\\_31](https://doi.org/10.1007/3-540-70733-6_31)
57. C. Wandrey, W. Jaeger, G. Reinisch, M. Hahn, G. Engelhard, H. Jancke, D. Ballschuh, *Acta Polym.* **1981**, 32, 177–179.  
<https://doi.org/10.1002/actp.1981.010320310>.
58. S. A. Ali, Z. A. Jamiu, *Polym. Bull.* **2016**, 73, 2179–2198.  
[DOI 10.1007/s00289-016-1602-x](https://doi.org/10.1007/s00289-016-1602-x).
59. F. Rullens, M. Devillers, A. Laschewsky, *Macromol. Chem. Phys.* **2004**, 205, 1155– 1166. <https://doi.org/10.1002/macp.200400081>.
60. Y. Yaagoob, H. A. Al-Muallem, S. A. Ali, *RSC Adv.* **2017**, 7, 31641–31653.  
<https://doi.org/10.1039/C7RA04418F>.
61. B. Lowe, C. L. McCormick, *Chem. Rev.* **2002**, 102, 4177-4189  
<https://doi.org/10.1021/cr020371t>.
62. S. Kudaibergenov, W. Jaeger, A. Laschewsky, *Adv. Polym. Sci.* **2006**, 201, 157–224,  
[DOI.10.1007/120\\_78](https://doi.org/10.1007/120_78).
63. P. G. Higgs, J. F. Joanny, *J. Chem. Phys.* **1991**, 94, 1543-1554.  
<https://doi.org/10.1063/1.460012>.

- A. V. Dobrynin, M. Rubinstein, *J. Phys. II* **1995**, 5, 677-695.  
<https://doi.org/10.1051/jp2:1995157>.
64. J. C. Salamone, W. Volksen, A. P. Olson, S. C. Israel, *Polymer* **1978**, 19, 1157-1162.  
[https://doi.org/10.1016/0032-3861\(78\)90064-2](https://doi.org/10.1016/0032-3861(78)90064-2).
65. D. N. Schultz, D. G. Peiffer, P. K. Agarwal, J. Larabee, J. J. Kaladas, L. Soni,  
*Polymer* **1986**, 27, 1734-1742. [https://doi.org/10.1016/0032-3861\(86\)90269-7](https://doi.org/10.1016/0032-3861(86)90269-7)
66. J. C. Salamone, W. Volksen, S. C. Israel, A. P. Olson, D. C. Raia, *Polymer* **1977**, 18,  
 1058-1062. [https://doi.org/10.1016/0032-3861\(77\)90013-1](https://doi.org/10.1016/0032-3861(77)90013-1).
67. V. M. S. Monroy, J. C. Galin, *Polymer* **1984**, 25, 254-262.  
[https://doi.org/10.1016/0032-3861\(84\)90334-3](https://doi.org/10.1016/0032-3861(84)90334-3).
68. J. Mosa, N. C. Rosero-Navarro, M. Aparicio, Active corrosion inhibitor of mild steel  
 by environmentally – friendly Ce-doped organic-inorganic sol-gel coatings, RSC  
 Adv. 6 (2016) 39577 –39586. <https://doi.org/10.1039/C5RA26094A>.
69. P. Mourya, S. Banerjee, R. B. Rastogi, M. M. Singh, The inhibition of mild steel  
 corrosion in hydrochloric acid and sulfuric acid media using thiosemicarbazone  
 derivative, Ind. Eng. Chem. Res. 52 (36) (2013) 12733 – 12747.  
<https://doi.org/10.1021/ie4012497>.
70. M. A. Kiani, M. F. Mousavi, S. Ghasemi, M. Shamsipur, S. H. Kazemi, Inhibitory  
 effect of some amino acids on corrosion of Pb–Ca–Sn alloy in sulfuric acid solution,  
 Corros. Sci. 50 (2008) 1035-1045. <https://doi.org/10.1016/j.corsci.2007.11.031>.
71. W. Revie, H. H. Uhlig, Corrosion and Corrosion Control: An Introduction to  
 Corrosion Science and Engineering, Wiley-Inter science, NY, USA, (2008).

<https://books.google.com.sa/books?hl=en&lr=&id=HJHMhOgrEiwC&oi=fnd&pg=PR5&dq=W>.

72. C. Verma, L.O. Olasunkanmi, E. E. Ebenso, M. A. Quraishi, I. B. Obot, Adsorption behavior of glucosamine-based, pyrimidine-fused heterocycles as green corrosion inhibitors for mild steel: experimental and theoretical studies, *J. Phys. Chem. C* 120 (2016) 11598 –11611. <https://doi.org/10.1021/acs.jpcc.6b04429>.
73. H. Zhao, X. Zhang, L. Ji, H. Hud, Q. Li, Quantitative structure –activity relationship model for amino acids as corrosion inhibitors based on the support vector machine and molecular design, *Corros. Sci.* 83 (2014) 261 –271. <https://doi.org/10.1016/j.corsci.2014.02.023>.
74. D-Q. Zhang, Q-R. Cai, X-M. He, L-X. Gao, G. S. Kim, Corrosion inhibition and adsorption behavior of methionine on copper in HCl and synergistic effect of zinc ions, *Mater. Chem. Phys.* 114 (2009) 612-617. <https://doi.org/10.1016/j.matchemphys.2008.10.007>.
75. H. Ashassi-Sorkhabia, M. R. Majidib, K. Seyyedi, Investigation of inhibition effect of some amino acids against steel corrosion in HCl solution, *Appl. Surf. Sci.* 225 (2004) 176 –185. <https://doi.org/10.1016/j.apsusc.2003.10.007>.
76. M. A. Amin, K. F. Khaled, Q. Mohsen, H. A. Arida, A study of the inhibition of iron corrosion in HCl solutions by some amino acids, *Corros. Sci.* 52 (2010) 1684–1695. <https://doi.org/10.1016/j.corsci.2010.01.019>.
77. G. Markevicius, S. Chaudhuri, C. Bajracharya, R. Rastogi, J. Xiao, C. Burnett, T. Q. Chastek, Polyoligomeric silsesquioxane (POSS)- hydrogenated polybutadiene

- polyurethane coatings for corrosion inhibition of AA2024, *Prog. Org. Coat.* 75 (2012) 319–327. <https://doi.org/10.1016/j.porgcoat.2012.08.001>.
78. S. Kumar, H. Vashisht, L. O. Olasunkanmi, I. Bahadur, H. Verma, M. Goyal, G. Singh, E. E. Ebenso, Polyurethane based triblock copolymers as corrosion inhibitors for mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>, *Ind. Eng. Chem. Res.* 56 (2017) 441–456. <https://doi.org/10.1021/acs.iecr.6b03928>.
79. R. Baskar, M. Gopiraman, D. Kesavan, K. Subramanian, Gopalakrishnan, S. Gopalakrishnan, Utilization of photo-cross-linkable polymer for mild steel corrosion inhibition in 1.0 M HCl medium. *J. Mater. Eng. Perform.* 24 (2015) 2847–2856. [DOI: 10.1007/s11665-015-1492-3](https://doi.org/10.1007/s11665-015-1492-3).
80. P. Kittisupakorn, P. Thitiyasook, M. A. Hussain, W. Daosud, *J. Process Control* 2009, 19, 579–590. <https://doi.org/10.1016/j.jprocont.2008.09.003>.
81. J. Curtis, L. Kalfayan, Improving wellbore and formation cleaning efficiencies with environmental solvents and pickling solutions, SPE, Latin American and Caribbean Petroleum Engineering Conference, OnePetro, 2003. <https://doi.org/10.2118/81138-MS>.
82. B. B. Tiu, R. C. Advincula, *React. Funct. Polym.* 2015, 95, 25–45. <https://doi.org/10.1016/j.reactfunctpolym.2015.08.006>.
83. C. Verma, M. Quraishi, K. Y. Rhee, *J. Mol. Liq.* 2021, 24, 118387. <https://doi.org/10.1039/D2NJ05978A>.
84. R. Ganjoo, C. Verma, A. Kumar, M. Quraishi, *Adv. Colloid Interface Sci.* 2023, 311, 102832. <https://doi.org/10.1016/j.cis.2022.102832>.

85. Singh A, Quraishi MA. Acidizing corrosion inhibitors: a review. J Mater Environ Sci 2015; 6:224–35. [https://www.jmaterenvironsci.com/Document/vol6/vol6\\_N1/28-JMES-564-2014](https://www.jmaterenvironsci.com/Document/vol6/vol6_N1/28-JMES-564-2014).
86. Singh A, Ansari K, Quraishi M, Lgaz H, Lin Y. Synthesis, and investigation of pyran derivatives as acidizing corrosion inhibitors for N80 steel in hydrochloric acid: theoretical and experimental approaches. J Alloy Compd 2018; 762:347–62. <https://doi.org/10.1016/j.jallcom.2018.05.236>.
87. Farag AA, Mohamed EA, Sayed GH, Anwer KE. Experimental/computational assessments of API steel in 6M H<sub>2</sub>SO<sub>4</sub> medium containing novel pyridine derivatives as corrosion inhibitors. J Mol Liq 2021;330:115705. <https://doi.org/10.1016/j.molliq.2021.115705>.
88. G. Koch, Cost of corrosion, Trends in oil and gas corrosion research and technologies, (2017) 3–30. <https://doi.org/10.1016/B978-0-08-101105-8.00001-2>.
89. Sait N, Aliouane N, Ait Ahmed N, Toukal L, Al-Noaimi M. Synergistic effect of potassium iodide on corrosion inhibition of copper by tetrakisphosphonic acid in hydrochloric acid solution. J Adhes Sci Technol 2022; 36:109–33. <https://doi.org/10.1080/01694243.2021.1916250>.
90. Khadom AA, Abd AN, Ahmed NA. Synergistic effect of iodide ions on the corrosion inhibition of mild steel in 1M HCl by cardaria draba leaf extract. Results Chem 2022; 4:100668. <https://doi.org/10.1016/j.rechem.2022.100668>.
91. Z. A. Jamiu, H. A. Al-Muallem, S.A. Ali, Aspartic acid in a new role: Synthesis and application of a pH-responsive cyclopolymer containing residues of the amino acid,

- React. Funct. Polym.**, 93, 120–129 (2015).  
<https://doi.org/10.1016/j.reactfunctpolym.2015.06.006>.
92. S.A. Ali, O.C.S. Al Hamouz, N.M. Hassan, Novel cross-linked polymers having pH-responsive amino acid residues for the removal of  $\text{Cu}^{2+}$  from aqueous solution at low concentrations, *J. Hazard. Mater.* 248–249 (2013) 47–58,  
<https://doi.org/10.1016/j.jhazmat.2012.12.052>.
93. H-S Byun, N. Zhong, R. Bittman, 6A-O-*p*-TOLUENESULFONYL- $\beta$ -CYCLODEXTRIN [ $\beta$ -Cyclodextrin, 6A-(4-methylbenzenesulfonate)] *Organic Syntheses*, Coll. Vol. 10, p.690 (2004); Vol. 77, p.225 (2000).  
<https://doi.org/10.15227/orgsyn.077.0225>.
94. S. A. Ali, S. A. Mubarak, I. Y. Yaagoob, Z. Arshad, M. A. J. Mazumder,  
*A sorbent containing pH-responsive chelating residues of aspartic and maleic acids for mitigation of toxic metal ions, cationic, and anionic dyes, RSC Advances*, 2022, 12, <https://doi.org/10.1039/d1ra09234k>.
95. H.A. Al-Muallem, M.A.J. Mazumder, M.K. Estaitie, S.A. Ali, A novel cyclopolymer containing residues of essential amino acid methionine: Synthesis and Application. *Iran Polym. J.* 24 (2015) 541–547. [DOI 10.1007/s13726-015-0344-1](https://doi.org/10.1007/s13726-015-0344-1).
96. Odewunmi NA, Mazumder MA, Ali SA. Tipping effect of tetra-alkylammonium on the potency of N-(6-(1H-benzo [d] imidazol-1-yl) hexyl)-N, N-dimethyldodecan-1-aminium bromide (BIDAB) as corrosion inhibitor of austenitic 304L stainless steel in oil and gas acidization: experimental and DFT approach. *J Mol Liq* 2022;360: 119431. <https://doi.org/10.1016/j.molliq.2022.119431>.

97. Chauhan DS, Quraishi MA, Mazumder MAJ, Ali SA, Aljeaban NA, Alharbi BG.  
Design and synthesis of a novel corrosion inhibitor embedded with quaternary ammonium, amide and amine motifs for protection of carbon steel in 1M HCl. J Mol Liq 2020; 317:113917. <https://doi.org/10.1016/j.molliq.2020.113917>.
98. O. C. S. Al Hamouz, S. A. Ali, Removal of heavy metal ions using a novel cross-linked polyphosphonate, Sep. Purif. Technol., 98, 94–101 (2012).  
<https://doi.org/10.1016/j.seppur.2012.07.019>.
99. O. C. S. Al Hamouz, S. A. Ali,  
*Novel Cross-linked Polyphosphonate for the Removal of Pb<sup>2+</sup> and Cu<sup>2+</sup> from Aqueous Solution,*
100. Ind. Eng. Chem. Res., 51, 14178–14187 (2012).  
<https://doi.org/10.1021/ie301231k>.
101. Pearson JF, Slifkin Ma. Spectrochim Acta part A 1977;28A;2403  
[https://doi.org/10.1016/0584-8539\(72\)80220-4](https://doi.org/10.1016/0584-8539(72)80220-4)
102. X. Cao, G. Fischer, Conformational and Infrared Spectral Studies of L-Methionine and Its N-Deuterated Isotopomer as Isolated Zwitterions, J. Phys. Chem. A2002,106,41-50, 10.1021/jp012908x  
<https://doi.org/10.1021/jp012908x>.
103. S. A. Ali, I. Y. Yaagoob, A. A. Al-Taq, H. A. Al-Muallem, M. A. J. Mazumder,  
*An antiscalant with chelating residues of amino acid glycine, Desalination*, 531, 2022, 115728, <https://doi.org/10.1016/j.desal.2022.115728>.
104. S. A. Ali, H.A. Al-Muallem, M.T. Saeed, S.U. Rahman, Hydrophobic-tailed bicycloisoxazolidines: a comparative study of the newly synthesized compounds on

- the inhibition of mild steel corrosion in hydrochloric and sulfuric acid media. *Corros. Sci.* 50 (3) (2008) 664–675, <https://doi.org/10.1016/j.corsci.2007.10.010>.
105. Frumkin, Electrocapillary curve of higher aliphatic acids and the state equation of the surface layer, *Z. Phys. Chem.* 116 (1) (1925) 466–470, <https://doi.org/10.1515/zpch-1925-11629>.
106. M.A.J. Mazumder, H.A. Al-Muallem, M. Faiz, S.A. Ali, Design and synthesis of a novel class of inhibitors for mild steel corrosion in acidic and carbon dioxide-saturated saline media, *Corros. Sci.* 87, 187–198 (2014), <https://doi.org/10.1016/j.corsci.2014.06.026>.
107. Bockris JO'M, Khan SUM (1993) Surface electrochemistry: a molecular level approach. Plenum, New York, <https://www.amazon.com/Surface-Electrochemistry-Molecular-Level-Approach/dp/0306443392>.
108. S. A. Ali, H. A. Al-Muallem S. U. Rahman, M. T. Saeed, Bis-Isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic media, *Corros. Sci.* 50 (11)3070-3078 (2008), <https://doi.org/10.1016/j.corsci.2008.08.011>.
109. Duan SZ, Tao YL (1990) Interface chemistry, Higher Education Press, Beijing, China <https://doi.org/10.3390/molecules170910614>.
110. S.A. Umoren, M.M. Solomon, S.A. Ali, H.D.M. Dafalla, Synthesis, characterization, and utilization of a diallylmethylamine-based cyclopolymer for corrosion mitigation in simulated acidizing environment, *Mater. Sci. Eng. C* 100 (2019) 897–914, <https://doi.org/10.1016/j.msec.2019.03.057>.
111. P. Han, C. Chen, W. Li, H. Yu, Y. Xu, L. Ma, Y. Zheng, Synergistic effect of mixing cationic and nonionic surfactants on corrosion inhibition of mild steel in HCl:

- experimental and theoretical investigations, *J. Colloid Interface Sci.* 516 (2018) 398–406, <https://doi.org/10.1016/j.jcis.2018.01.088>.
112. M. K. Aldahdooh, S. A. Ali, *Synthesis and application of a poly(bis-zwitterion) containing chelating motifs of N-(2-aminoethyl)iminodiacetic acid*, **European Polymer Journal** 141 (2020) 110071, <https://doi.org/10.1016/j.eurpolymj.2020.110071>.
113. Richardson, S. D., & Ternes, T. A. (2014). Water Analysis: Emerging Contaminants and Current Issues. *Analytical Chemistry*, 86(6), 2813–2848. <https://doi.org/10.1021/ac500508t>.
114. Schwarzenbach, R. P., Escher, B. I., Fenner, K., Hofstetter, T. B., Johnson, C. A., Von Gunten, U., & Wehrli, B. (2006). The Challenge of Micropollutants in Aquatic Systems. *Science*, 313(5790), 1072–1077. <https://doi.org/10.1126/SCIENCE.1127291>.
115. Gidwani, B., & Vyas, A. (2014). Synthesis, characterization and application of Epichlorohydrin- $\beta$ -cyclodextrin polymer. *Colloids and Surfaces B: Biointerfaces*, 114, 130–137. <https://doi.org/10.1016/J.COLSURFB.2013.09.035>.
116. Morin-Crini, N., & Crini, G. (2013). Environmental applications of water-insoluble  $\beta$ -cyclodextrin–epichlorohydrin polymers. *Progress in Polymer Science*, 38(2), 344–368. <https://doi.org/10.1016/J.PROGPOLYMSCI.2012.06.005>.
117. V.A. Santhi, N. Sakai, E.D. Ahmad, A.M. Mustafa, Occurrence of bisphenol A in surface water, drinking water and plasma from Malaysia with exposure assessment from consumption of drinking water, *Science of The Total Environment*, 427–428, 2012, 332–338, <https://doi.org/10.1016/j.scitotenv.2012.04.041>.

# **Resume**

Of

## **Sabri Saghieron Al-Shiekh Abdelkreem**

**Nationality** : [ Sudanese ]

**Date of Birth** : [1/1/1994]

**Email** : [ [sabrisig118@gmail.com](mailto:sabrisig118@gmail.com) ]

**Address:** [P.O. Box 11111 /Khartoum, Sudan /phone +24903220305 ]

### **Education:**

October 2014-November 2020 : B.Sc (Hons) Chemistry, University of Khartoum, Sudan

### **Experience:**

- At present Research Assistant at King Fahd University of petroleum and minerals
- Determination of concentration of Gold by Atomic absorption spectroscopy( AAS) and titration, gold shining company, Niger.
- Determination of concentration of gold by using AAS, Noosh mining for Waste treatment and gold extraction, Sudan
- Determination of concentration of gold in geological samples with titration, Sudan.

### **Publication:**

Sabri S. A. Abdelkreem, Sk. Asrof Ali “Synthesis and application of polymers containing biogenic motifs of methionine and  $\beta$ -cyclodextrin to mitigate toxic contaminants”(Manuscript under Preparation).