

**BIO-INSPIRED pH-RESPONSIVE
POLYELECTROLYTES CONTAINING MOTIFS
OF CATECHOL AND BETA-CYCLODEXTRIN:
SYNTHESIS AND APPLICATION**

BY

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A Dissertation Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

ORGANIC CHEMISTRY

MAY 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

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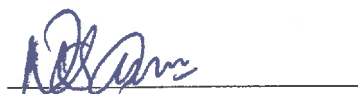
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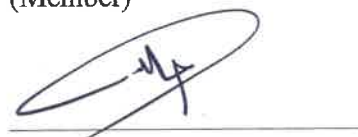
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ORGANIC CHEMISTRY

May 2024

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2024

**Dedicated to my Wife (Nausheen Zeeshan), Beloved
Kids (Haniyyah Zeeshan, Mohammed Ismayl),
Parents and Siblings**

ACKNOWLEDGMENTS

All praise belongs to Allah, lord of all that exists in the world, who blessed me with the courage to complete my Ph.D. All the praises for Him, the Merciful, Kind, Beneficent. After that, All the prodigious esteem for the greatest leader of the world, the messenger of Almighty Allah, our Holy Prophet Hazrat Muhammad (PBUH), the benefactor of humanity empowered mankind to know the creator and to comprehend the way of life.

I would like to express my sincere gratitude to my supervisor Dr. Shaikh Asrof Ali, for the continuous support of my course work and research, for his enthusiasm, patience, insightful comments, helpful information, practical advice, and unceasing ideas that have always helped me tremendously in my research and writing of this thesis. His immense knowledge, profound experience and professional expertise in polymer science has enabled me to complete this research successfully. Without his support and guidance, this work would not have been possible. I could not have imagined having a better supervisor in my Ph.D.

I would also like to thank my committee members Dr. Khalid R. Alhooshani, Dr. Nisar Ullah, Dr. M. Jafar Mazumder, and Dr. Hassan Al-Muallem for their valuable comments, suggestions, and feedback to improve my thesis work.

I am greatly thankful to the King Fahd University of Petroleum and Minerals (KFUPM) for supporting my Ph.D. by providing a fully funded scholarship. I also wish to express my sincere thanks to Dr. Jameel R. Al-Thagfi (Chairman of Chemistry) for providing me excellent learning and research environment at KFUPM. I would like to acknowledge all

the faculty members who improved my Chemistry knowledge. I would like to acknowledge Dr. Nadeem Baig from IRC-MWS, KFUPM for his collaborative work in one of my thesis works. I would like to thank my lab mentor Dr. M. Ibrahim Y. Yaagoob and lab members Lipiar Khan Goni, Sabri Abdelkreem, Khaled Ossoss, Hamza Jasim for the stimulating discussions, and cooperative support during lab work. My special thanks to M. Arif Baba and MJ Baylon for being very helpful and cooperative during my work in the department. I am grateful to entire staff of Department of Chemistry KFUPM, Mansour Al-Zaki, Sowrirajan, Mohammed Al-Ghushairy Mohammad Sebaa, Malak Al-Khaldi Abdul Nasir, Nadir Osman, Abdullah Alsubaie and M. Luquman for their help and services. I would like to thank Pakistani community in KFUPM for their help and support during this journey.

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ABSTRACT

Full Name : [Zeeshan Arshad]

Thesis Title : [Bio-inspired pH-responsive polyelectrolytes containing motifs of catechol and Beta-cyclodextrin: synthesis and application]

Major Field : [Chemistry]

Date of Degree : [May 2024]

A series of copolymers containing bio-inspired catechol and Beta-cyclodextrin (β -CD) motifs as backbone pendants using Butler's cyclopolymerization protocol involving diallyl amine salts $[(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)\text{N}^+\text{R}^1\text{R}^2 \text{X}^-]$ has been synthesized for the first time to use in various applications. The identification of the basic design principles employed by common marine organisms such as *mussels* and then translate key functional group to synthetic systems has been carried out. Dopamine hydrochloride was converted to monomer *N,N*-diallyldopamine hydrochloride [(3,4-(HO)₂C₆H₄CH₂CH₂NH⁺(CH₂CH=CH₂)₂ Cl⁻) (I), while its copolymerization and terpolymerization with other monomers gave respective alternate copolymers and terpolymers. Solution properties of synthesized polymers including viscosity have been examined. Bio-inspired polymers were demonstrated as acidic corrosion inhibitors for mild steel and shown improved separation efficiencies and anti-fouling characteristics for the membrane, while treating the oil-in-water emulsions.

A diallyl amine salt monomer bearing β -CD substituent has been cyclopolymerized for the first time. Thus, 6-O-toluenesulfonyl- β -cyclodextrin -[(C₆H₁₀O₅)₆-(C₅H₇)]-CH₂OTs upon reaction with diallylamine followed by protonation afforded diallylamine salt

monomer $-(\text{C}_6\text{H}_{10}\text{O}_5)_6-(\text{C}_5\text{H}_7)]-\text{CH}_2\text{NH}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2 \text{Cl}^-$ (**I**). Cyclopolymerization of monomer **I** and its copolymerization with monomers $[\text{Me}_2\text{N}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2 \text{Cl}^-]$ (**II**) or $[\text{O}_2\text{CCH}_2\text{NH}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2]$ (**III**) or $[\text{H}_2\text{O}_3\text{PCH}_2\text{NH}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2 \text{Cl}^-]$ (**IV**) or $[\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{NH}^+(\text{CH}_2\text{CH}=\text{CH}_2)_2 \text{Cl}^-]$ (**V**) gave a series of copolymers having residues of β -CD and glycine or methyl phosphonate or aspartic acid. Terpolymerization in the presence of SO_2 afforded polymers with alternate placement of the SO_2 units. Solution properties of the pH-responsive polyelectrolytes including viscosity have been examined. Water-insoluble terpolymer **I/V/SO₂** having 20 mol% β -CD residues has been shown to remove organic micropollutant 2-naphthol by host/guest complexation. This work paved the way to synthesize cross-linked polymers for water treatment application. The synthesized cross-linked resin demonstrated simultaneous removal of polyaromatic hydrocarbons (encapsulation by β -CD) and toxic metal ions (by complexing with chelating ligands of glycine, aspartic acid, aminomethyl phosphonate) from contaminated aqueous bodies.

ملخص الرسالة

الاسم الكامل: زيشان أرشد

عنوان الرسالة: إلكترونيات متعددة مستوحاة من الحيوية المستجيبة للأس الهيدروجيني تحتوي على زخارف من الكاتيول وبيتا سيكلودكسترين: التوليف والتطبيق

التخصص: كيمياء

تاريخ الدرجة العلمية: مايو 2024

تم تصنيع سلسلة من البوليمرات الثنائية التي تحتوي على زخارف الكاتيول المستوحاة من الحياة وزخارف بيتا سيكلودكسترين (بيتا س د) كمعلقات أساسية باستخدام بروتوكول بلمرة حلقيّة بتلر الذي يشتمل على أملاح ثنائي الأليل أمين $[-(H_2C=CH-CH_2)N^+R^1R^2 X^-]$ لأول مرة من أجل إستخدامها في مختلف التطبيقات. تم تحديد مبادئ التصميم الأساسية التي تستخدمها الكائنات البحرية الشائعة مثل بلح البحر ثم ترجمة المجموعات الوظيفية الرئيسية إلى أنظمة اصطناعية. تم تحويل هيدروكلوريد دوبامين إلى مونومر N,N -ثنائي أليل دوبامين هيدروكلوريد $[(3,4-$ إلى $(HO)_2C_6H_4CH_2CH_2NH^+(CH_2CH=CH_2)_2 Cl^-]$ (I) في حين أن البلمرة الثنائية والبلمرة الثلاثية مع المونومرات الأخرى أعطت بوليمرات ثنائية وبوليمرات ثلاثية متبادلة. خواص المحاليل للبوليمرات المصطنعة بما في ذلك اللزوجة تم فحصها. البوليمرات المستوحاة من المواد الحيوية برهنت كمثبطات للتآكل الحمضي للفولاذ الطري وأظهرت كفاءة فصل محسنة وخصائص مضادة للحشف للعشاء أثناء معالجة مستحلبات الزيت في الماء.

مونومر ملح ثنائي اليل أمين الذي يحمل بديل بيتا-س د تم بلمرته حلقياً لأول مرة. وهكذا، O-6-تولوين سلفونيل-بيتا-سيكلوديكسترين $[(C_6H_{10}O_5)_6-(C_5H_7)]-CH_2OTs$ عند التفاعل مع ثنائي اليل أمين متبوعاً بالبرتنة أعطت مونومر ملح ثنائي اليل أمين (I) $[(C_6H_{10}O_5)_6-(C_5H_7)]-CH_2NH^+(CH_2CH=CH_2)_2 Cl^-$. البلمرة الحلقيّة للمونومر I وبلمرته ثنائياً مع المونومرات (II) $[Me_2N^+(CH_2CH=CH_2)_2 Cl^-]$ أو $[-$ (III) $O_2CCH_2NH^+(CH_2CH=CH_2)_2]$ أو

(IV) $[H_2O_3PCH_2NH^+(CH_2CH=CH_2)_2 Cl^-]$ أو $[HO_2CCH_2CH(CO_2H)NH^+(CH_2CH=CH_2)_2]$ (V) أعطت سلسلة من البوليمرات الثنائية التي تحتوي على بقايا بيتا س د والجلاليسين أو فوسفونات الميثيل أو

حمض الأسبارتيك. البلمرة الثلاثية في وجود ثاني أكسيد الكبريت توفر بوليمرات مع وضع متبادل لوحداث ثاني أكسيد الكبريت. خصائص المحاليل الزيتية متعددة الأيونات المستحبة للأس الهيدروجيني، بالإضافة الي خاصية اللزوجة التي قد تم فحصها. البوليمر الثلاثي غير القابل للذوبان في الماء $I/V/SO_2$ الذي يحتوي على نسبة مولية 20% من بقايا بيتا س د قد تبين أنه يزيل الملوثات العضوية الميكرونية 2-نفثول بواسطة المركب المعقد المضيف/الضيف. هذا العمل مهد الطريق لإصطناع البوليمرات المترابطة لتطبيقات معالجة المياه. الراتنج المترابط المصطنع أظهر الإزالة المتزامنة للهيدروكربونات متعددة العطريات (المغلقة بواسطة بيتا س د) وأيونات المعادن السامة (عن طريق التعقيد باستخدام بروابط مخلبة من الجلايسين، وحمض الأسبارتيك، وفوسفونات أمينوميثيل) من الأجسام المائية الملوثة.

CHAPTER 1

INTRODUCTION

1.1 Bio-inspired polymers

Moisture-resistant adhesive proteins, secreted by holdfast of marine mussels, contain 1-28% of -L-alanine (L-DOPA), form strong adhesives on solid surfaces in the turbulent sea (Fig. 1.1) [1]. The presence of catecholic 3,4-dihydroxyphenyl functionality in the proteins is responsible for covalent interfacial interactions. This adhesive chemistry provided by marine mussels has become the inspiration to mimic in the chemistry laboratories. The DOPA-containing proteins have substantial amount of anionic phosphoserine residues that can form complex such as coacervates with other proteins having cationic 4-hydroxyarginine moieties. For wet adhesion, this phase-separated coacervates feature is crucial [2–4].

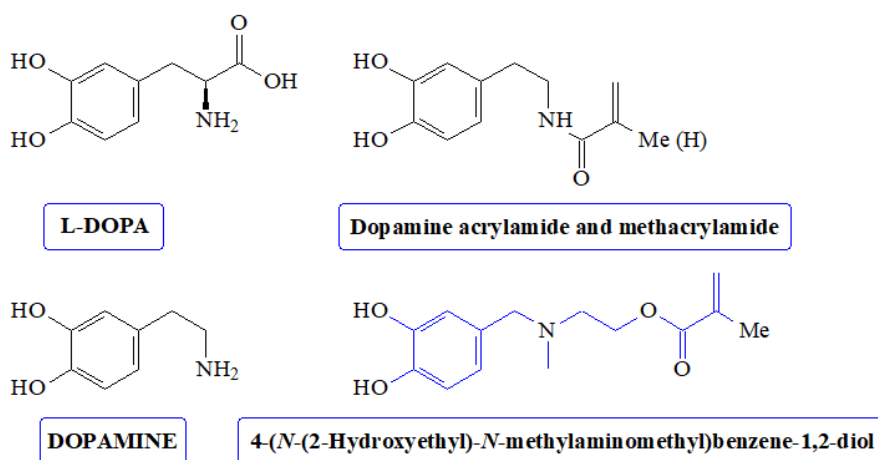


Figure 1.1. Chemical structure of L-DOPA, dopamine, methylacrylamide, and methacrylate monomers having residues of dopamine and catechol motifs

3,4-Dihydroxyphenethylamine, known as Dopamine (DA), a hormone and neurotransmitter, is commonly used in clinical medicine. DA possesses the vital functional motifs of catechol present in mussel's adhesive proteins. At pH value > 8.5 , the catechol groups are oxidized into the quinone form, which can react with amine and self-polymerize to polydopamine (PDA) that can adhere to various substrates [5]. DA [6] and 3,4-dihydroxystyrene [7] have been utilized to synthesize mussel mimetic adhesive polymers [4,8]. The catecholamines deposited on the surface of membranes led to their improved performance [9]. Cross-linking of polydopamine attached graphene oxide by polyethylenimine paved further the applications of graphene [10].

The biomimetic designs have been articulated in several reviews, which describe the incorporation of catechol moiety to use in different applications such as drug delivery and anti-biofouling due to its adhesive nature [11–13]. Researchers were attracted to imitate the adhesive chemistry used by the mussels. Synthesis of mussel-inspired biomimetic materials having catechol functionalities and their applications in fields such as underwater adhesives [14,15], coatings [14,16], biological adhesives [17], self-healing of hydrogels [18,19], anti-biofouling [20], have been reported. The mechanical strength of polymers having catechol has been shown to improve by coordinating with metal cations commonly found in seawater [19]. A Review articles describe the biomedical importance of mussel-inspired polymers and mechanism of wet adhesion [12,21]. Numerous biomimetic polymers bearing catechol or dopamine motifs have been synthesized via 2,2-azodiisobutyronitrile (AIBN)-initiated free radical polymerization. Copolymerization of methacrylate and polyethylene glycol (PEG)-methacrylate led to polymers with excellent coat ability on various surfaces [17]. Acrylic terpolymers bearing pendant catechol,

oligo(ethylene glycol), and perfluoroalkyl groups in varying ratios gave low-biofouling polymeric coatings [20]. Dopamine acrylamide and butyl acrylate monomers led to copolymers that can self-heal in seawater through hydrogen bonding and coordination [19]. The copolymer of 2-(methacryloyloxy) ethyl phosphonate and dopamine methacrylamide (DMA), having negative charges on the phosphonate, can form nanocomposite complex coacervate on positively aminated gelatin [22]. A copolymer of dopamine methacrylamide and 2-methoxyethyl acrylate has been shown to reduce failure of dental restorations due to saliva contamination [23]. A pH-Responsive molecularly imprinted polymer (MIP) hydrogel, to control the release of a drug, was synthesized by polymerization of dopamine acrylamide and acrylic acid [24]. Gecko adhesion, which allows the gecko to cling onto vertical and even inverted surfaces, is greatly diminished under wet conditions. A hybrid adhesive of gecko-mimetic and mussel-mimetic polymers (of dopamine methacrylamide (DMA) and methoxyethyl acrylate) is shown to maintain its adhesive performance in both dry and wet environments [4]. The polymers derived via acrylic monomers (*vide supra*) have the pendants of catechol or dopamine motifs linked to the polymer backbone via ester or amide linkage. However, the polymers derived via Butler's protocol will have the pendant dopamine attached to the polymer backbone by a robust N-C bond, which will not be susceptible to hydrolysis like the cases of ester and amide linkages (in proteins). Moreover, the dopamine will keep intact the original functionality of the basic amine in the polymer.

1.2 Polymers containing β -Cyclodextrin pendants

Cyclic oligosaccharide β -Cyclodextrin (β -CD), composed of seven glucopyranose units bonded by α -1,4 glycosidic linkage, takes the shape of a truncated cone where the apex is replaced by a plane parallel to the base (Fig.1.2) [25]. The secondary OH groups remain in the bigger cavity while the primary OH groups stay in the smaller cavity (Scheme 1, inset). U.S. FDA considers the cyclodextrin as safe [26,27]. β -CD, produced by enzymatic degradation of starch, has an inner lipophilic cavity having a diameter of 0.60-0.65 nm wrapped up by hydrophilic peripheral [27,28]. The hydrophilic nature of the exterior of cyclodextrin or its complexes imparts water-solubility and insolubility in typical organic solvents.

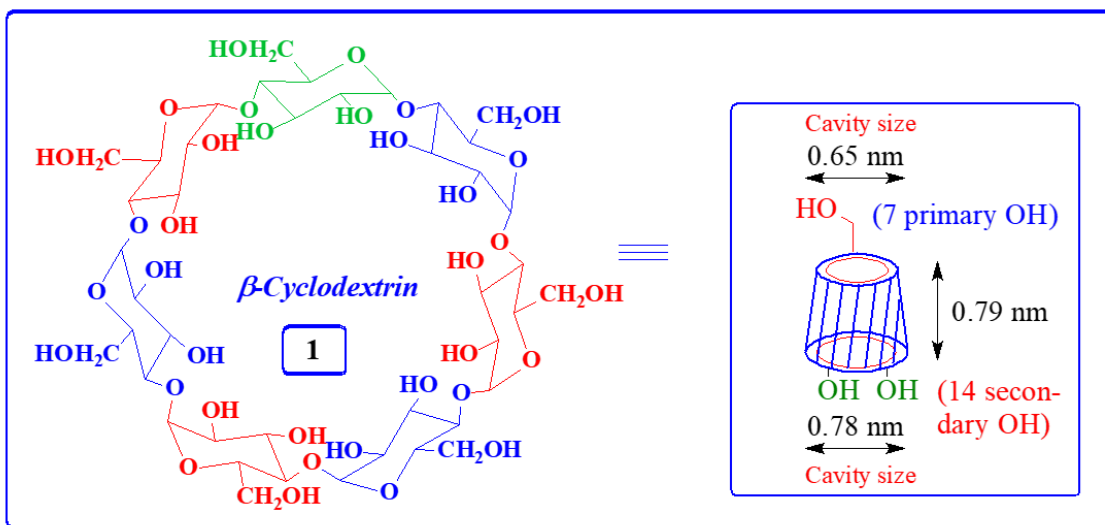


Figure 1.2. β -cyclodextrin structure and shape

Easy availability and applications in the fields of drug delivery, pharmaceutical industry, biosensors, tissue engineering, water treatment, etc. make β -CD an attractive natural material [25]. β -CD is used as a stationary phase in HPLC chromatography [29]. In drug

delivery, the cyclodextrins confer solubility and stability to a variety of hydrophobic drugs in the process of formation of inclusion compounds, which are then able to penetrate body tissues to deliver biologically active functional groups [30,31]. β -CD forms intramolecular H-bonds involving secondary OH groups owing to which it has poor water-solubility [32,33]. Each glucopyranose unit has sterically crowded two secondary OH groups, while the primary OH at C-6 faces less steric encumbrance. Chemical modification of cyclodextrins via methylation, tosylation, etc. helps to manipulate their host-guest behavior [30,34]. The water-soluble inclusion complexes were made by β -CD with cholesterol to manufacture cholesterol-free products. The cholesterol moiety (hydrophobic) does go into the interior of the cyclodextrin [35]. A book chapter describes the emerging usage of cyclodextrin systems in the food industry [36]. Host-guest inclusion complexes of β -CD with several vitamins have been explored [37]. The use of cyclodextrins primarily as a reliable and powerful mode of transport for drug delivery has been reviewed [38]. Crosslinked hydrogels of β -CD and poly β -CDs have been synthesized via reaction of -OH groups with -COOH, -COCl, epoxides, and -NCO [39–41]. Modification of hydroxyl groups of β -CD to accommodate vinyl motifs and their free radical polymerization (FRP) leads to poly(β -CDs) bearing CD motifs as pendants [42–44]. ‘Click’ reaction involving azide/alkyne cycloaddition has been explored for the probable formation of a thermoresponsive hydrogel [45]. The inner hydrophobic cavity of the β -CD in CD-based polymers can play host to numerous organic compounds [46]. The -OH of β -CD groups has been modified using common organic reagents [47]. A methyl methacrylate monoester of β -CD has been copolymerized with N-isopropyl acrylamide via FRP [48]. A bis-acrylate ester of β -CD

upon polymerization with acrylic acid and N-isopropyl acrylamide led to the formation of thermo and pH-responsive hydrogels [49].

1.3 Butler's cyclopolymerization protocol

Butler's cyclopolymerization protocol [50,51] using homo- [52] and co-cyclopolymerization [53–55] of *N,N*-diallyl quaternary ammonium salts led to numerous synthesis of industrially important polyelectrolytes [56–58] (Fig.1.3). This protocol leads to polymer backbone, embedded with pyrrolidine rings, known as the eighth most important polymer architecture [51,59]. Poly(diallyldimethylammonium chloride), documented in over 1000 patents and publications; is extensively used for water treatment [50]. The polymers from diallylamine salts $[(CH_2=CH-CH_2)_2NH^+R Cl^-]$, bearing pH-responsive nitrogens and functionalities (R), can be transformed to polyzwitterions (PZs) ($\pm$) [58,60,61]. The bio-mimicking polyampholytes (+ –) [62,63] and PZs [64] have found applications in various fields [65].

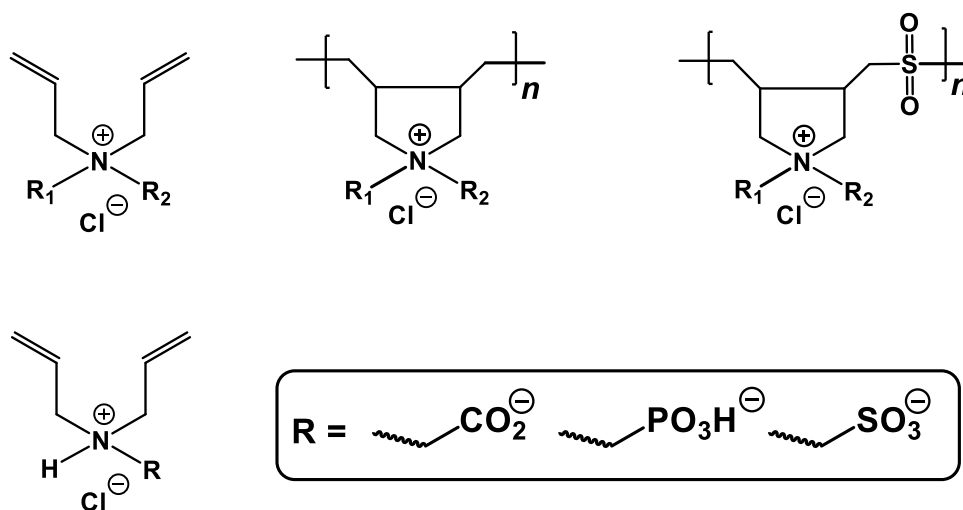


Figure 1.3. Diallylamine salt monomers and their polymers

1.4 Statement of the problem and objectives

The literature does not report any document describing the synthesis of polymeric materials containing bio-inspired catechol and β -cyclodextrin motifs using Butler's cyclopolymerization. Thus, the objective of the proposed project is the synthesis of a series of copolymers containing bio-inspired catechol and β -cyclodextrin motifs as backbone pendants using Butler's cyclopolymerization protocol for use in various applications.

Metal corrosion is an expensive process and industries using mild steel components lose billions of dollars each year. The presence of atoms like O, N, S, P in inhibitor molecules [66] impedes metal corrosion upon adsorption above metal surface doing so interfering with cathodic or anodic reactions causing corrosion loss [67–69]. Low carbon steel (LCS) is less expensive as such used in the constructions for mechanical parts, pipes [70,71] and several industrial processes in oil and gas sectors [72,73]. However, LCS is susceptible to undergo corrosion process over time [74,75]. During acid cleaning using concentrated acids (HCl, H₂SO₄), corrosion of LCS remains a major threat [76]. In acidizing application involving mostly used 15% HCl, heteroatom containing organic inhibitors are often used to minimize LCS corrosion [77,78]. Three benzimidazole derivatives imparted 89.5-96.4% inhibition of LCS corrosion [79,80]. Two benzimidazole derivatives were reported as a corrosion inhibitor for LCS in 1.0 M HCl solution [81]. Our objective is to use polymers containing catechol motifs to test in 15% solution of HCl by using weight loss methods to confirm the minimization of LCS corrosion.

Oily wastewater produced by petrochemical, oil and gas, food, and pharmaceutical industries has now become the most serious environmental challenge worldwide [82]. It is affecting ecology, the ecosystem, and human health negatively. Therefore, it is important to develop effective methods for the treatment of oily wastewater [83]. The membrane technology is considered the most effective for water-oil separation due to process simplicity and low cost. PVDF membranes have been used extensively for the treatment of oily wastewater but due to hydrophobic nature of these membranes, the membrane fouling blocks the pores caused by the attachment of hydrophobic solutes present in the waste during separation process. PVDF membrane can be modified to reduce the membrane fouling by fabricating with polymer that will enhance the hydrophilicity of the membrane. A terpolymer containing catechol motifs will be synthesized and incorporated into the membrane to enhance the antifouling and permeability properties of PVDF membranes.

Water resources are under threat owing to the presence of micropollutants (organic moieties in low concentration). A porous polymer based on cyclodextrins has been demonstrated to have a high affinity towards micropollutants resulting in high uptake of them [84]. A mesoporous polymer of high surface area having stiff aromatic groups has been generated by crosslinking β -CD [85]. The encapsulation and removal of micropollutants from the water via adsorption method have been reported for the polymer. Environmental toxicants such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) have been frequently found in contaminated water and have attracted great concerns in recent years due to their persistent toxicological risk to humans and wildlife. Recent studies have stated the occurrence of organic pollutants,

such as PAHs, and inorganic HMs in various aquatic systems such as influent and effluent from wastewater treatment plants, groundwater, surface waters or seawater. For removing both PAHs and HMs from water, a new adsorbent will be designed. A novel cross-linked resin will be synthesized, in which β -cyclodextrin and metal chelating motifs (aspartic acid and aminophosphonate) will be incorporated in a polymer network via Butler's cyclopolymerization.

The specific objective for this work is to synthesize several precursor molecules, monomers, their copolymers, terpolymers and cross-linked resin.

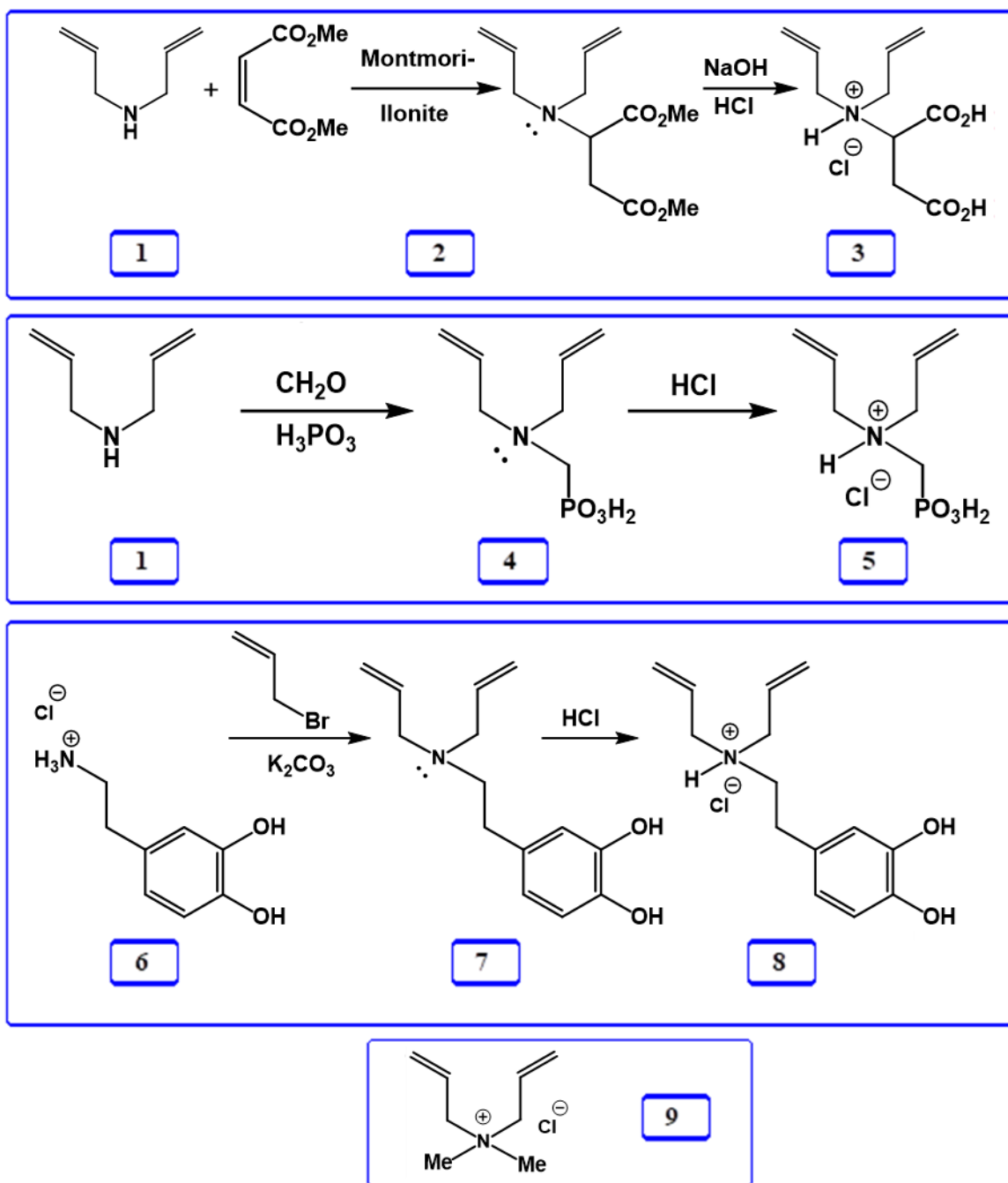
1. Synthesis of several diallyl amine salt monomers including the one containing catechol motifs.
2. Polymerization and copolymerization of the catechol-derived monomer with various diallyl amine salt monomers.
3. Co- and/or terpolymerization of catechol-derived monomer with SO_2 .
4. Synthesis of a diallyl salt monomer including containing β -cyclodextrin motifs as a substituent.
5. Polymerization and copolymerization of the β -cyclodextrin-derived monomer with various diallyl amine salt monomers.
6. Analysis of the synthesized polymers using NMR, IR, TGA, elemental analysis, viscosity, etc

7. Application of catechol-derived polymers for membrane surface modification and as inhibitor of mild steel corrosion.
8. Application of β -cyclodextrin-derived polymers for simultaneous trapping priority metal contaminants as well as organic contaminants.

1.5 General description and the work plan

1.5.1 Synthesis of monomers especially the one having catechol motifs

The synthesis of several monomers **3**, **5** and **8** is outlined in Scheme 1.1. The synthesis of monomer **3** will be achieved by reacting diallyl amine **1** with dimethyl maleate [86]. Diallylamine **1** upon treatment with formaldehyde in the presence of phosphorous acid will afford **4** which on acid treatment will be converted to monomer **5** [87]. Dopamine hydrochloride **6** upon dialylation followed by treatment with HCl gas is expected to generate new monomer **8**. Monomer **9** will be purchased from Sigma-Aldrich.

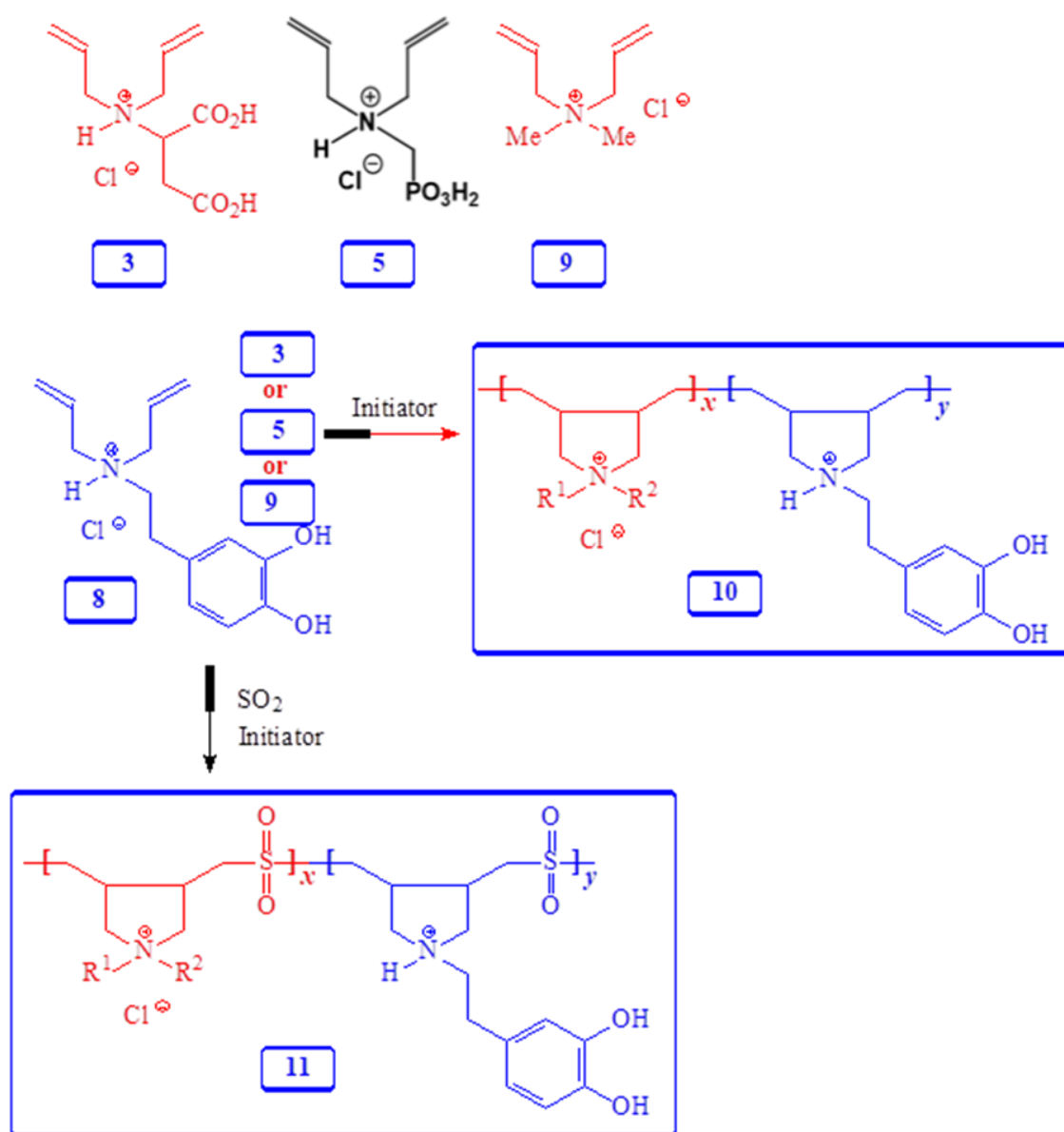


Scheme 1.1. Synthetic plan of monomers

The monomers **3** and/or **5** and/or **9** will be subjected to undergo copolymerization with **8** (in various proportions) and terpolymerization with SO_2 to give the polymer **10** and **11**, respectively (Scheme 1.2). The polymerization conditions will be varied to obtain

polymer with higher yields and viscosity. The polymer will be identified by the ^1H and ^{13}C NMR spectra.

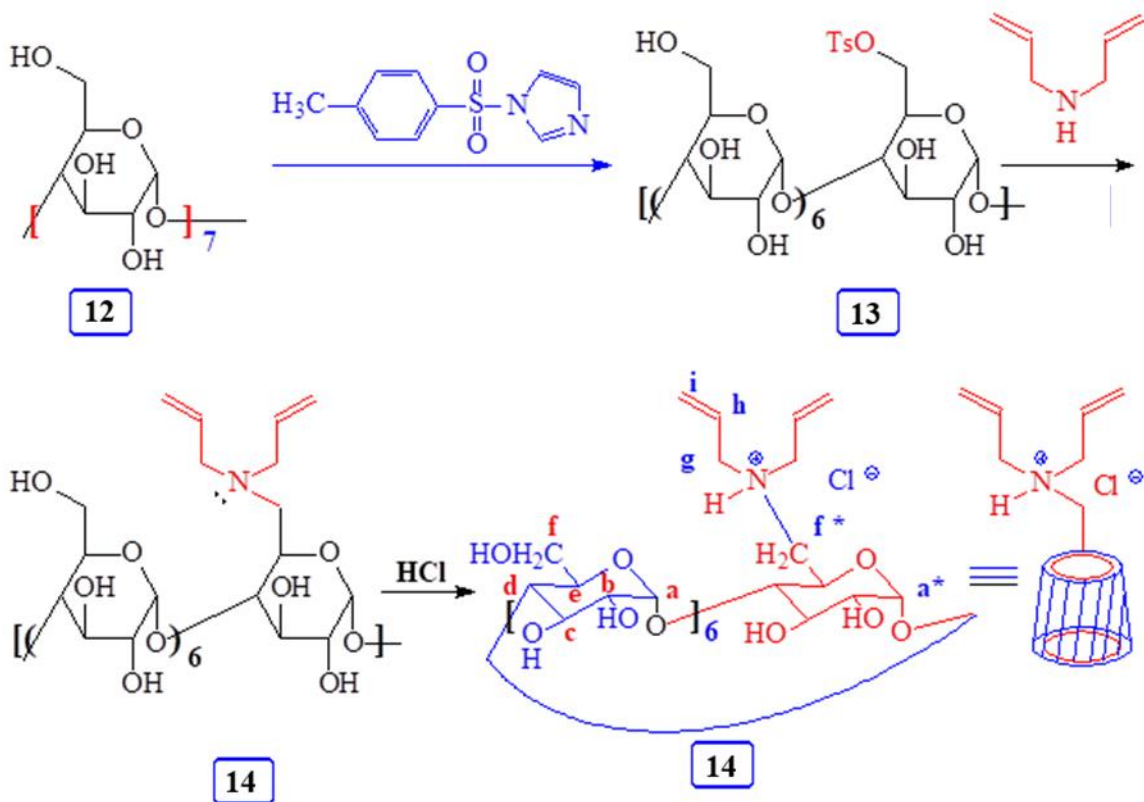
Polymerization reactions will be carried out using monomers and SO_2 in the presence of AIBN and ammonium persulfate [55,60,61]. The resultant polymers will be characterized using various physical techniques.



Scheme 1.2. Cyclopolymerization of **8** with various diallyl amine salt monomers

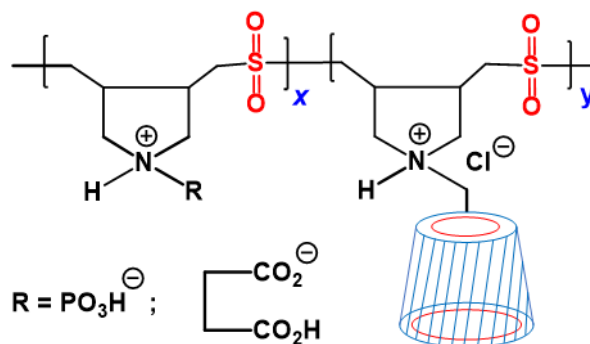
1.5.2. Synthesis of monomer having β -Cyclodextrin motifs

β -Cyclodextrin **12** upon selective tosylation [88] would lead to **13** which upon treatment with diallylamine followed HCl treatment is expected to give monomer **14** (Scheme 1.3).



Scheme 1.3. Synthesis of diallylamine salt containing β -cyclodextrin motifs

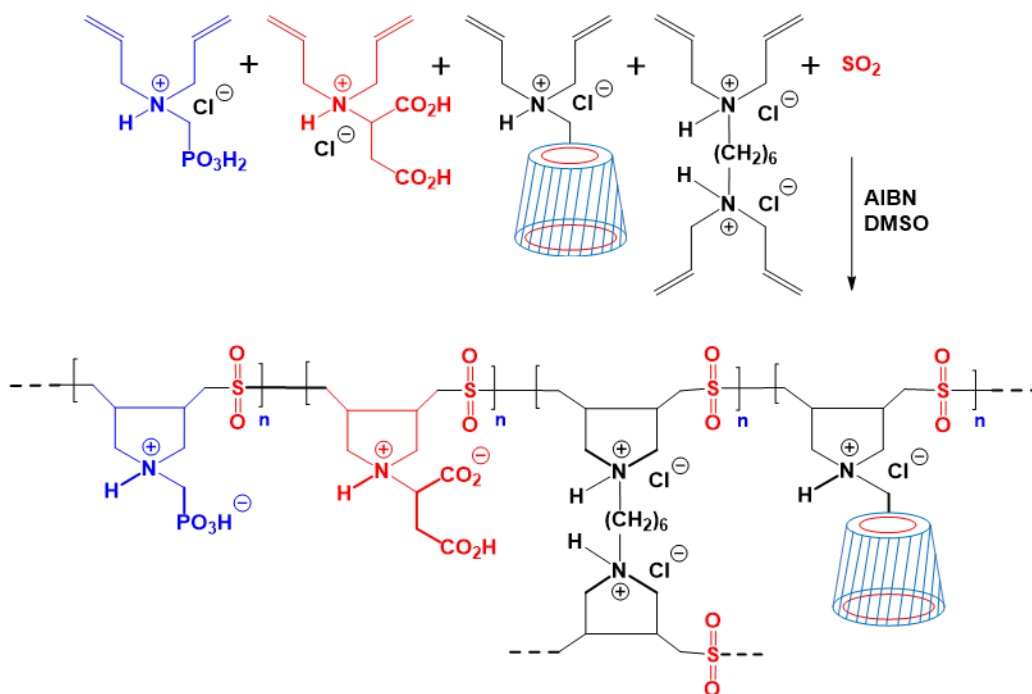
Diallylamine salts **3** and **5** will be cyclopolymerized with SO₂ and monomer **14** (Scheme 1. 4).



Scheme 1.4. Terpolymerization of **14** with **3** and **5**

1.5.3. Synthesis of cross-linked resin

A cross-linked polymer will be obtained by polymerizing **14**, and cross-linker to obtain a novel resin which could be used to capture and remove lethal metal ions and organic contaminants from wastewater (Scheme 1.5).



Scheme 1.5. Cross linked resin containing β -cyclodextrin motifs

1.5.4. Assessment of toxic metal ion and organic pollutant removal proficiency

Toxic metal removal efficiency [89,90] and removal of organic contaminants will be tested using known protocol in the literature [85,91].

CHAPTER 2

Synthesis and anticorrosive application of biomimetic dopamine-based cationic polyelectrolytes derived from diallylammonium salts

Taken from Zeeshan Arshad, Shaikh A. Ali, Synthesis and anticorrosive application of biomimetic dopamine-based cationic polyelectrolytes derived from diallylammonium salts, *Polymer*, 264 (2023), 125537

Abstract

Dopamine hydrochloride was converted to monomer *N,N*-diallyldopamine hydrochloride [(3,4-(HO)₂C₆H₄CH₂CH₂NH⁺(CH₂CH=CH₂)₂ Cl⁻] (**I**). Polymerization of diallyldimethylammonium chloride (**II**) monomer gave homocyclopolymer **III**, while its copolymerization with 5-20 mol% **I** afforded copolymers **IV**. Likewise, **II**/SO₂ copolymerization and **I**/**II**/SO₂ terpolymerization gave respective alternate copolymer **V** and terpolymers **VI**. At a concentration of 10 and 20 ppm **IV** (containing 20 mol% dopamine motifs) imparted respective 94.1 and 98% inhibitions of mild steel corrosion at 60 °C in 1 M HCl. Increasing mol% of dopamine motifs in **IV** resulted in increasing corrosion protection and demonstrated better efficiency than monomer **II** and its homopolymer **III**. Polymer **IV** at 20 ppm imparted inhibitions of 85.2%. in 15% HCl at 60 °C, while a mixture of 20 ppm **IV** and 400 ppm iodide ions provided synergistic

inhibition of 95.1%. Cationic polyelectrolyte **IV** has been shown to form polyelectrolyte complex/coacervate with three model anionic polyelectrolytes.

Keywords: Diallylamine salts; Polyelectrolyte complex; Coacervate; Mild steel corrosion; Dopamine; Cyclopolymerization

2.1. Introduction

Clasp of marine mussels release diverse moisture-reluctant sticking proteins, known as nature's water-resistant glue, having $\approx 1\text{--}28$ mol% 3,4-dihydroxyphenyl-L-alanine (L-DOPA) (Fig. 2.1), which twig swiftly and firmly to solid surfaces in the areas of turbulent sea [92] by virtue of covalent type strong interfacial interactions involving the catechol moieties (i.e., dihydroxyphenyl groups). The DOPA-containing proteins have substantial amount of anionic phosphoserine residues that can form complex such as coacervates with other proteins having cationic 4-hydroxyarginine moieties. For the wet adhesion, this phase-separated coacervates feature is crucial [2–4]. 3,4-Dihydroxyphenethylamine, known as Dopamine (DA), a hormone and neurotransmitter, is commonly used in clinical medicine. DA possesses the vital functional motifs of catechol present in mussel's adhesive proteins. At pH value > 8.5 , the catechol groups are oxidized into the quinone form, which can react with amine and self-polymerize to polydopamine (PDA) that can adhere to various substrates [10].

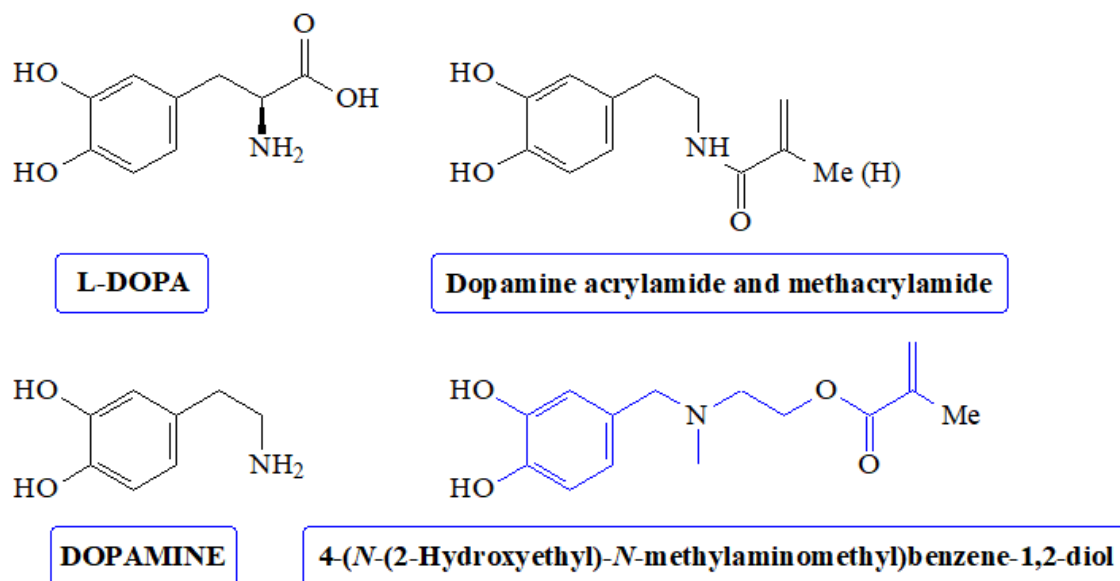


Figure 2.1. Chemical structure of L-DOPA, dopamine, methyl acrylamide, and methacrylate monomers having residues of dopamine and catechol motifs

Researchers were attracted to imitate the adhesive chemistry used by the mussels. Synthesis of mussel-inspired biomimetic materials having catechol functionalities and their applications in fields such as drug delivery [13], underwater adhesives [11,14,15], coatings [14,16], biological adhesives [17], self-healing of hydrogels [18,19], surface modification of membranes [9], and anti-biofouling [20] have been reported. The mechanical strength of polymers having catechol units has been shown to improve by coordinating with metal cations commonly found in seawater [19]. A Review article describe the biomedical importance of mussel-inspired polymers and mechanism of wet adhesion [12,21].

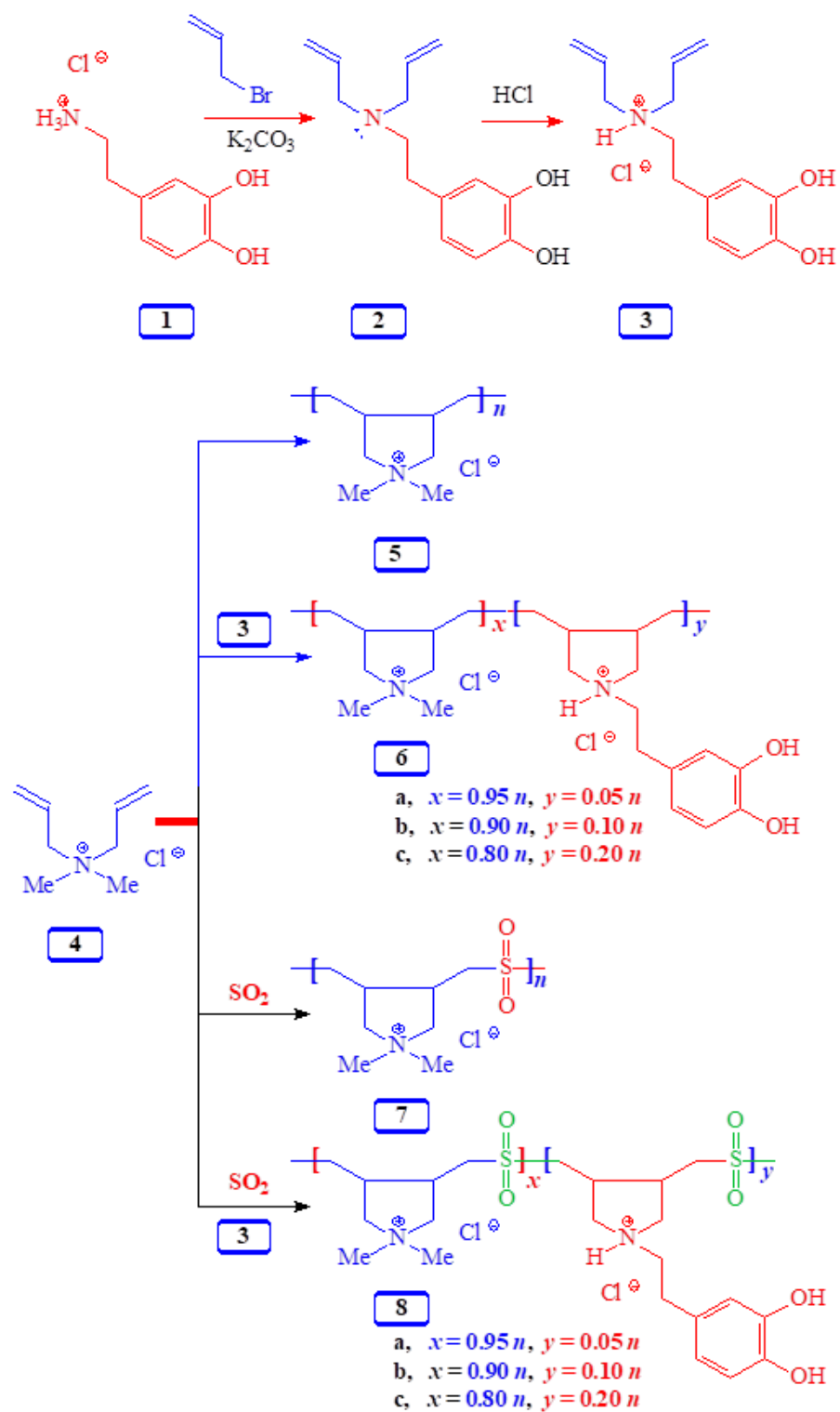
Numerous biomimetic polymers bearing catechol or dopamine motifs have been synthesized *via* 2,2-azobisisobutyronitrile (AIBN)-initiated radical polymerization of acryl-based monomers containing dopamine motifs (Fig. 2.1). Polymerization of a dopamine-derived methacrylate monomer and poly(ethylene glycol)-methacrylate

macromonomer led to copolymers with excellent coatability on various surfaces [16]. The polymers having catechol or dopamine motifs are shown to have strong adhesion in the wet environment [4,6–8] and low-biofouling property [20] on various surfaces. Dopamine acrylamide and n-butyl acrylate monomers led to copolymers that can self-heal in seawater through hydrogen bonding and coordination (Fig. 2.1) [19]. The copolymer of 2-(methacryloyloxy) ethyl phosphonate and dopamine methacrylamide, having negative charges on the phosphonate, can form nanocomposite complex coacervate on cationized gelatin [22]. A dopamine methacrylamide /2-methoxyethyl acrylate copolymer has been shown to reduce failure of dental restorations due to saliva contamination [23]. A pH-responsive hydrogel of dopamine acrylamide/acrylic acid copolymer has been used to control the release of a drug [24]. Gecko adhesion, which allows the gecko to cling onto vertical and even inverted surfaces, is greatly diminished under wet conditions. A hybrid adhesive of gecko-mimetic and mussel-mimetic polymers based on dopamine methacrylamide is shown to maintain its adhesive performance in both dry and wet environments [4].

The current work has three main objectives: (i) synthesis of a new class of water-soluble mussel-mimetic polymers via Butler’s cyclopolymerization protocol involving diallylamine salts having residues of dopamine, (ii) exploitation of catechol motifs’ chelation ability to mild steel surface to inhibit corrosion in acidic media, and (iii) use of Butler’s dopamine-containing cyclopolymers having cationic backbones to form polyelectrolyte complex/coacervate with some zwitterionic/anionic polyelectrolytes.

Butler’s cyclopolymerization protocol of *N,N*-diallyl quaternary ammonium salts $[H_2C=CHCH_2)_2N^+R^1R^2]$ led to the synthesis of numerous industrially important

polyelectrolytes [56–58,93]. We intend to synthesize a dopamine-derived monomer **3** and co-polymerize it using the cyclopolymerization protocol to obtain a series of homo- and co- and ter-polymers as outlined in Scheme 2.1. The polymers would then be used as corrosion inhibitors in well acidizing [76] and as a component to form technologically important polyelectrolyte complex/coacervate with zwitterionic/anionic polyelectrolytes [94–96].



Scheme 2.1. Synthesis of dopamine-derived monomer 3 and Cyclopolymerization of monomers 3, 4, and SO_2

2.2. Materials and Methods

2.2.1. Physical Methods

Elemental analyses were performed using a Perkin Elmer instrument (Model 2400). Thermogravimetric analyses (TGA) under N₂ were performed by an SDT analyzer (Q600: TA Instruments). The FTIR spectra (Transmittance mode) of the synthesized materials were recorded by a Thermo Scientific Nicolet iS10 spectrometer and are reported in wave numbers (cm⁻¹) (Spectral resolution, 4 cm⁻¹; number of scans, 64). An Ubbelohde viscometer having a Viscometer Constant of 0.005 cSt/s was utilized to perform viscosity measurements at 30.0±0.1 °C using a CT72/P water bath (SI Analytics, Germany). The bath contained an automatic viscoclock to record the time. Viscosity values were determined in triplicate having an error in time of < 0.2%. ¹H and ¹³C NMR spectra were recorded in a 400 MHz spectrometer (Bruker AvanceIII) using the residual D₂O protons (HOD) at δ 4.65 ppm, and ¹³C dioxane signal at δ 67.4 ppm as internal standards. For quantitative analysis, a pulse width of 14 μs for 90° pulse (hard pulse) with a power level of 9.9 watts and a delay time of 5 s was employed to make sure the full relaxation of ¹H NMR signals (which usually have a T₁ of 1 s). An Olympus optical microscope (SZX16), fitted with a SC-50 Q-Imaging Retiga EXi digital camera and Olympus cellSens Entry software, was used to take optical microscope images of polyelectrolyte complexes.

2.2.2. Materials

2,2'-Azobisisobutyronitrile (AIBN) ($\geq 98\%$) was purchased from Fluka Chemie AG and crystallized from chloroform-ethanol. Diallyldimethylammonium chloride, dopamine hydrochloride, Dimethylsulfoxide (DMSO) ($\geq 99.5\%$), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPD), allyl bromide, and Poly(4-styrenesulfonic acid) lithium salt (PSS) 9 solution (30 wt. % in H₂O) (MW 75000 g mol⁻¹) were purchased from sigma Aldrich. Zwitterionic 10 [97] and zwitterionic/anionic 11 [98] were prepared as described. All water used was of Milli-Q quality. A Spectra/Por (Spectrum Lab., Inc.) membrane (MWCO 3500 and 6000-8000) was used for dialyses.

2.2.3. Synthesis of *N,N*-diallyldopamine 2

To a stirred mixture of DA-HCl **1** (9.5 g, 50 mmol) in acetonitrile (200 mL) containing anhydrous K₂CO₃ (24.3 g, 175 mmol) was added dropwise (N₂) a solution of allyl bromide (12.7 g, 105 mmol) in acetonitrile (25 mL) at room temperature for 30 min. After stirring under N₂ at 50 °C overnight, the mixture was filtered while hot, and hot 1:1 MeOH/CH₃CN mixture (150 mL) was used to wash the solid residue. After removal of the solvent, the residue upon silica gel chromatography in a short column using ether followed by 9:1 MeOH/CH₃OH mixture as eluant to give diallyl dopamine **2** as a white solid (7.3 g, 63%) (Scheme 2.1). For analysis, a pure sample was prepared by crystallization from hot MeOH, mp 129-131 °C, (Found: C 71.8; H 8.1; N 5.9%. C₁₄H₁₉NO₂ requires C 72.07; H 8.21; N 6.00%); ν_{max} (KBr): 3283, 3076, 3015, 2933, 2852, 2712, 2562, 1750 (very broad), 1589, 1519, 1458, 1373, 1283, 1206, 1118, 1077, 935, 809, 674 and 584 cm⁻¹; δ_{H} (DMSO-d₆) 2.51 (4H, s), 3.09 (4H, d, *J* 6.3 Hz), 5.11

(4H, m), 5.80 (2H, m), 6.40 (1H, d, J 8.0 Hz), 6.54 (1H, s), 6.61 (1H, d, J 8.0 Hz) (Note that the residual DMSO- d_6 proton signal also appeared overlapping at δ 2.51 ppm); δ_C (DMSO- d_6) 31.89 (1C), 54.96 (1C), 56.11 (2C), 115.43 (1C), 116.00 (1C), 117.10 (2C, $\text{CH}=\underline{\text{C}}\text{H}_2$), 119.19 (1C), 131.24 (1C), 136.09 (2C, $\underline{\text{C}}\text{H}=\text{CH}_2$), 143.26 (1C), 144.97 (1C) (DMSO- d_6 middle C:39.51). DEPT 135 NMR spectrum was recorded to assign the ^{13}C signals. The compound was water-insoluble, slightly soluble in CHCl_3 but soluble in hot (45 °C) CH_3CN , MeOH, and DMSO.

2.2.4. Synthesis of N, N-diallyldopamine hydrochloride 3

To a stirred solution of *N, N*-diallyldopamine **2** (6.30 g, 27 mmol) in hot MeOH (20 mL) was added dropwise conc HCl (37 wt%) (3.94 g, 40 mmol). The solvent was removed, and monomer dried in vacuum to yield **3** as a white solid which was crystallized from MeOH/Et₂O (6.8 g, 93%). Mp 164-166 °C; (Found: C 62.1; H 7.6; N 5.1%. $\text{C}_{14}\text{H}_{20}\text{ClNO}_2$ requires C 62.33; H 7.47; N 5.19%). This monomer was soluble both in water and methanol. ν_{max} (KBr): 3342, 2938, 2818, 2743, 2642, 1604, 1519, 1453, 1353, 1270, 1179, 1112, 1056, 1000, 945, 870, 786, 664, and 609 cm^{-1} ; δ_H (D_2O) 2.78 (2H, t, J 7.8 Hz), 3.17 (2H, t, J 7.8 Hz), 3.64 (4H, d, J 7.2 Hz), 5.47 (4H, m), 5.75 (2H, m), 6.57 (1H, d, J 8.0 Hz), 6.65 (1H, s), 6.72 (1H, d, J 8.0 Hz) (residual HOD proton signal appeared at δ 4.65 ppm); δ_C (D_2O) 29.69 (1C), 53.67 (1C), 55.78 (2C), 117.32 (1C), 117.34 (1C), 121.93 (1C), 126.26 (2C, $\underline{\text{C}}\text{H}=\text{CH}_2$), 127.49 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 129.51 (1C), 144.00 (1C), 145.10 (1C), (dioxane: δ 67.4 ppm). DEPT 135 NMR spectrum was recorded to assign the ^{13}C signals.

2.2.5. Homopolymerization of diallyldimethylammonium chloride **4**

A solution of monomers **4** (1.62 g, 10 mmol) and AMPD (75 mg) in water (0.87 g) was heated at 65 °C in a closed flask under N₂ for 24 h. The reaction mixture becomes solidified within 4 h. Thereafter, upon dialysis against distilled water by using 3500 MWCO dialysis bag for 24 h and freeze-drying gave white solid of polymer **5** (1.4 g, 86%).

2.2.6. Copolymerization of diallyldimethylammonium chloride **4** and N, N-diallyldopamine hydrochloride **3**

2.2.6.1 Using monomers **4/3** in a 95:5 ratio

A solution of monomers **4** (1.54 g, 9.5 mmol), **3** (135 mg, 0.5 mmol), and AMPD (75 mg) in water (0.9 g) was heated in a closed flask under N₂ for 24 h at 65 °C. The reaction mixture becomes solidified within 4 h. Thereafter, upon dialysis against distilled water by using 3500 MWCO dialysis bag for 24 h and freeze-drying gave polymer **6a** as a white solid (1.4 g, 84%). (Found: C 59.2; H 9.9; N 8.0%. monomers **4** and **3** incorporated in a respective ratio of 95:5 requires C 59.67; H 9.77; N 8.38%).

2.2.6.2 Using monomers **4/3** in a 90:10 ratio

A solution of monomers **4** (1.46 g, 9.0 mmol), **3** (270 mg, 1.0 mmol), and AMPD (75 mg) in water (1.10 g) was heated (65 °C, 24 h) in a closed flask under N₂. The reaction mixture becomes viscous within 4 h. Thereafter, upon dialysis against distilled water by

using 3500 MWCO dialysis bag for 24 h and freeze-drying gave polymer **6b** as a white solid (1.54 g, 89%). (Found: C 58.9; H 9.7; N 7.7%. monomers **4** and **3** incorporated in a respective ratio of 90:10 requires C 59.89; H 9.58; N 8.12%). $\nu_{\max}$ (KBr): 3658, 3381, 3164, 2976, 2898, 2346, 1636, 1466, 1383, 1250, 1152, 1074, 955, 815, 648, and 536 cm^{-1} .

2.2.6.3 Using monomers **4/3** in a 80:20 ratio

A solution of monomers **4** (1.293 g, 8.0 mmol), **3** (541 mg, 2.0 mmol), and AMPD (100 mg) in water (987 mg) was heated (65 °C, 24 h) in a closed flask under N_2 for 24 h. The reaction mixture becomes viscous within 4 h. Thereafter, upon dialysis against distilled water by using 3500 MWCO dialysis bag for 24 h and freeze-drying gave polymer **6c** as a white solid (1.6 g, 87%). (Found: C 59.1; H 9.6; N 7.3%. monomers **4** and **3** incorporated in a respective ratio of 80:20 requires C 60.29; H 9.24; N 7.64%). $\nu_{\max}$ (KBr): 3650, 3388, 2967, 2574, 1622, 1462, 1376, 1259, 957, 809, 678, and 538 cm^{-1} .

2.2.7. Cyclopolymerization of **4** with SO_2

SO_2 (0.737 g, 11.5 mmol) was adsorbed on **4** (1.62 g, 10.0 mmol) in DMSO (2.8 g). After adding AIBN (100 mg), the mixture was heated under N_2 at 65 °C for 24 h. The resultant mixture was dialyzed against distilled water using 6000-8000 MWCO dialysis bag for 24 h and freeze dried to obtain white copolymer **7** (2.1 g, 93%).

2.2.8. Terpolymerization of monomers **3**, **4** and SO₂

2.2.8.1 Using monomers **4**/**3**/SO₂ in a 95:5:100 ratio

SO₂ (0.737 g, 11.5 mmol) was adsorbed on **4** (1.54 g, 9.5 mmol), **3** (135 mg, 0.5 mmol) in DMSO (2.8 g). After adding AIBN (100 mg), the mixture was heated under N₂ at 65 °C for 24 h. The resultant solidified mixture was dialyzed in distilled water using 6000-8000 MWCO dialysis bag for 24 h and freeze-dried to get white terpolymer **8a** as (2.15 g, 93%). (Found: C 42.0; H 7.2; N 5.8; S 13.0%. monomer **4**, **3** and SO₂ incorporated in a respective ratio of 95:5:100 requires C 43.13; H 7.06; N 6.06; S 13.87%). $\nu_{\max}$ (KBr): 3433, 3024, 2962, 2876, 1636, 1472, 1309, 1204, 1127, 948, 770, 660, and 515 cm⁻¹.

2.2.8.2 Using monomers **4**/**3**/SO₂ in a 90:10:100 ratio

SO₂ (0.737 g, 11.5 mmol) was adsorbed on a mixture of **4** (1.46 g, 9.0 mmol) and **3** (270 mg, 1.0 mmol) in DMSO (2.8 g). After adding AIBN (180 mg), the mixture was heated under N₂ at 65 °C for 24 h. The resultant solidified mixture was dialyzed in distilled water using 6000-8000 MWCO dialysis bag for 24 h and freeze-dried to obtain white solid of **8b** (2.23 g, 94%). [Note that the above polymerization does not proceed well in the presence of a smaller amount of AIBN (100 mg) for 5 h]. (Found: C 42.8; H 7.4; N 5.7; S 12.8%. monomer **4**, **3** and SO₂ incorporated in a respective ratio of 90:10:100 requires C 43.67; H 6.99; N 5.92; S 13.55%). $\nu_{\max}$ (KBr): 3458, 3027, 2911, 1637, 1529, 1473, 1410, 1309, 1127, 1041, 950, 869, 769, 660, and 510 cm⁻¹.

2.2.8.3 Using monomers 4/3/SO₂ in a 80:20:100 ratio

SO₂ (0.737 g, 11.5 mmol) was adsorbed on a mixture of **4** (1.29 g, 8.0 mmol), **3** (540 mg, 2.0 mmol) in DMSO (2.8 g). AIBN (180 mg) was added, and the mixture was heated under N₂ at 65 °C for 24 h. Thereafter, the solidified mixture was dialyzed against distilled water by 6000-8000 MWCO dialysis bag for 24 h and freeze-dried to obtain white solid of **8c** (2.32 g, 94%). (Found: C 43.2; H 7.1; N 5.4; S 12.0%. monomer **4**, **3** and SO₂ incorporated in a respective ratio 2853, 2705, 1631, 1528, 1470, 1408, 1305, 1195, 1127, 1037, 950, 872, 770, 658, and 517 cm⁻¹).

2.2.9. Corrosion inhibition of mild steel in 1 M and 15% HCl by polymers 5 and 6

Gravimetric weight-loss method [99] was utilized in 1 M HCl (250 mL) for a duration of 24 h at 60 °C by hanging mild steel coupons (2.5 × 2.0 × 0.1 cm³) having composition (wt%): C (0.082), Si (0.032), Ni (0.062), Mn (0.207), Cr (0.16), Al (0.045), Cu (0.029), W (0.042), Sn (0.048), Zn (0.017), Fe (≈ 99.3). For 15% HCl (250 mL) for a duration of 6 h at 60 °C, mild steel coupons of greater dimension (2.9 × 2.9 × 0.7 cm³) having composition (wt%): Fe (≈ 97.8), Mn (0.84), Si (0.39), C (0.33), Cr (0.16), Cu (0.15), Ni (0.075), Al (0.043), S (0.033), W (0.015), Co (0.014), Mo (0.03) were used. After scraping the coupons with grades of silicon carbide papers, the coupons were washed with acetone, dried with warm air, and kept in a desiccator. Concentrated HCl (37%) was diluted with distilled water to prepare the corrosive medium of 15% HCl. A stock solution (1000 ppm) of the polymers in 15% HCl was diluted with 15% HCl to obtain concentrations of 0.5–50 ppm.

The corrosion tests were run in triplicate. For similar size of the coupons, the %IE (% η) was calculated using **Eq. 2.1**, where W_{lb} and W_{li} are taken as the respective weight-loss in the uninhibited (blank) and polymer-inhibited solutions. In the cases of the significantly differing coupon-masses, % η was determined using relative weight-loss method [99].

$$\% \eta = \frac{W_{lb} - W_{li}}{W_{lb}} \times 100 \quad (2.1)$$

2.2.10. Polyelectrolyte complex

For coacervation of cationic polyelectrolyte **6c**, its 1 wt% aqueous solution was mixed with the 1 wt% aqueous solution of anionic/zwitterionic polyelectrolytes **9**, **10**, and **11** in equimolar quantity as described in **Table 2.1**. For instance, in entry 1, using repeating unit molar masses of **6c** and **9** as 183.3 and 190.3 g mol⁻¹, respectively, 1 mL solution of **9**- and 0.96-mL solution of **6c** were calculated to have the same 0.0526 mmol of anionic and cationic centers, respectively. After mixing, the solution was shaken for 20 min during which the mixture was separated into two layers, thereby leading to the formation of the CC (liquid-liquid phase separation), which was visualized by an optical microscope.

Table 2.1 Concentration (mL) of each PE used for coacervation

Entry	Polyelectrolyte A (mL)	Volume of 1.0 wt% Polyelectrolyte A (mL)	Volume of 1.0 wt% Polyelectrolyte B (6c) (mL)
1	9	1.0	0.96
2	10	1.0	0.68
3	11	1.0	0.61

2.3. Results & Discussion

2.3.1. Synthesis and characterization of monomer **3** and polymers **5-8**

Dopamine underwent dialkylation with allyl bromide to give *N, N*-diallyldopamine **2**, which upon treatment with HCl afforded monomer *N, N*-diallyldopamine hydrochloride **3** in 93% yield (**Scheme 2.1**). The current work represents the first example of a cyclocopolymerization involving diallylammonium salt containing dopamine motifs. The homopolymerization of monomer **4** and its copolymerization with **3** afforded cyclopolymers **5** and **6**, respectively, in well over 80% yields (**Scheme 2.1, Table 2.2**, entries 1-4). Monomers **4/3** feed ratios of 95:5, 90:10, and 80:20, led to respective copolymers **6a**, **6b**, and **6c**, in which the incorporated monomers were expected to match the feed ratios as expected for such high conversions to polymers. This was confirmed by calculating the monomer incorporation using area integrations of the aromatic protons versus the rest of the protons in the ^1H NMR spectra of the polymers. We observed that the presence of 20 mol% comonomer **3** (entry 4) necessitated the use of higher amount of

initiator AMPD, implying that the excessive presence of catechol motifs presumably inhibits the rate of polymerization. The copolymers are not block copolymers as suggested by the structure (**Scheme 2.1**), rather the monomers are randomly placed owing to the similar reactivities of the diallyl monomers **3** and **4**.

The **4**/SO₂ copolymerization and **3/4**/SO₂ terpolymerization afforded respective cyclopolymers **7** and **8** (**Scheme 2.1**, **Table 2.2**, entries 5-8) in excellent yields (93-94%). Diallylamine salt/SO₂ pair having reactivity ratios $r_1 \approx 0$, $r_2 \approx 0$ invariably lead to alternate placement of SO₂, while monomers **3** and **4** are randomly placed [100,101].

Table 2.2 Homo- and co-polymerization of monomers 3 and 4 and their co- and ter-polymerization with SO₂ at 65 °C for 24 h.

Entry	3 (mmol)	4 (mmol)	SO ₂ (mmol)	Solvent (g)	Initiator ^a (mg)	Yield ^b Polymer (%)	3/4 ratio in poly- mer ^c	Intrinsic Viscosity ^d (dL g ⁻¹)	$\overline{M}_v$ ^e & $\overline{M}_n$ ^f
1	–	10	–	Water (0.87)	AMPD (75)	5 (86)	–	0.787	28800 ^d
2	0.5	9.5	–	Water (0.90)	AMPD (75)	6a (84)	4:96	0.913	31260 ^d
3	1.0	9.0	–	Water (1.10)	AMPD (75)	6b (89)	8:92	0.501	14030 ^d
4	2.0	8.0	–	Water (0.98)	AMPD (100)	6c (87)	17:83	0.386	7850 ^d
5	–	10	11.5	DMSO (2.8)	AIBN (100)	7 (93)	–	0.297	11500 ^e
6	0.5	9.5	11.5	DMSO (2.8)	AIBN (100)	8a (93)	4:96	0.268	10800 ^e
7	1.0	9.0	11.5	DMSO (2.8)	AIBN (180)	8b (94)	8:92	0.199	9200 ^e
8	2.0	8.0	11.5	DMSO (2.8)	AIBN (180)	8c (94)	19:81	0.0898	6800 ^e

^aAMPD = 2,2'-azobis(2-methylpropionamidine) dihydrochloride, AIBN = 2,2'-Azobisisobutyronitrile.

^bYields (by gravimetry) are written under parentheses.

^cBy ¹H NMR spectroscopy.

^dViscosity of 1-0.125 % in 0.1 M NaCl at 30 °C.

^eViscosity average molar mass $\overline{M}_v$ was obtained using $[\eta] = 1.12 \times 10^{-4} \overline{M}_v^{0.82}$ [102], where $[\eta]$ was determined in 1 M NaCl at 30 °C and found to be 0.508, 0.543, 0.282, and 0.175 dL g⁻¹ for **5**, **6a**, **6b**, and **6c**, respectively.

^f $\overline{M}_n$ calculated by end group analysis.

The TGA curves for several polymers displayed in **Fig. 2.2**, reveal their stability up to ≈210 °C with an average 10% weight-loss attributed to the removal of moisture. For **5** and **6c**, two losses of 38% and 43% in the ranges 280-400 °C and 400-470 °C, can be

attributed to the loss of the parts of pyrrolidine rings. For **7** and **8c** a loss of 45% in the range of 240-325 °C does point toward the combined losses of SO₂ and ring pendants.

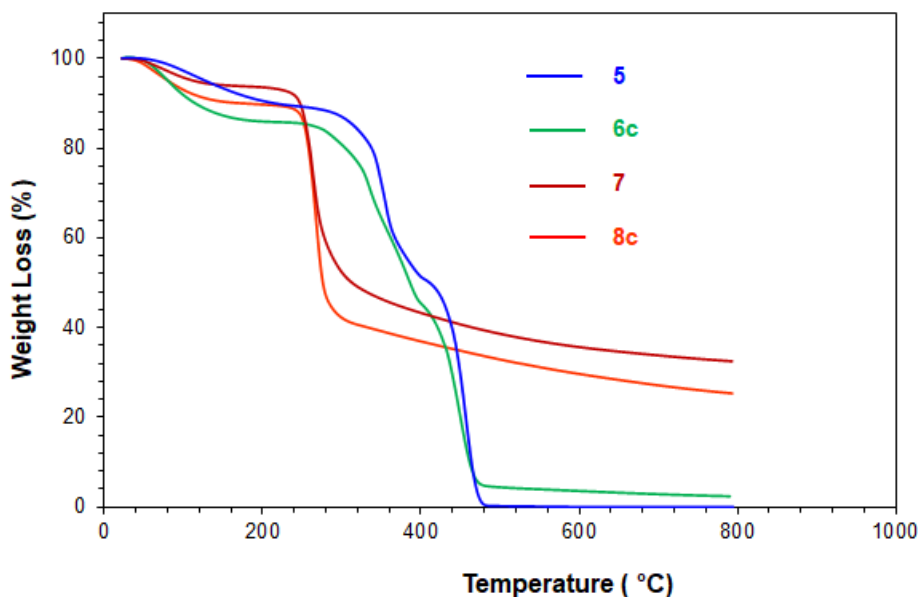


Figure 2.2. TGA curves of **5**, **PZ 6c**, **7**, and **PZM 8c**

FTIR spectrum of monomer **3** and monomer **3**-incorporated polymers showed an absorption at $\approx 950\text{ cm}^{-1}$ assigned to the aromatic ring stretch. The NH and phenolic OH vibrations appeared at $3650\text{--}3400\text{ cm}^{-1}$ range. Terpolymers **8a-c** showed strong IR bands at 1309 and 1127 cm^{-1} owing to the asymmetric and symmetric vibrations of SO₂ unit [103].

Figs. 2.3 - 2.6 display the NMR spectra of monomers and polymers. Assignment of ¹H and ¹³C signals are based on substituent effects. The absence of residual signals of the alkene protons at $\delta 5.5\text{--}6$ ppm in the polymers (**Fig. 2.3c, d**) suggests the termination process by degradative chain transfer via abstraction of the allylic proton of the monomers to yield unreactive allylic radicals [104]. Note that the alkene carbon signals at $\approx \delta 126$ and 127 ppm (**Fig. 2.4a,b**) disappeared in the polymers (**Fig. 2.4c,d**). The

incorporation of the catechol motifs is confirmed by the appearance of signals for six aromatic carbons in the range δ 115-145 ppm (**Fig. 2.4d**). The three aromatic protons of monomer **3** appeared as sharp signals at δ 6.57, 6.65, 6.72 ppm (**Fig. 2.3b**), while the corresponding protons in copolymer **6c** are shown in the same chemical shifts as broad signals (**Fig. 2.3d**). Likewise, ^1H NMR spectra of terpolymers **8b** and **8c** polymers having SO_2 units (**Fig. 2.5b, c**) and ^{13}C NMR spectrum of **8c** (**Fig. 2.6b**) also demonstrated the incorporation of the catechol motifs and disappearances of signals of the alkene protons and carbons.

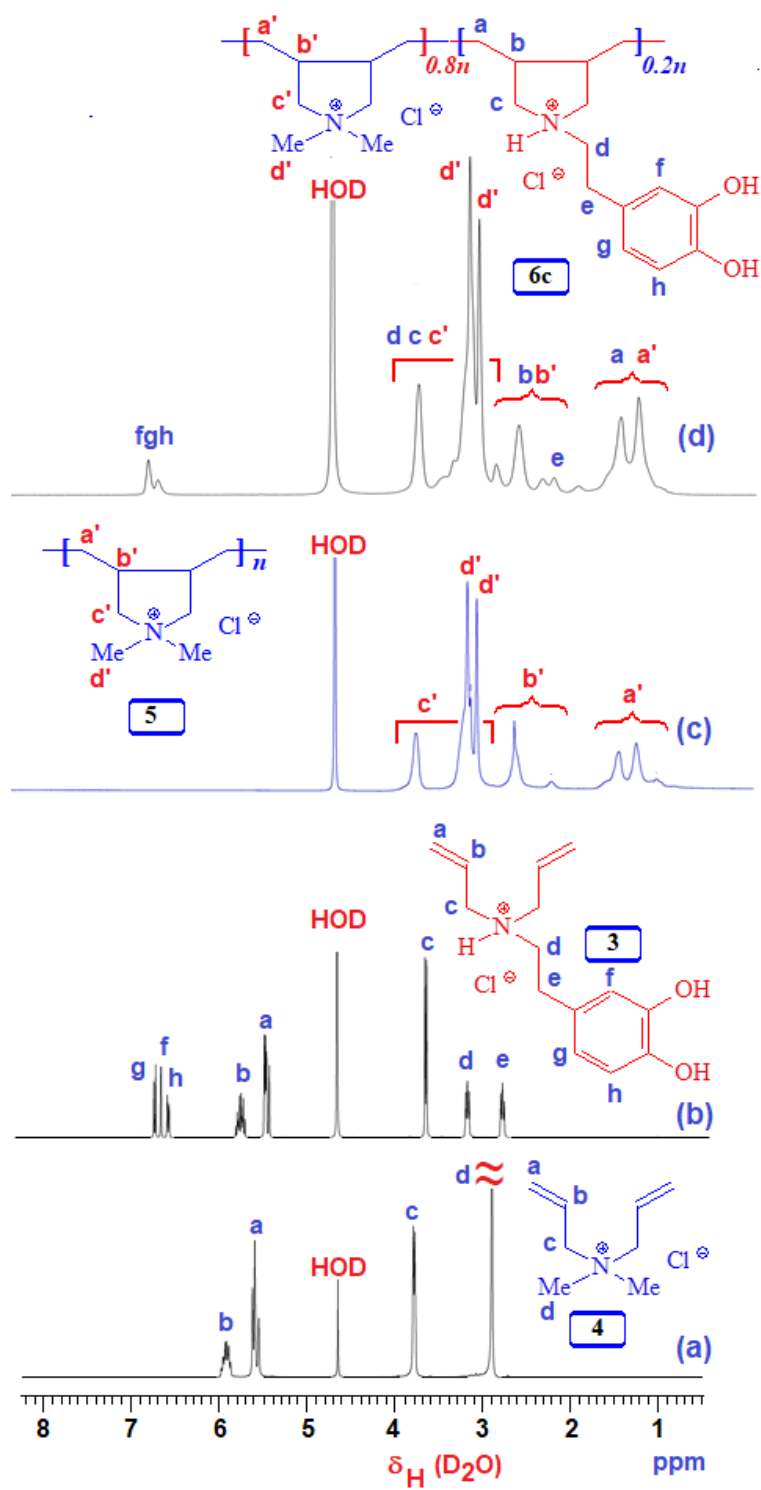


Figure 2.3. ^1H NMR spectra in D_2O of (a) monomer 4, (b) Monomer 3, (c) polymer 5, and (d) polymer 6c

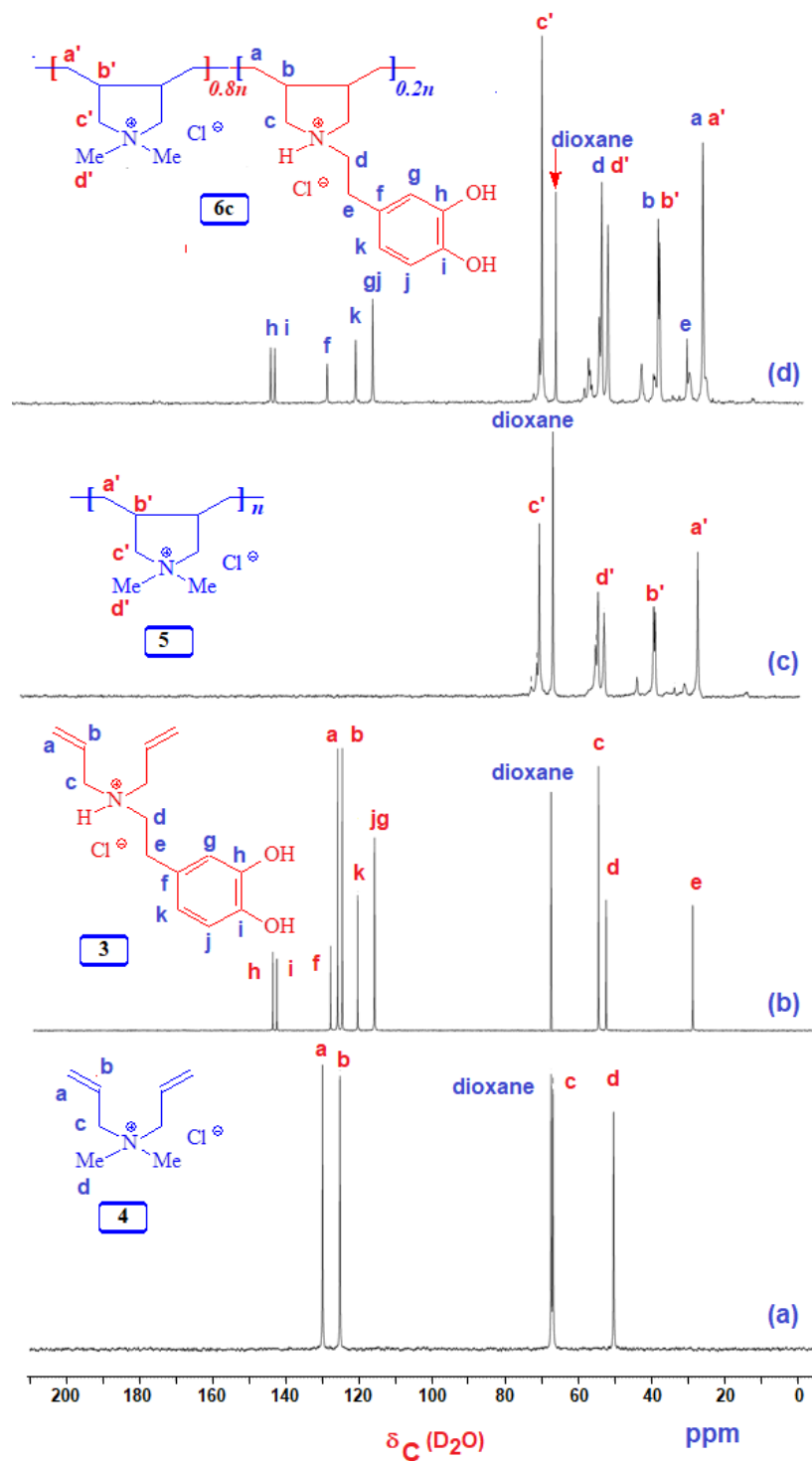


Figure 2.4. ^{13}C NMR spectra in D_2O of (a) monomer 4, (b) Monomer 3, (c) polymer 5, and (d) polymer 6c

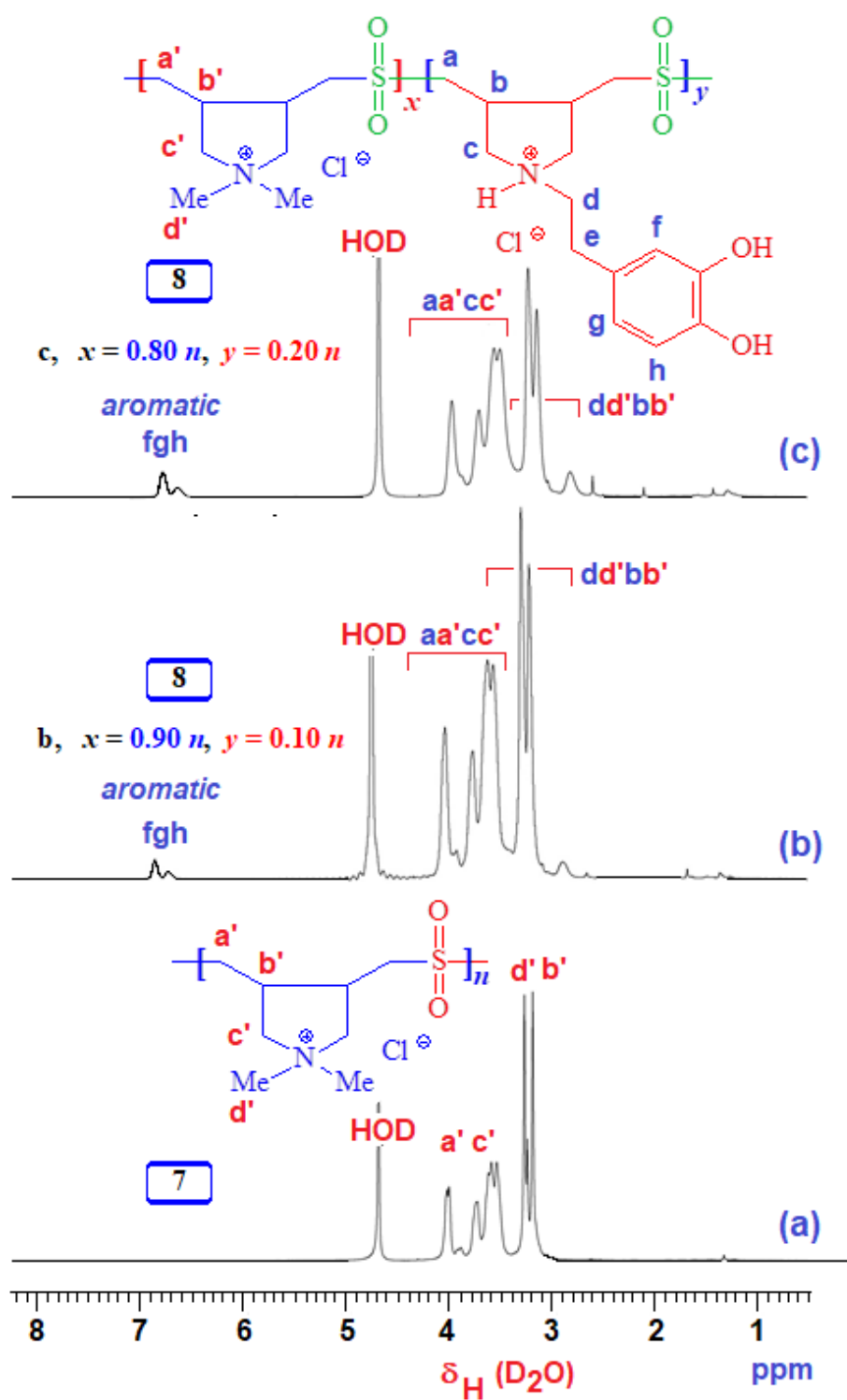


Figure 2.5. ^1H NMR spectra in D_2O of (a) polymer 7, (b) polymer 8b, and (c) polymer 8c

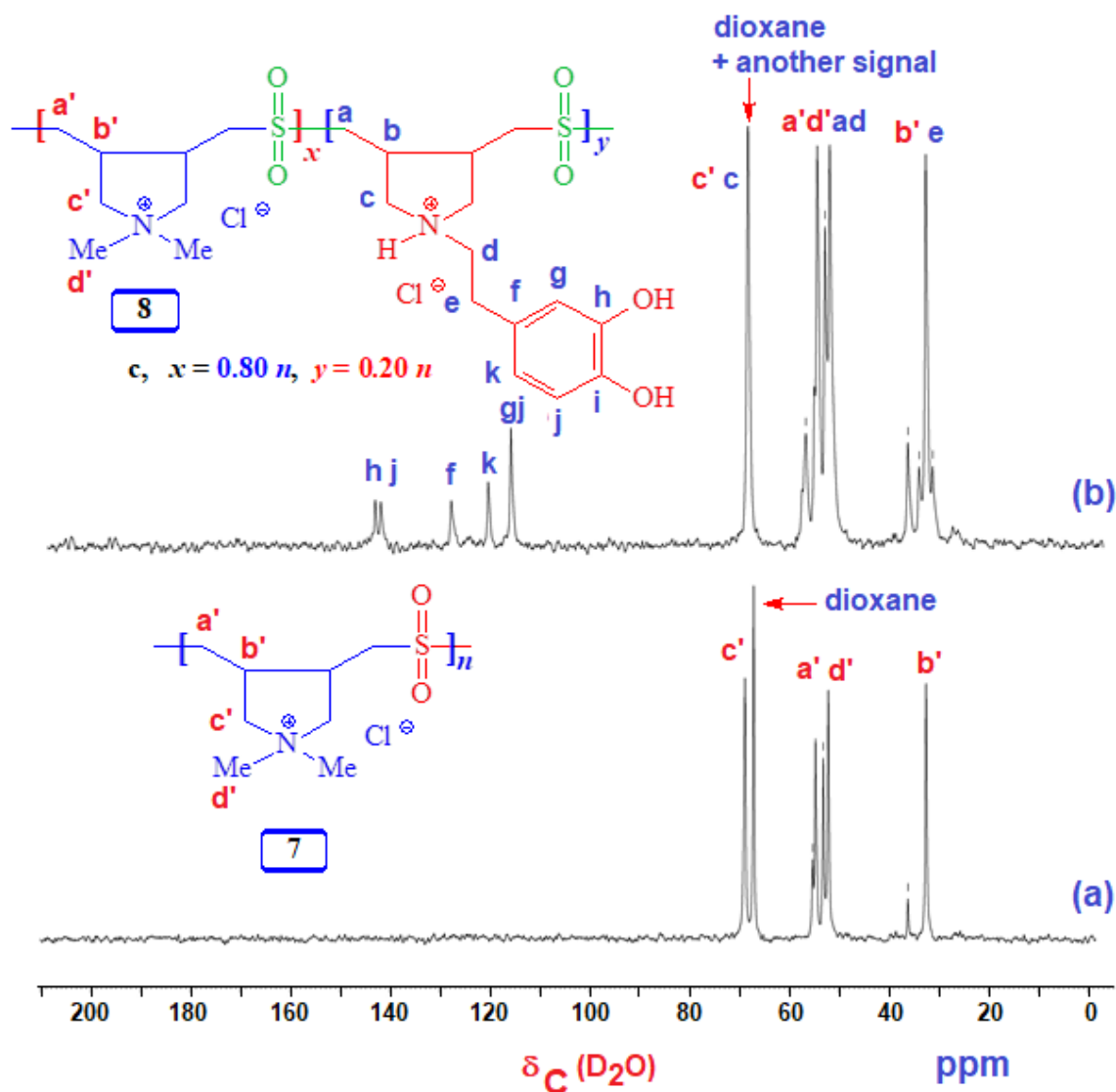


Figure 2.6. ^{13}C NMR spectra in D_2O of (a) polymer 7, (b) polymer 8b, and (c) polymer 8c

All the synthesized polymers are water-soluble. For instance, a 20-mg sample in 1 mL water (i.e., 2 wt%) gives a homogeneous solution within 2 min. The viscosity plots for the polymers in aqueous solutions in salt-free and 0.1 M NaCl are shown in **Figs. 2.7** and **2.8**. In salt-free water, the viscosity plots become concave upward as expected of polyelectrolytes (**Figs. 2.7i** and **2.8i**), while normal linear plots were obtained in 0.1 M NaCl because of shielding of the positive charges on the polymer backbone by Cl^- ions.

Intrinsic viscosities $[\eta]$ are given in **Table 2.2**. Viscosity average molar mass $\overline{M}_v$ was calculated using Mark-Houwink equation: $[\eta] = K\overline{M}_v^a$ where $[\eta]$ values of were 0.508, 0.543, 0.282, and 0.175 dL g⁻¹ for **5**, **6a**, **6b**, and **6c**, respectively, in 1 M NaCl at 30 °C. Mark-Houwink parameters ‘K’ was taken as 1.12×10⁻⁴ dL g⁻¹ and ‘a’ as 0.82 [102]. Note that the parameters used are for homopolymers **5** not for copolymers **6** containing dopamine residues. This could be a source of error for the $\overline{M}_v$ of the copolymers **6**. The $\overline{M}_v$ values are given in **Table 2.2**. Polymer **6c** with highest incorporation of catechol motifs was found to have the lowest molar mass, presumably because of higher rate of chain termination. For the SO₂ polymers, the $\overline{M}_n$ values (**Table 2.2**) were estimated by end group analysis using area integration of the protons for initiator fragment (CH₃)₂C(CN) which appeared at δ 1.30 ppm (**Fig. 2.5**) [100]. Polymer **8c** having highest incorporation of catechol motifs was found to have the lowest molar mass.

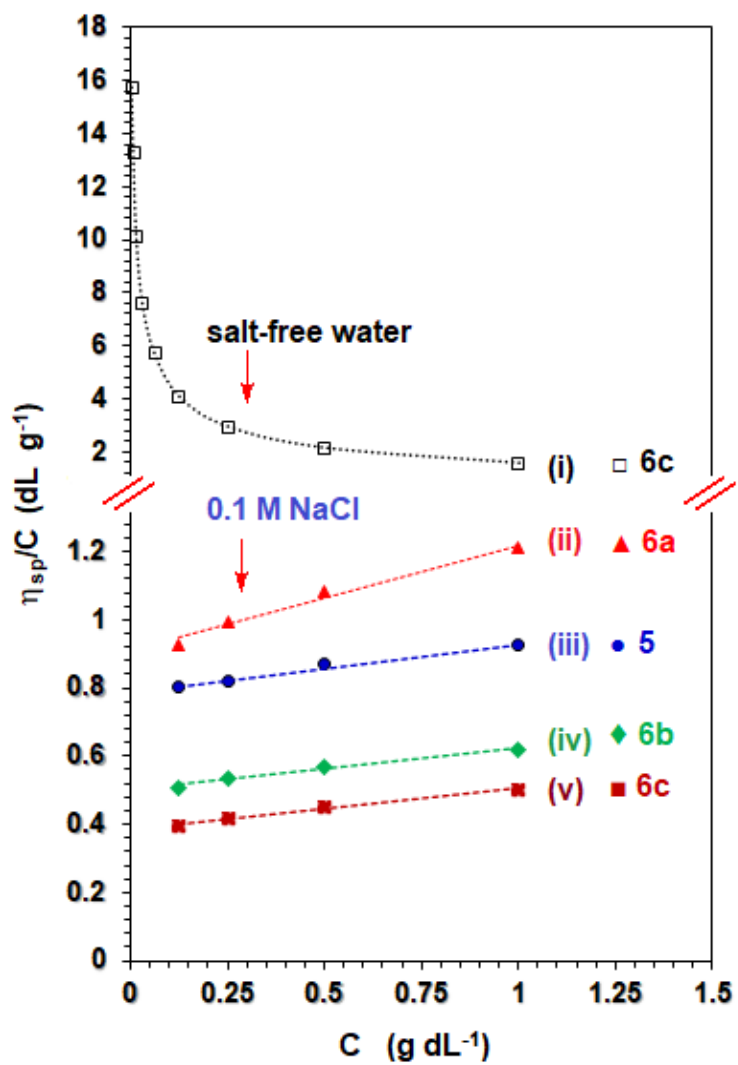


Figure 2.7. Viscosity plots at 30 °C of (i) 6c in salt-free water, and in 0.1 M NaCl (ii) 6a, (iii) 5, (iv) 6b and (v) 6c

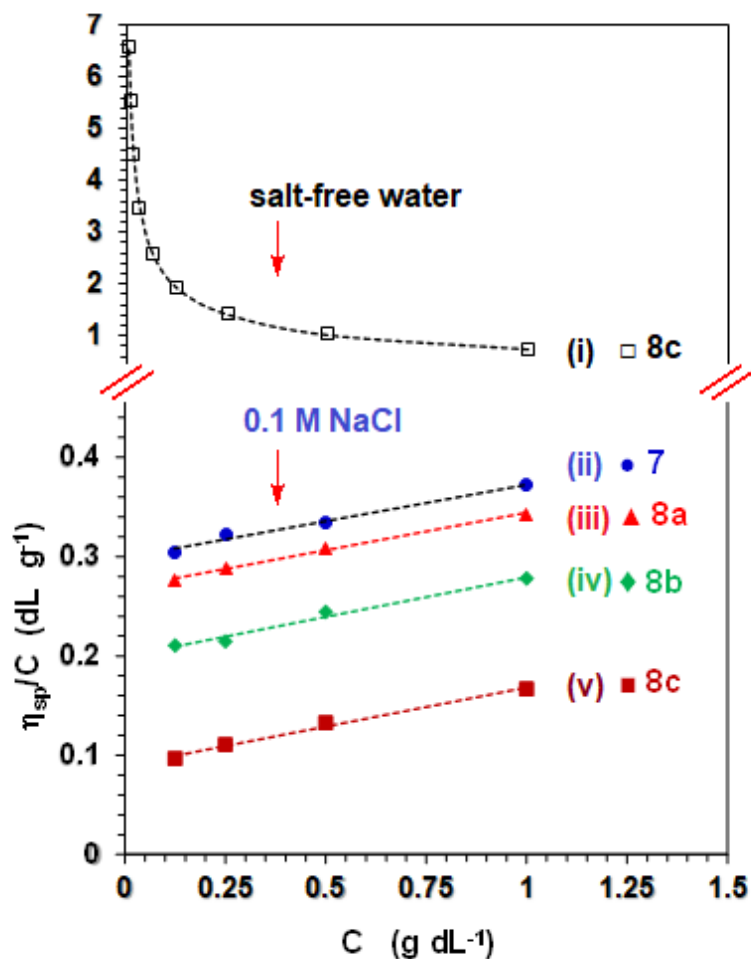


Figure 2.8. Viscosity plots at 30 °C of (i) 8c in salt-free water, and in 0.1 M NaCl (ii) 7, (iii) 8a, (iv) 8b and (v) 8c.

2.3.2. Some of the synthesized polymers as corrosion inhibitors

Gravimetric weight-loss method is the simplest yet more reliable technique as compared to electrochemical methods to study the mild steel corrosion in corrosive environments since the former process is carried out over a much longer duration. The results of the corrosion inhibition efficiency (IE) ($\eta\%$) monomer **4**, polymers **5** and **6c** in 1 M HCl (60 °C, 24 h) are included in **Table 2.3**.

Table 2.3 Inhibition efficiency (IE) (h%) imparted by homopolymer 5 and copolymers 6 to inhibit mild steel corrosion in 1 M HCl for 24 h at 60 °C.

Entry	Sample (ppm)	IE ($\eta\%$)
	Polymer 6c	
1	0.5	48.9 ± 1.7
2	1	65.0 ± 1.1
3	1.5	73.4 ± 0.9
4	2.5	83.1 ± 0.6
5	5	89.5 ± 0.5
6	10	94.1 ± 0.6
7	20	98.0 ± 1.0
	Polymer 5	
8	10	81.2 ± 1.3
	Monomer 4	
9	10	37.1 ± 1.7

Inhibitors **4**, **5**, and **6c** at a concentration of 10 ppm imparted %IE of 37.1, 81.2, and 94.1, respectively, thereby confirming the superior effectiveness of **6c** having 20% catechol motifs. In general, the increased effectiveness of the polymers as compared to monomer **4** is facilitated by the former's multiple adsorption sites which resist desorption from the metal surface. The %IE increases with increasing concentrations of **6c** in the range 0.5-20 ppm, achieving a remarkable %IE of 98.4 at 20 ppm. Inhibitor **6c** has fared well as compared to some recent polymeric inhibitors [105].

The surface coverage data, θ , which are equated to fractional IEs (i. e., $\eta\%/100$) imparted by copolymer **6c**, in the concentration (C) range 0.5-10 ppm were used to

construct several isotherm models of Temkin ($K_{ads} C = e^{f\theta}$), Langmuir ($\frac{\theta}{1-\theta} = K_{ads} C$), Frumkin [106] ($K_{ads} C = \frac{\theta}{1-\theta} e^{-2a\theta}$), and Freundlich [107] ($\theta = K_{ads} C^n$), where equilibrium adsorption constant is denoted as K_{ads} , and C is expressed in mol L⁻¹. The linear plots, shown in **Fig. 2.9**, revealed the best fit for the Langmuir model with a R^2 value of 0.9969 (**Fig. 2.9b**). K_{ads} was obtained from the slope which was equated to free energy of adsorption using **Eq. (2.2)** where 55.5 is the molar concentration of water in solution [108]. ΔG^0_{ads} value of (-) 45.9 kJ mol⁻¹ indicates favorable adsorption of the polymeric inhibitor on the metal surface. Note that the Temkin plot (**Fig. 2.9a**) is shown to have a moderate fit with R^2 value of 0.941 (**Fig. 2.9a**). The relatively high value of 6.66 for the molecular interaction constant f , extracted from the slope ($1/f$) of the Temkin plot, indicates the electrostatic repulsion among positive nitrogens are of moderate significance [109].

$$K_{ads} = \frac{1}{55.5} e^{\frac{-\Delta G^0_{ads}}{RT}} \quad (2.2)$$

Corrosion inhibition study was also conducted in 15% HCl (6 h, 60 °C), and the %IE in the presence of various concentrations of inhibitors are included in **Table 2.4**. At a concentration of 20 ppm, homopolymer **5**, copolymers **6a**, **6b**, and **6c** imparted %IEs of 67.2, 74.2, 81.4, and 85.2, respectively. The %IE thus increased with the increase in the incorporation of dopamine motifs. Under the influence of such a harsh corrosive environment of 15% HCl, the inhibitory action was quite significant; a %IE of 93.1 was achieved in the presence of 50 ppm of copolymer **6c**. Several isotherm plots, shown in **Fig. 2.10**, revealed the best fit for the Langmuir model which gave a ΔG^0_{ads} value of (-) 41.2 kJ mol⁻¹.

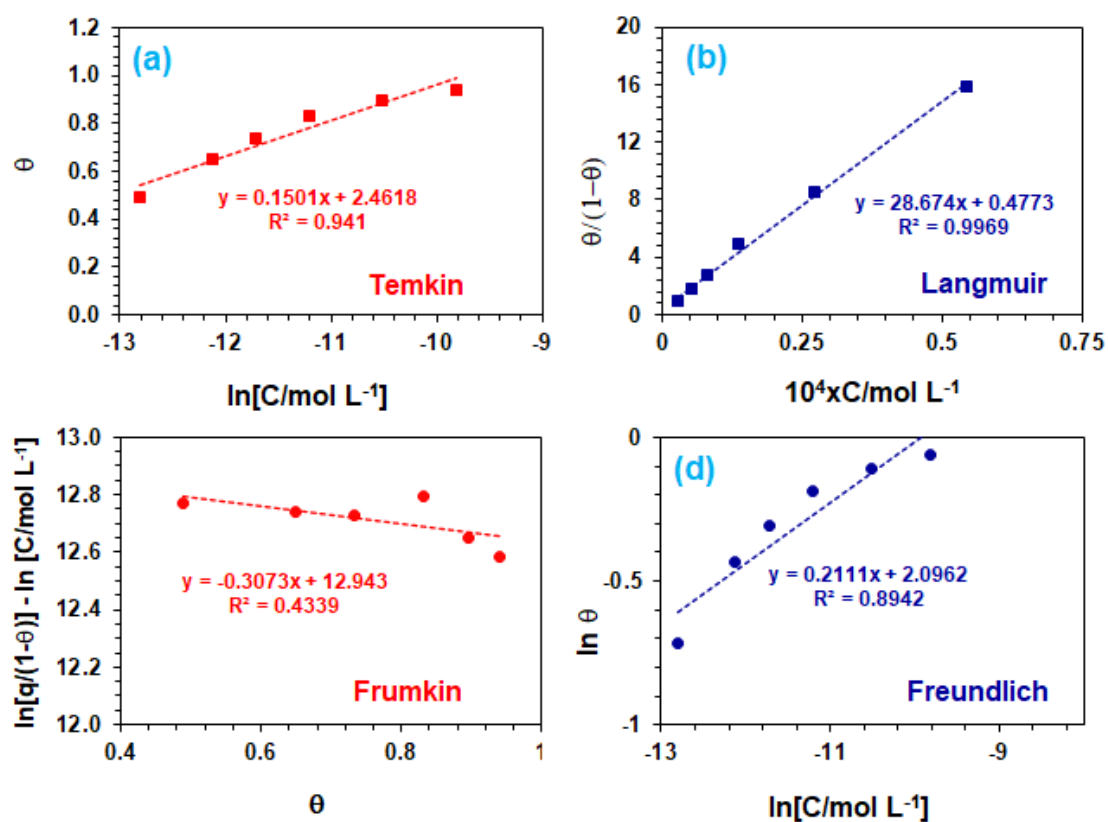


Figure 2.9. Adsorption isotherms of 6c in 1 M HCl at 60 °C: (a) Temkin, (b) Langmuir, (c) Frumkin, and (d) Freundlich.

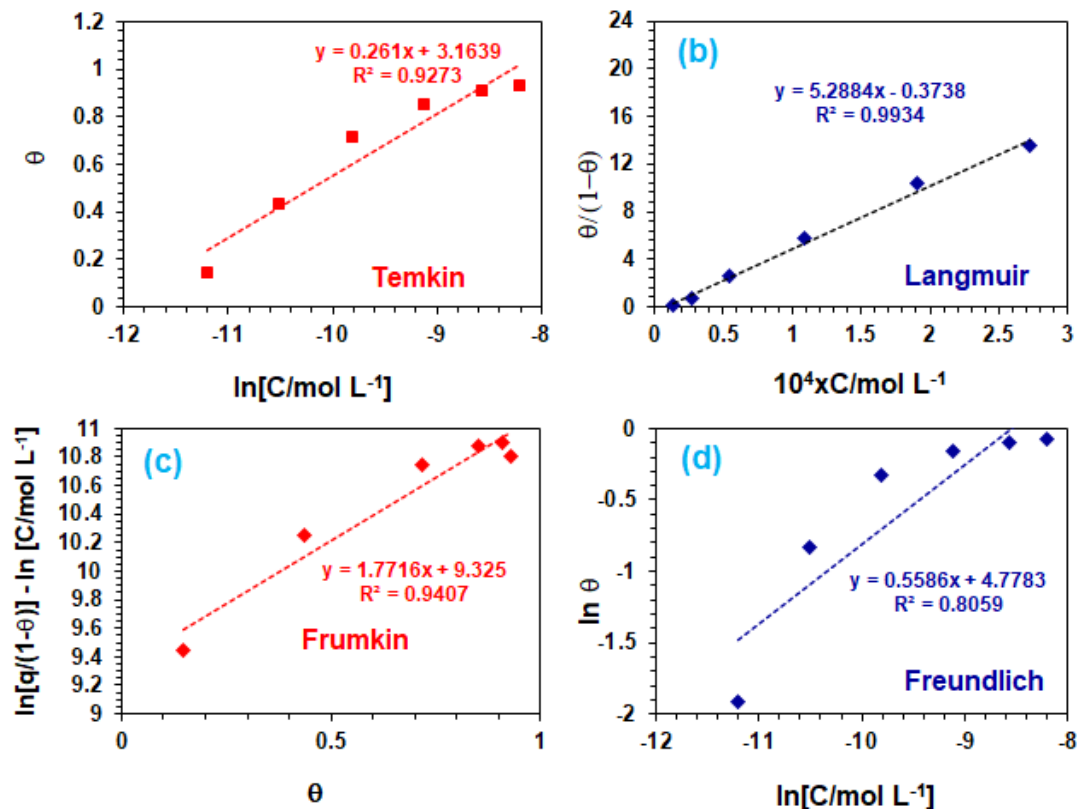


Figure 2.10. Adsorption isotherms of **6c** in 15% HCl at 60 °C: (a) Temkin, (b) Langmuir, (c) Frumkin, and (d) Freundlich.

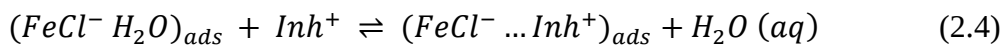
The %IE of **6c** is further improved in the presence of KI. While KI (400 ppm) imparted a surface coverage θ_2 of 0.317 for iodide ions, a mixture of **6c** (20 ppm) and KI (400 ppm) improved the surface coverage θ_1 for **6c** from 0.852 to an excellent θ_{1+2} value of 0.933 for (**6c** + KI) (Table 2.4, entries 7 versus 11). Synergistic parameter (S_θ) was calculated using Eq. (2.3) [110]. S_θ value of 2.06 (i.e., >1) reflects the corrosion inhibition process as guided by the synergistic cooperative co-adsorption. Note that $S_\theta < 1$ would have implied antagonistic competitive co-adsorption [110].

$$S_\theta = \frac{1 - (\theta_1 + \theta_2 - \theta_1\theta_2)}{1 - \theta_{1+2}} \quad (2.3)$$

Table 2.4 Inhibition efficiency (IE) ($\eta\%$) imparted by homopolymer 5 and copolymers 6c to inhibit mild steel corrosion in 15% HCl for 6 h at 60 °C.

	Sample (ppm)	KI (ppm)	IE ($\eta\%$)
Entry	Polymer 5		
1	20		67.2±0.4
	Polymer 6a		
2	20		74.2± 0.6
	Polymer 6b		
3	20		81.4± 0.4
	Polymer 6c		
4	2.5	—	14.7 ± 2.1
5	5	—	43.5 ± 1.4
6	10	—	71.8 ± 0.8
7	20	—	85.2 ± 0.5
8	35	—	91.2 ± 0.4
9	50	—	93.1 ± 0.3
	Polymer 6c and KI		
10	—	400	31.7 ± 1.2
11	20	400	95.1 ± 0.3

The positively charged Fe surface induces the adsorption of a layer of Cl^- ions, which facilitate the co-adsorption of positively charged inhibitor molecules (Inh^+) (**Eq. (2.4)**) [111–113]. The adsorption of Inh^+ and Cl^- ions displaces the H_2O molecules accumulated on the surface, thereby requiring the inclusion of molar concentration of water as 55.5 (**Eq. 2.2**).



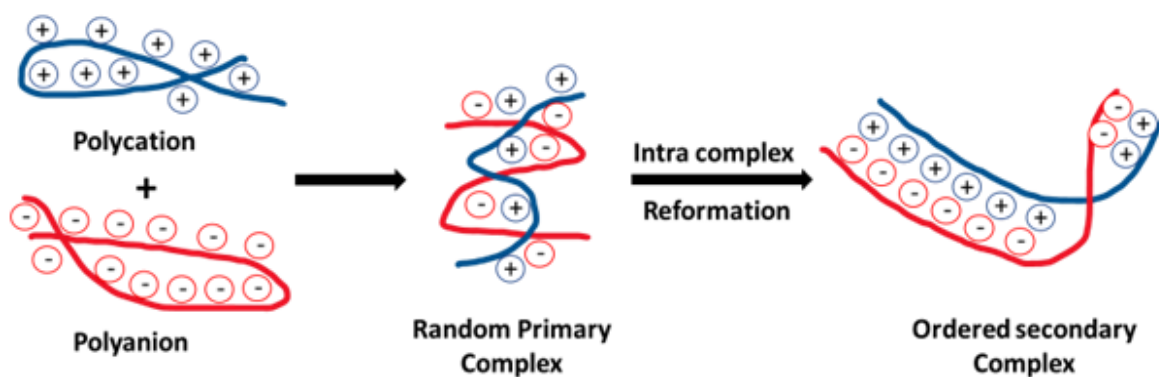
Usually, $\Delta G^{\circ}_{\text{ads}}$ values $- < 20 \text{ kJ mol}^{-1}$ point toward physisorption. A $\Delta G^{\circ}_{\text{ads}}$ value of $(-) 45.9 \text{ kJ mol}^{-1}$ in 1 M HCl and $(-) 41.2 \text{ kJ mol}^{-1}$ in 15% HCl may point towards both physisorption involving Inh^+ adsorption on FeCl^- layers, and chemisorption using the interaction of catechols $\text{Ar}(\text{OH})_2$ in dopamine motifs with the vacant iron d-orbitals [109,114] or accumulated Fe^{2+} on the metal surface leading to the formation of chelated species $\text{Ar}(\text{O})_2\text{Fe}$.

The polymers derived *via* acrylic monomers (*vide supra*, *Introduction*) have the pendants of catechol or dopamine motifs linked to the polymer backbone via ester or amide linkage (**Fig. 2.1**). However, the polymers derived *via* Butler's cyclopolymerization protocol [56–58,93] involving dopamine-derived monomer **3** (**Scheme 2.1**) have the pendant dopamine attached to the polymer backbone by a robust N-C bond, which will not be susceptible to acid hydrolysis like the cases of ester and amide linkages (in proteins). The dopamine has kept intact the original functionality of the basic amine in the synthesised polymers and their stability under acidic environment makes them efficient corrosion inhibitor. The polymers, having multiple adsorption sites to anchor on the metal surface, - thereby imposing a barrier to the corrosive environments - quite often give better protection to the metal surface than their monomeric counterparts [114–118].

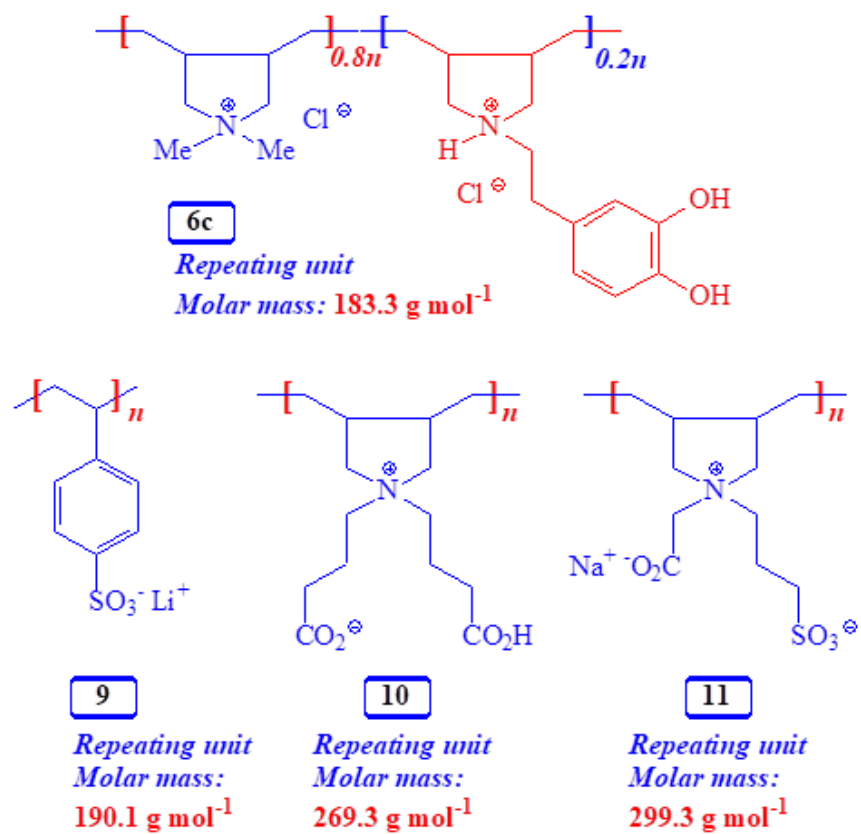
2.3.3. Polyelectrolyte Complex: Encapsulation of Oils with Complex Coacervates

Several interesting articles described the theoretical and application points of view regarding the polyelectrolyte complexes of pairs of polyampholytes/polyelectrolytes [94],

polyanions/polycations and polyelectrolyte complexes (PEC), which can be in the form of layer-by-layer assembly, solid precipitate, liquid coacervates (complex coacervate [CC]), or soluble complex (**Scheme 2.2**) [119,120]. Herein, the preliminary CC study of cationic **6c** containing catechol pendants was carried out with three model anionic/zwitterionic PEs: anionic polystyrene sulfonate (PSS) **9**, zwitterionic **10** [97], and zwitterionic/anionic **11** [98] (**Scheme 2.3**).



Scheme 2.2. Schematic representation of the formation of polyelectrolyte complex (PEC): (i) Random primary complex. (ii) Ordered secondary complex



Scheme 2.3. Ionic polymers for polyelectrolyte complexes

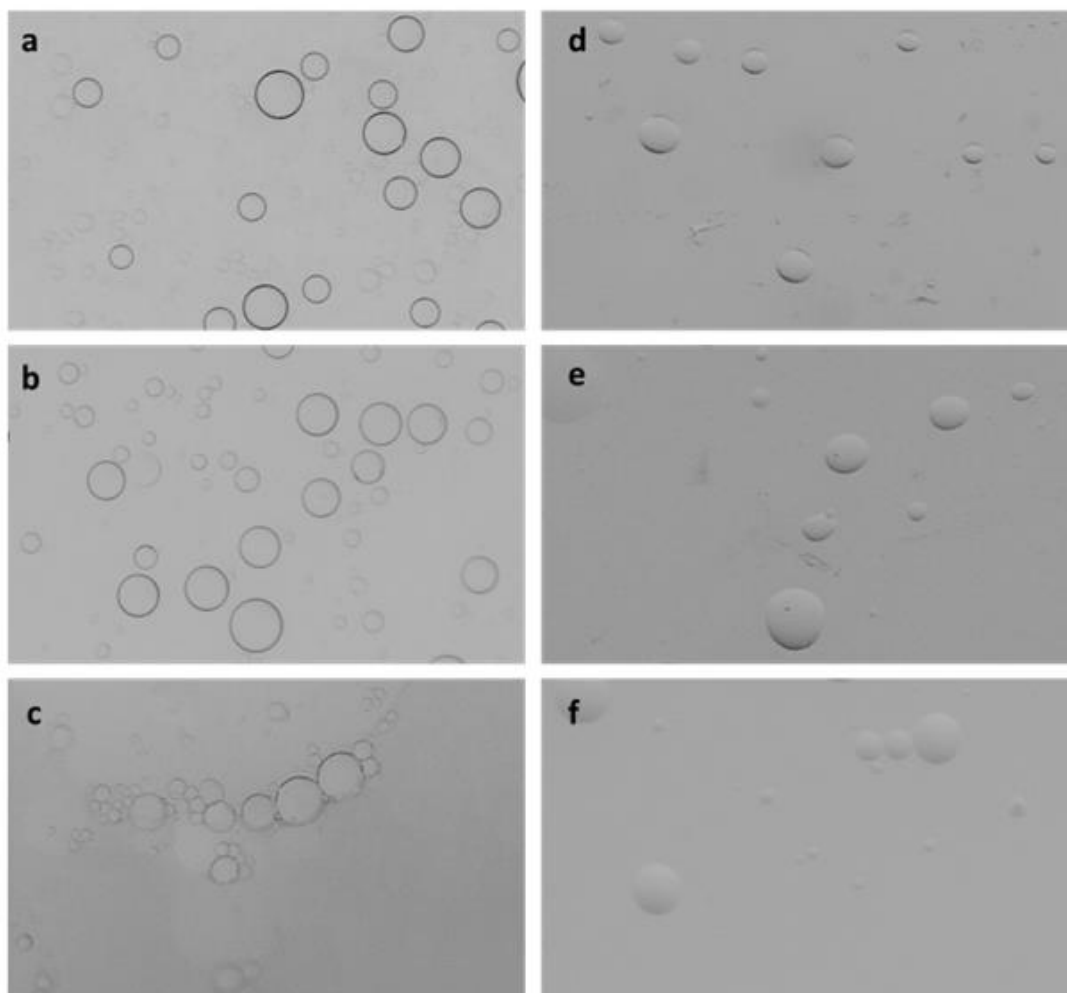


Figure 2.11. Optical microscope images of polyelectrolyte complexes in the absence of NaCl (a) **6c/9, (b) **6c/10**, (c) **6c/11** and in the presence of NaCl (d) **6c/9**, (e) **6c/10**, (f) **6c/11****

The Pfeiffer P3 mineral oil (2-3 drops) was added into the coacervate pairs of **6c/9**, **6c/10**, and **6c/11** which were prepared in aqueous solutions in 1:1 mol ratio of the repeating units. When oppositely charged PEs are neutralized in the system, the separation of the liquid-liquid phase led to the formation of complex coacervate (CC) [121]. A mixture of the layers was taken for optical microscope study. The encapsulation by CC was observed as the dark bold lines around the drops (**Fig. 2.11a-c**). Addition of NaCl - amounts written under parentheses - to the CC pairs **6c/9** (293.0 mg), **6c/10** (112.1

mg) and **6c/11** (224.1 mg), disrupts the electrostatic interactions among the positive and negative charges in the PEs chains since Cl^- and Na^+ ions bind with the respective positive nitrogens and negative centers and thereby shielding them from interchain interactions [56]. The CC was observed to be broken down and dissolved ultimately to a single layer. The bold lines therefore disappeared after the addition of NaCl (**Fig. 2.11d-f**). The quantity of salt was different for each PEC according to the nature of the complex; **6c/9** pair showed strong interaction since it required the greatest amount of salt to break the CC. In **6c/10** and **6c/11** pairs, the negative charge densities in zwitterionic **10** and zwitterionic/anionic **11** are less owing to internal charge neutralization in the zwitterionic dipoles.

Encapsulation of hydrophobic liquid droplets with a complex coacervates have been used for several applications. The coacervate walls can protect volatile oils from evaporation [120] and can be used to encapsulate particles or droplets to protect the inside material. In pharmaceutical industries, PECs are used as coatings materials (for sustained delivery, as binder for formulation of drug) [122]. This study thus confirmed that cationic copolymer **6c** can form complex coacervates with anionic PE **9**, zwitterionic **10** and zwitterionic/anionic **11**, that can be further explored for desired applications.

2.4. Conclusion

Dopamine hydrochloride (**1**) upon alkylation with two equivalents of allyl bromide in acetonitrile in the presence of K_2CO_3 afforded *N,N*-diallyldopamine (**2**), which upon treatment with HCl gave cationic monomer *N,N*-diallyldopamine hydrochloride (**3**). While the AMPD-initiated cyclopolymerization of monomer diallyldimethylammonium chloride (**4**) gave polymer **5**, the copolymerization of **4** and **3** in ratios of 95:5, 90:10, and

80:20 led to water-soluble random copolymers **6a**, **6b**, and **6c**, respectively, in excellent yields. To our knowledge, these copolymers represent the first examples of cyclopolymers containing various proportions of dopamine motifs as generated by Butler's cyclopolymerization protocol. Likewise, monomers **4/3**/SO₂ in ratios of 100:0:100, 95:5:100, 90:10:100, and 80:20:100, afforded respective water-soluble copolymer **7** and terpolymers **8a**, **8b**, and **8c** having alternate placement of SO₂ units and random distribution of monomers **4** and **3**. TGA analysis revealed the stability of these polymers up to ≈ 210 °C. NMR spectra revealed the absence of residual alkene double bonds, thereby implying the chain termination by abstraction of allylic 'H' from the monomers. Viscosity average molar masses $\overline{M}_v$ of polymers **5** and **6** and number average molar masses $\overline{M}_n$ of polymers **7** and **8** have been determined by viscosity measurements and end-group analysis by ¹H NMR, respectively.

Some of the bio-mimetic polymers, decorated with various proportions of dopamine motifs, have been tested as inhibitors of corrosion of mild steel in 1 M and 15% HCl at 60 °C. At a concentration of 10 ppm, monomer **4**, polymers **5** and **6c** imparted corrosion inhibitions of 37.1, 81.2, and 94.1% at 60 °C in 1 M HCl, while at 20 ppm **6c** demonstrated excellent inhibition of 98%. Polymers **5**, **6a**, **6b**, and **6c** at 20 ppm containing 0, 5, 10, and 20 mol% dopamine residues were also effective in 15% HCl, imparting respective inhibitions of 67.2, 74.2, 81.4, and 85.2%, while 20 ppm **6c** aided by KI demonstrated enhanced synergistic inhibition of 95.1%. Corrosion inhibitions followed Langmuir isotherm model giving favorable $\Delta G^{\circ}_{\text{ads}}$ values of (-) 45.9 and (-) 41.2 kJ mol⁻¹ in 1 M and 15% HCl, respectively, thereby indicating an association of

physisorption of cationic motifs and chemisorption by catechol groups on the metal surface.

Cationic polyelectrolyte **6c** has been shown to form polyelectrolyte complex/coacervate with three model anionic polyelectrolytes **9**, **10**, and **11**. This study confirms that the synthesized co-polymer can form CC with different polyelectrolytes, that have a potential to be explored in various applications. PECs can be used to encapsulate particles or droplets. The coating of PEC can protect the inside material, control the release, and alter the colloidal properties.

CHAPTER 3

Fabrication of a New Rationally Designed Mussel-Inspired Cationic Amphiphilic Terpolymer to Enhance the Separation and Anti-Fouling Performance of Membranes

Taken from Zeeshan Arshad, Billel Salhi, Nadeem Baig*, Isam H. Aljundi, Shaikh A. Ali* Fabrication of a New Rationally Designed Mussel-Inspired Cationic Amphiphilic Terpolymer to Enhance the Separation and Anti-Fouling Performance of Membranes, *Langmuir*, 39 (2023), 9186-9199.

Abstract

Polyvinylidene fluoride (PVDF) membrane based systems for treating oily wastewater are prone to fouling. Herein, we introduced a novel mussel-inspired cationic amphiphilic terpolymer consisting of monomers: *N,N*-diallyldimethylammonium chloride (DADMAC), *N,N*-diallyltetradecan-1-ammonium chloride (DTDAC), and mussel-inspired *N,N*-diallyldopamine hydrochloride (DADAHC) to improve the performance and characteristic of the PVDF membranes for oil-in-water emulsion separations. The cationic terpolymer, poly(DADMAC-co-DTDAC-co-DADAHC), shortened as PDDD, synthesized in excellent yield via free radical polymerization, has good compatibility with the PVDF owing to the presence of hydrophobic long alkyl chain in DTDAC. The presence of dopamine motifs helps to stabilize the PDDD-PVDF membrane by chelating with Fe^{3+} ions. The water contact angle on the PDDD-incorporated PVDF membranes was reduced from 87.6° to 54.6° , demonstrating improved hydrophilicity than pristine PVDF (M-0). The incorporation of PDDD into the PVDF improved the separation

efficiencies of the membrane, which reached up to 99% while treating the oil-in-water emulsions. Incorporating PDDD into PVDF has significantly enhanced the anti-fouling characteristics of the membranes, which are indicated by their remarkable flux recovery ratio (FRR) (up to 92%). The hydrophobic and hydrophilic groups worked synergetically to enhance the performance of the fabricated membrane.

KEYWORDS: PVDF Membrane, amphiphilic terpolymer; oil/water separation, anti-fouling, Diallylamine salts.

3.1. Introduction

Oily wastewater produced by petrochemical, oil and gas, food, and pharmaceutical industries has become the most severe worldwide environmental challenge.[123,124] Oil wastage in wastewater negatively impacts the economy, ecosystem, and human health. Therefore, it is crucial to develop effective methods for treating oily wastewater.[125] Skimming is considered a conventional technique to separate heterogeneous oily wastewater. Alternatively, absorption, adsorption, and chemical processes were found to be inefficient for oil-water emulsions.[126–129] Membrane-based technology is considered the most effective for water-oil separation over conventional techniques. Usually, the separation technique is adopted based on the oil droplet size in water; oil is called free oil when the size is $>150\mu\text{m}$, dispersed oil when the size is between 20 -150 μm , and emulsified oil when the size is $< 20\mu\text{m}$.[130] Free and dispersed oil are easy to separate, but separating the emulsion is a critical challenge, and as such a suitable membrane design is required to treat emulsions.[126,131] Due to the importance of the subject, several kinds of polymeric membranes, including pine nut shell membrane

(PNSM)[132], polyethersulfone (PES), polysulfone (PS), polyvinylidene fluoride (PVDF), cellulose acetate (CA) and polyacrylonitrile (PAN), are used to deal with the oil/water emulsions. [133]

PVDF membranes have been used extensively in various applications such as membrane distillation, ultrafiltration, microfiltration, and for a broad range of water treatment applications owing to their high mechanical strength, excellent thermal and chemical stability, and well-controlled porosity in various operational conditions.[134,135] Despite such advantages, these membranes have hydrophobic polymeric backbone, which leads to low water permeation and increased membrane fouling. The hydrophobic biological moieties, organic compounds, oily contaminants, and colloidal particles attached to the surface of the membrane during the separation process lead to pore blockage.[136,137] Structural modification of the membrane with hydrophilic additives reduces fouling by developing a strong interaction with water to enhance membrane performance and fouling resistance.

Hydrophilic polymers are commonly used to improve the performance of PVDF membranes. Directly using hydrophilic polymers in PVDF membranes has limitations, such as being soluble in water, it may leach out during the phase inversion process. Moreover, the incompatibility between PVDF matrix and polymers results in decreased mechanical strength.[138,139] Recently,[140] it has been found that using amphiphilic copolymers in PVDF membranes can improve their hydrophilicity and overall anti-fouling performance. Amphiphilic copolymers are unique to conventional polymers, containing both hydrophobic and hydrophilic groups. Hydrophobic groups make the polymers insoluble in water, keeping them intact within the hydrophobic PVDF

membrane matrix and preventing phase separation during the phase inversion process. The high compatibility of the modifier with the PVDF membranes does not compromise with the mechanical strength of the membranes.[141,142] In 2018, it was reported that the PVDF blended with poly(methacrylamido benzene sulfonic acid) enhances the hydrophilicity and anti-fouling properties of the membrane.[143] Furthermore, the increase in the mechanical stability of PVDF membranes after blending with poly(ethylene glycol methyl ether methacrylate) was investigated to evaluate its performance.[144]

The use of mussel-inspired bioadhesive, 3,4-dihydroxy-L-phenylalanine (DOPA), and its derivative dopamine (DA) (**Fig. 3.1**), for surface modification has drawn considerable attention because of their interactions with various functionalities and outstanding biocompatibility.[145][146] The application of DOPA or DA as adhesives or co-deposition reagents is commonly employed to produce separation materials, including sponges,[147,148] metal meshes,[149–151] aerogels,[152] fabrics,[153] and polymer membranes.[154–156] The presence of catechol functionality in DA makes it susceptible to interacting with various metal ions.[157] The catechol-iron complexation is well studied and documented in several articles.[157–159] A comprehensive physio-chemical study of the catechol-containing compound with Fe (III) chelation was reported.[160] Moreover, the hydrophilic nature of DA can inhibit fouling formation.[161] Therefore, DA can help further along with the hydrophobic moiety to enhance the stability of the amphiphilic polymer in the PVDF membrane.

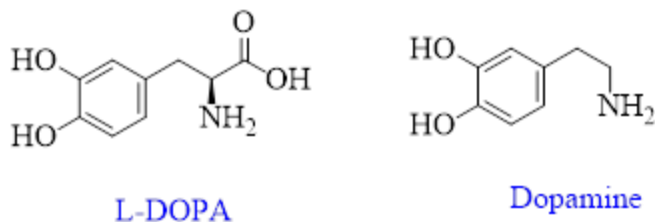


Figure 3.1. Chemical structure of L-DOPA and Dopamine

Free radical polymerization of *N,N*-diallyl quaternary ammonium salts $[H_2C=CHCH_2)_2N^+R^1R^2]$ led to the synthesis of various linear homo- and co-cyclopolymer.[162–164] The five-membered ring embedded in the polymer backbone is the eighth-most vital structural design of synthetic polymer.[165] Poly(diallyldimethylammonium chloride) p(DADMAC) alone is covered in ≈ 1000 patents and journal articles and is extensively used for water treatment.[164] In this work, cycloaterpolymerization of a hydrophilic monomer DADMAC, a hydrophobic monomer *N,N*-diallyltetradecan-1-aminium chloride (DTDAC), and dopamine-derived *N,N*-diallyldopamine hydrochloride (DADAHC) monomer led to an amphiphilic linear terpolymer poly(DADMAC-co-DTDAC-co-DADAHC) i.e., (PDDD). The PDDD is used to design high-performance PDDD-PVDF membranes for oil-in-water emulsion separation. The hydrophobic groups of DTDAC are expected to improve the compatibility between the polymer and membrane, while the DADMAC and DADAHC are expected to reduce the fouling formation.

3.2. Experimental Section

3.2.1. Materials

2,2'-Azobis(2-methylpropionamidine) dihydrochloride (AMPD) ($\geq 97\%$), Diallyldimethylammonium chloride (DADMAC), allyl bromide, dimethylacetamide (DMA) and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. ACS reagent grade hydrochloric acid (37%) was purchased from Fluka AG, Buchs, Switzerland, and used as received. All water used was of Milli-Q quality. A Spectra/PorTM (SpectrumTM) membrane having 3500 molecular weight cutoff (MWCO) was used for dialysis. DTDAC,[166] and DADAHC,[167] were synthesized as described. The diesel with 100% purity was obtained from the Industrial & Mechanical Services Co. Ltd. The PVDF (MW350 KDa) was acquired from Alfa Aesar. The Tween-80 was purchased from LOBA Chemie Pvt. Ltd.

3.2.2. Physical Methods

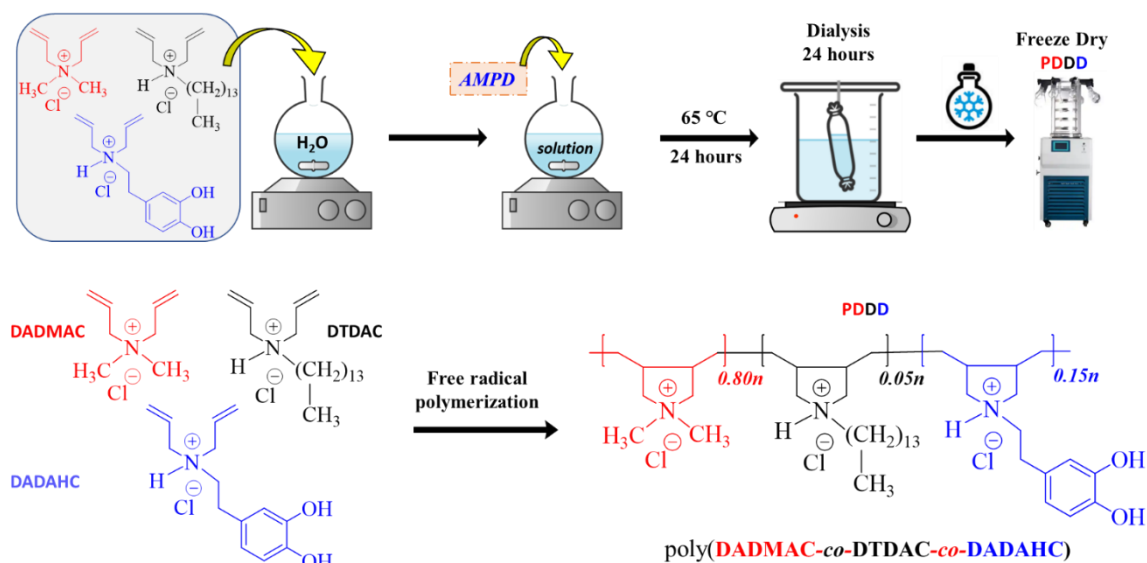
Perkin Elmer instrument (Model 2400) was used to determine atomic compositions. Thermogravimetric analyses (TGA) were performed under a flow of N₂ using an SDT analyzer (Q600: TA Instruments). Fourier transform infrared (FTIR) spectra of materials were acquired using a Thermo Scientific Nicolet iS10 spectrometer. For Nuclear magnetic resonance (NMR), a Bruker Avance III 400 MHz spectrometer was utilized to measure ¹H, and ¹³C, spectra using the residual D₂O protons (HOD) at δ 4.65 ppm, and ¹³C dioxane signal at δ 67.4 ppm as internal standards.

The water contact angle of the membranes was obtained by Goniometer DSA25 KRÜSS. The membranes' cross-section and surface morphology were performed using the Thermo Scientific™ Quattro field-emission scanning electron microscope (FE-SEM). The cross-section of the membranes was prepared using liquid nitrogen. Prior to analysis, the cross-section and surfaces of the membranes coated with Au using sputtering to improve image quality. Malvern Zetasizer instrument was used to measure the size distribution of the feed. Atomic force microscopy (AFM) was used to investigate the roughness and the topography of the PVDF membranes using the Agilent 550 instrument. The JASCO V-750ST UV-VIS Spectrophotometer was used to compute the $\lambda_{\max}$ of the various complexes. The Bona TYLG -19 cross-flow system was used to evaluate the anti-fouling characteristics of the membranes. The Olympus Microscope was used to capture the images of the feed and the permeate of the different PVDF membranes. A digital camera with a 25 megapixels resolution sensor was used to take photographs of the feed and the filtrate.

3.2.3. Synthesis of PDDD

DADMAC (1.30 g, 8.0 mmol), DTDAC (0.15 g, 0.5 mmol), and DADAHC (0.41 g, 1.5 mmol), were dissolved in water (1 g) in round bottom flask. Initiator AMPD (100 mg) was added to the solution and stirred at 65 °C for 24 h. Thereafter, upon dialysis against distilled water, using a 3500 MWCO dialysis bag for 24 h and freeze-drying gave polymer PDDD (**Scheme 3.1**), as a white solid (1.6 g, 86%). Required elemental analysis: C, 66.52; H, 10.26; N, 5.41 %, (Found: C 66.2; H 10.4; N 5.3%). $\nu_{\max}$ (KBr): 3641 (phenol O–H [H-bonded] stretching), 3428 (amine N–H stretching), 3076 (aromatic C–H stretching), 2927 (alkyl C–H stretching), 2854 (alkyl C–H stretching), 2796, 1636 (amine

N–H bending), 1459 (C–H bending), 1259 (amine C–N stretching), 1118, 917 (aromatic ring stretching), 631, and 540 cm^{-1} .

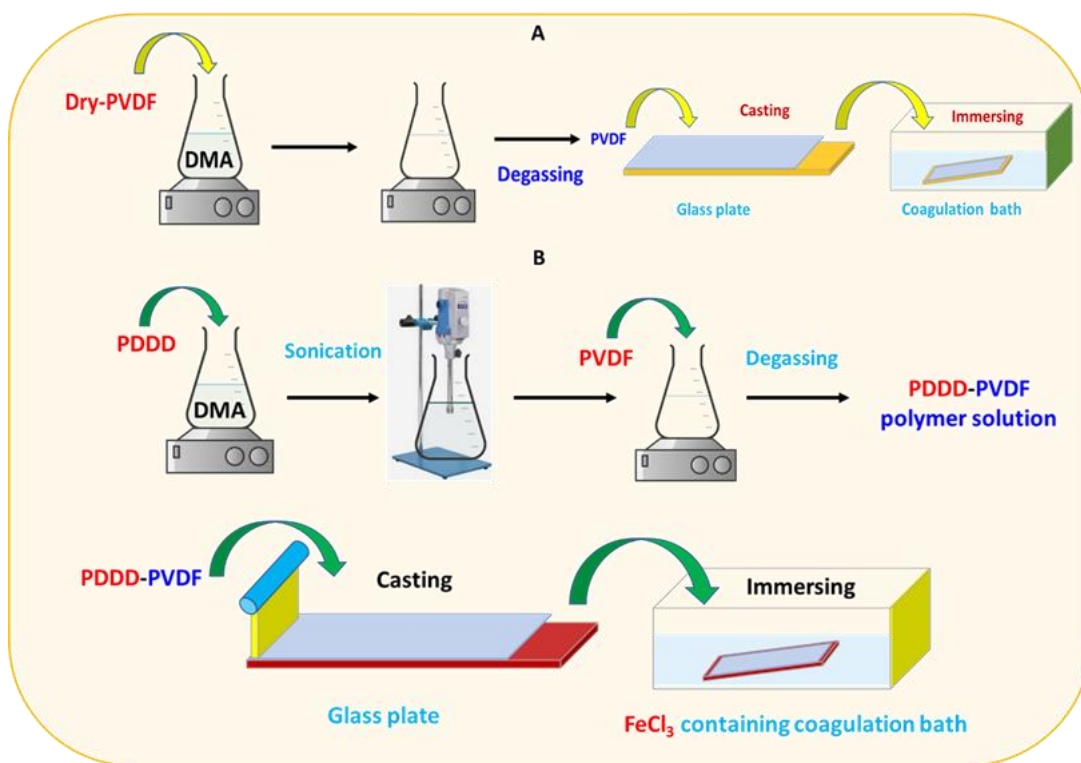


Scheme 3.1. Synthesis of PDDD

3.2.4. Synthesis of the membranes

PVDF membranes were synthesized using the phase inversion method. Firstly, the PVDF powder was dried in a vacuum oven at 60 °C for 12 hours to remove any moisture. Then, the dried PVDF powder was dissolved at 60 °C in anhydrous DMA to create a homogeneous PVDF dope solution. The dope solution was then degassed for 30 minutes in a sonicator and allowed to rest for 24 hours to eliminate any trapped bubbles. The dope solution was cast on a glass plate using a membrane applicator, and the resulting thin film was immediately immersed in a coagulation bath to solidify the membrane. After 10 minutes, the membrane was removed and placed in deionized water for 24 hours to complete the phase inversion process.

The poly(DADMAC-co-DTDAC-co-DADAHC) incorporated PVDF membranes were also synthesized in similar fashions, except a few additional steps were involved. Before the addition of the PVDF, the DMA was heated at 60 °C, and the PDDD was added into the DMA to get a uniform solution, and after that, the PVDF was added into it to prepare the PDDD doped PVDF uniform solution. For PDDD-PVDF membrane fabrication, a coagulation bath containing 0.002 M of FeCl_3 was prepared. The thin films of the various PDDD doped PVDF solutions were dipped into the coagulation baths. The rest of the steps were the same as those adopted for synthesizing the pristine PVDF membrane (**Scheme 3.2**). The details of the composition of the PVDF and the PDDD-PVDF membranes are provided in **Table 3.1**.



Scheme 3.2. (A) Schematic representation of (A) Pristine PVDF and the (B) PDDD incorporated PVDF membranes

Table 3.1. Composition of the various PVDF solutions used to synthesize the pristine PVDF and the PDDD-PVDF membranes.

Membrane code	Concentration of PDDD (%)	PVDF (%)	DMA (%)
M-0	0	15	85
M-1	0.25	15	84.75
M-2	0.5	15	84.5
M-3	1	15	84

3.2.5. Evaluation of the membrane performance

The stabilized milky oil-in-water emulsions were prepared by adding 0.25 g/L of diesel oil to the water. The oil-in-water emulsion was stabilized with the help of the Tween-80 by stirring at a high rate for 24 hours. Before the evaluation of the membranes, the membrane was kept in deionized water overnight and, after that, fitted into the dead-end cell. Argon gas was used to control the trans-membrane pressure across the membranes. The Oakton turbidity meter was used to measure the turbidity of the feed and the filtrate.

3.3. Results & Discussions

3.3.1. Synthesis and characterization of polymer

In this work, DADMAC, DTDAC, and DADAHC underwent AMPD-initiated cyclopolymerization to afford PDDD in an excellent yield of 86%. The monomer ratios incorporated were taken as 80:5:15 same as the feed ratio. TGA was used to investigate the thermal stability of PDDD. The TGA curve shows two significant 40 % and 44 % losses in the temperature range of 260-400 °C and 400-470 °C, respectively, due to the

loss of pyrrolidine rings. The weight loss of 12 % up to 210 °C was due to moisture escape. The synthesized PDDD is stable up to 210 °C (**Fig. 3.2**).

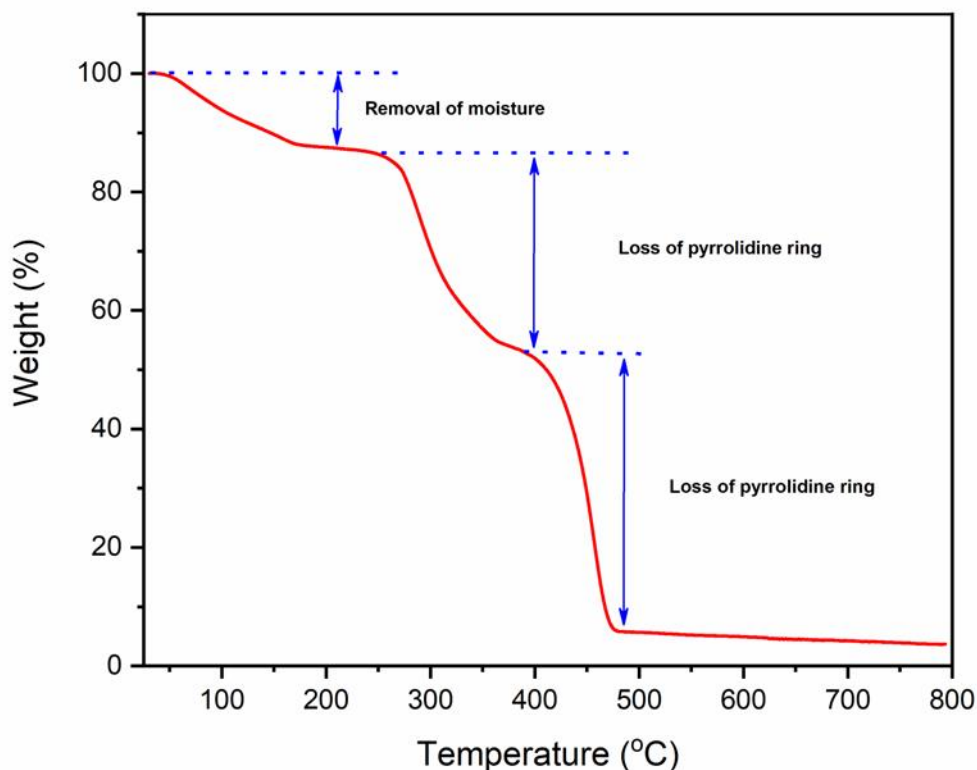


Figure 3.2. TGA of PDDD

The FTIR peaks for PDDD (**Fig. 3.3**), at 3641 and 3428 cm^{-1} were attributed to phenol O–H stretching and amine N–H stretching, respectively. Absorptions at 3076 and 2927 cm^{-1} were due to the respective aromatic C–H stretching and alkyl C–H stretching.[168] The strong peak at 1459 cm^{-1} was assigned to C–H bending. The absence of a strong peak of C=C (alkene) at $\approx 1604 \text{ cm}^{-1}$ indicates the formation of the polymer with the disappearance of the alkene motifs.[167]

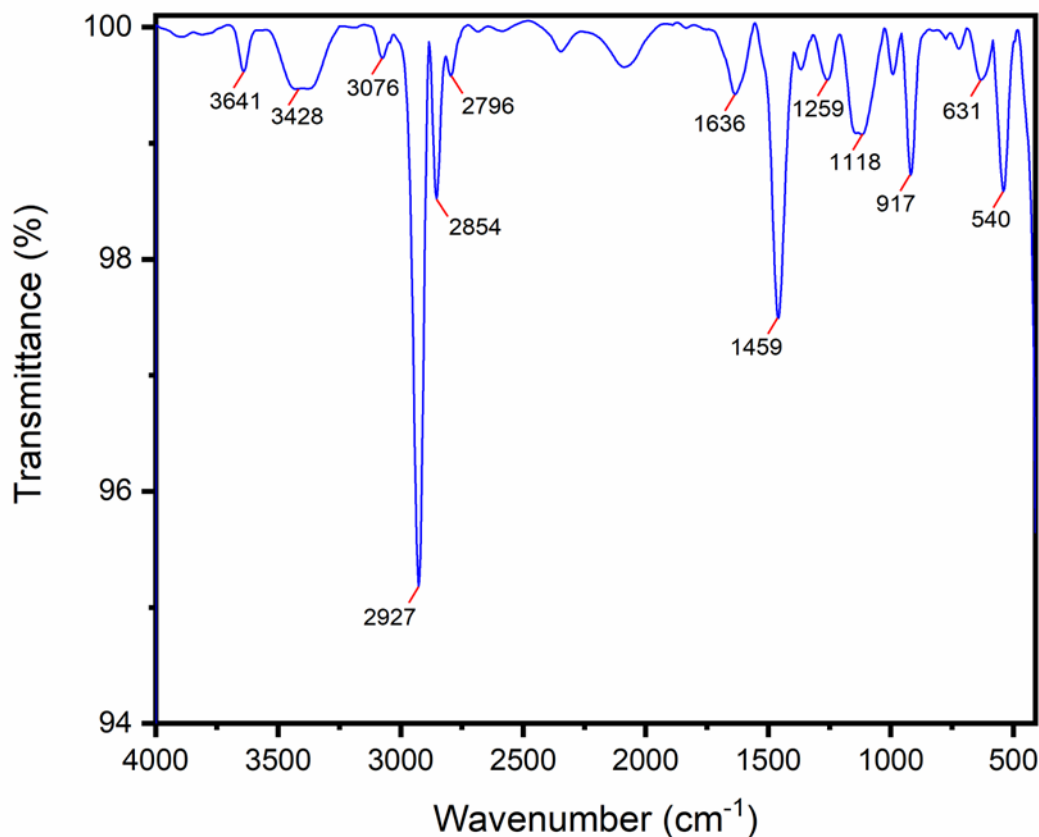


Figure 3.3. FTIR spectrum of PDDD

The proton (^1H) NMR has provided information regarding the successful synthesis of the poly(DADMAC-*co*-DTDAC-*co*-DADAHC). The disappearance of alkenes protons is key in successfully recognizing the synthesis. The absence of alkene protons in the range of 5-6 ppm confirms the absence of any residual double bond in the polymer, which suggests degradation chain transfer as the termination process involving allylic hydrogen of the monomers.[169] The three aromatic protons of DADAHC appeared as strong signals at δ 6.57, 6.65, and 6.72 ppm (**Fig. 3.4c**), while the corresponding protons in PDDD 4 (**Fig. 3.4d**), are shown in the same chemical shifts as broad signals (j, k, l). The signal of methyl protons marked 'g' is broad and overlapping in D_2O ; however, the signal is separated as a triplet in CD_3OD (**Fig. 3.4d**, inset).

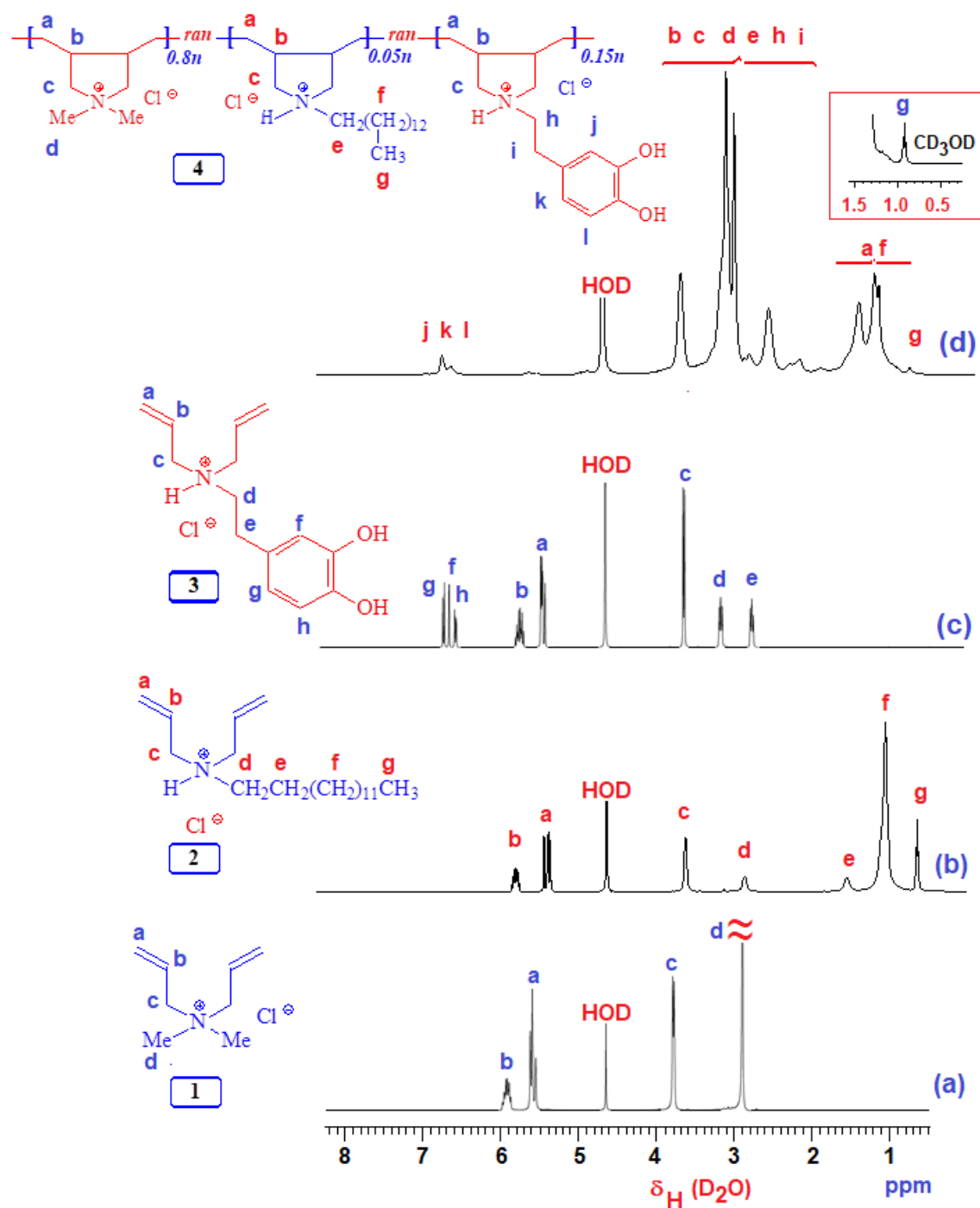


Figure 3.4. ^1H NMR spectra in D_2O of (a) DADMAC 1, (b) DTDAC 2, (c) DADAHC 3, and (d) PDDD 4.

PDDD is turbid (partially soluble) in water because it contains hydrophobic groups, so its solution viscosities were not measured.

3.3.2. Characterization of PVDF membranes

The FTIR spectra of bare PVDF and PDDD-incorporated PVDF membranes were qualitatively analyzed. The C-F stretching vibration was observed at 825 cm^{-1} for PVDF. For the pristine PVDF (M-0), the asymmetrical stretching band for the carbon backbone appeared at a vibration of 954 cm^{-1} , and for $-\text{CF}_2$, it appeared prominently at 1154 cm^{-1} .^[170] The absorption range for the fluoride-containing compound is usually exhibited strongly within $1000\text{--}1400\text{ cm}^{-1}$ (**Fig. 3.5A**). The two solid forms of α and β PVDF show the characteristic absorption bands for both phases. The β phase PVDF showed the characteristic peak at 1250 cm^{-1} .^[171] For the α phase, several absorption bands were observed at 530 cm^{-1} , 1073 cm^{-1} , 1155 cm^{-1} , and 1385 cm^{-1} as major peaks.^[172] The symmetric C-H stretching absorption peak appeared at 2887 cm^{-1} , while the asymmetric C-H stretching absorption peak was observed at 2977 cm^{-1} .^[172] The PDDD-incorporated PVDF membranes (M-1, M-2, and M-3), exhibited all the characteristic peaks of pristine PVDF membrane in the FTIR spectrum (**Fig. 3.5**). The most absorption bands of PDDD appeared within the range of the PVDF absorption bands and eventually merged with them. In the PDDD-incorporated PVDF, however, the catechol (phenol C-H stretching) absorption band was noticeable (*vide infra*). In the case of M-2, the relatively more intense absorption band appeared at 3428 cm^{-1} owing to the presence of catechol in the Polymer. This absorption band is nearly absent in the pristine PVDF (**Fig. 3.5A**).

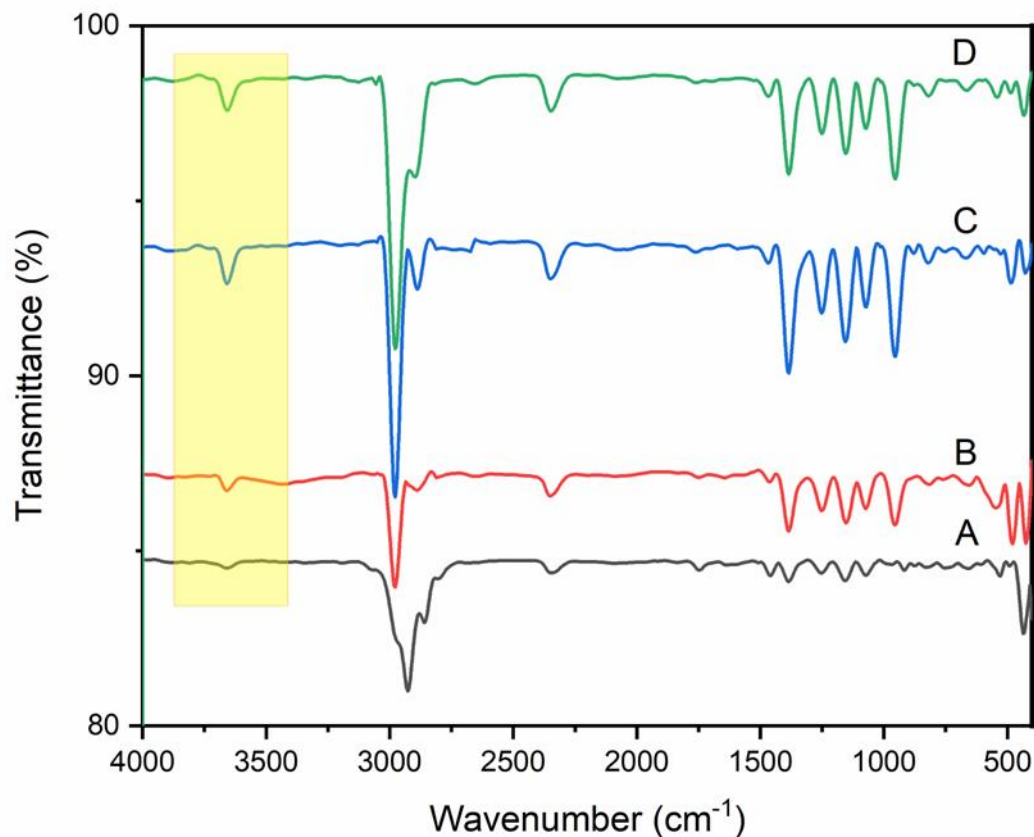


Figure 3.5. FTIR spectra of (A) M-0, (B) M-1, (C) M-2, and (D) M-3.

The TGA of modified PVDF membranes was compared with the pristine PVDF membrane. A sharp weight loss was observed at 430 °C for the pristine membrane. The modified membranes also followed the same trend (**Fig. 3.6**). This analysis confirmed that PDDD-containing PVDF membranes maintain their thermal strength, and no significant change was observed after the incorporation of PDDD. Moreover, fluorocarbon-based polymers present in PVDF membranes are thermally more stable than hydrocarbons-based due to C-F bond strength.⁵¹ The thermal stability of the pristine and modified PVDF membranes remains similar.

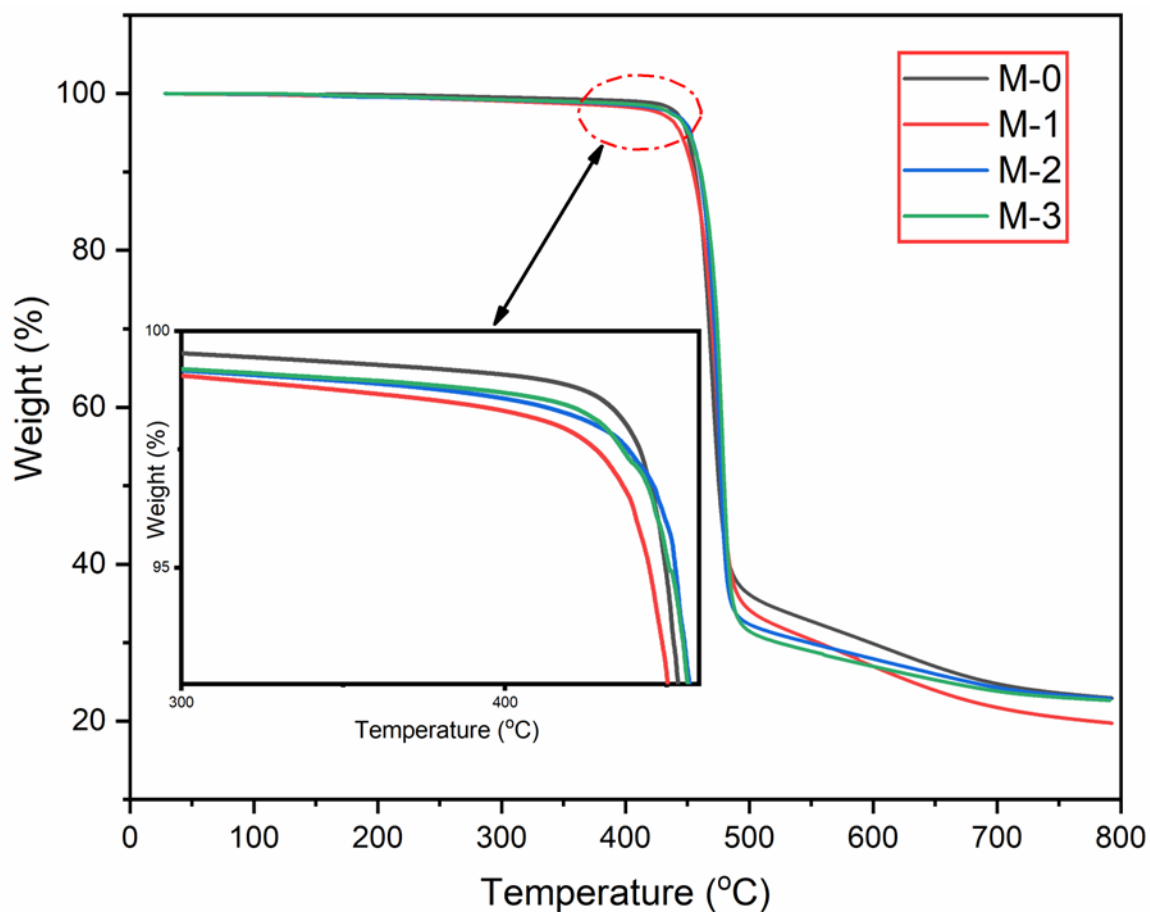


Figure 3.6. TGA curves of pristine PVDF (M-0) and PDDD-PVDF membranes (M-1, M-2 and M-3), (inset showing similar thermal stability for all membranes)

3.3.3. Morphological Analysis

The top surface and cross-section of the pristine PVDF and amphiphilic copolymer-containing membranes with various concentrations were examined by SEM, and the results are shown in **Fig. 3.7**. As shown, the top surface of pristine PVDF has relatively less porosity because of the absence of amphiphilic PDDD. The SEM images of modified PVDF membranes indicated the surface micropores as well. The size and the number of surface pores for PDDD-PVDF membranes were increased, as noticed due to the presence of functional groups present in the amphiphilic polymer. In fact, as the

concentration of PDDD is raised in the PVDF membranes, the porosity of the membranes also increases owing to the enhancement in phase inversion rate. The gradual increase in the number of pores can be observed in **Fig.3.7**, in the order: M-3>M-2>M-1.

The SEM images of the cross-section of the membranes demonstrated an asymmetric structure. The top skin layer has a finger-like structure and a spongy sub-layer. The bare PVDF membrane has shown a thick skin layer and relatively high porosity with fewer finger-like projections.[133,173] The finger-like structures in PDDD-PVDF-modified membranes developed more as the concentration of PDDD increased (**Fig.3.7**). The phase inversion mechanism described the changes in the structure and morphology of the membranes. The casting solution's thermodynamic stability declined due to the amphiphilic PDDD, leading to a higher phase separation rate. The polymer containing amphiphilic groups influenced the kinetics of phase separation [174,175]. The pristine PVDF consists of a more sponge-like structure, indicating a slow exchange of the solvent and non-solvent during the phase inversion process due to the low hydrophilicity of the PVDF polymer. The SEM results proved that the PDDD-PVDF membranes showed high porosity on the top surface and more extended finger-like channels in the cross-section. The high pores on the top surface indicated the presence of amphiphilic groups in the PDDD, while longer-developed finger-like structures are due to the faster mass transfer that occurred during the phase inversion mechanism. The rapid mass transfer is due to the amphiphilic copolymer system, and a major role is played by its hydrophilic moieties. The presence of the hydrophobic group enhances the compatibility with the PVDF membrane, while the hydrophilic groups improve the overall flux and mechanical strength of the PDDD-PVDF membranes.

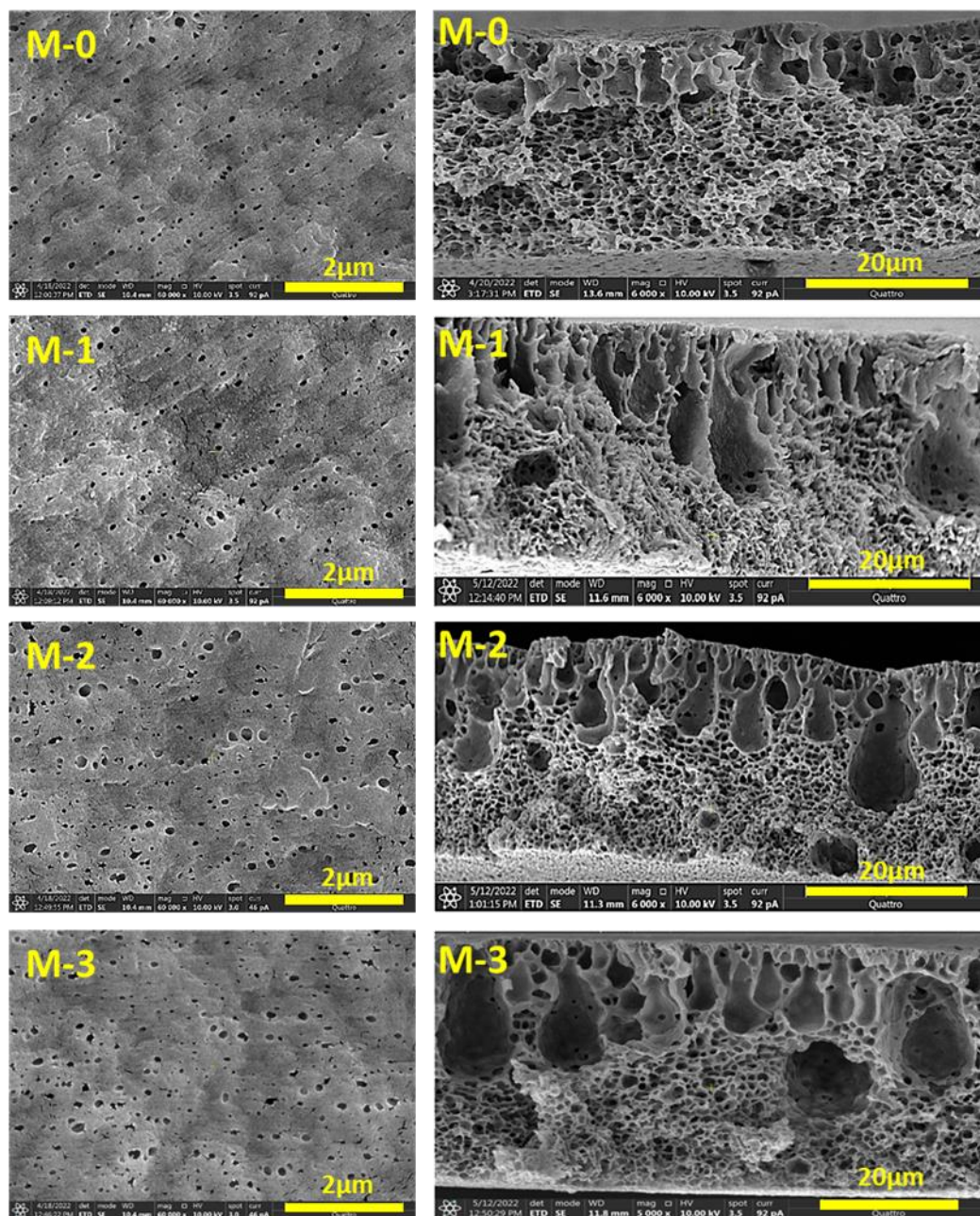


Figure 3.7. The SEM images of various membranes' top surface (Left) and Cross-section (Right)

The elemental mapping of pristine PVDF and modified PDDD-PVDF was conducted to confirm the presence of specific elements in the membranes. The pristine PVDF showed only carbon (49.0 wt %) and fluorine (51.0 Wt %), as expected for PVDF (C-F) structure. The gold (Au) coating on the membrane was used for conductance (**Fig.3.8**).

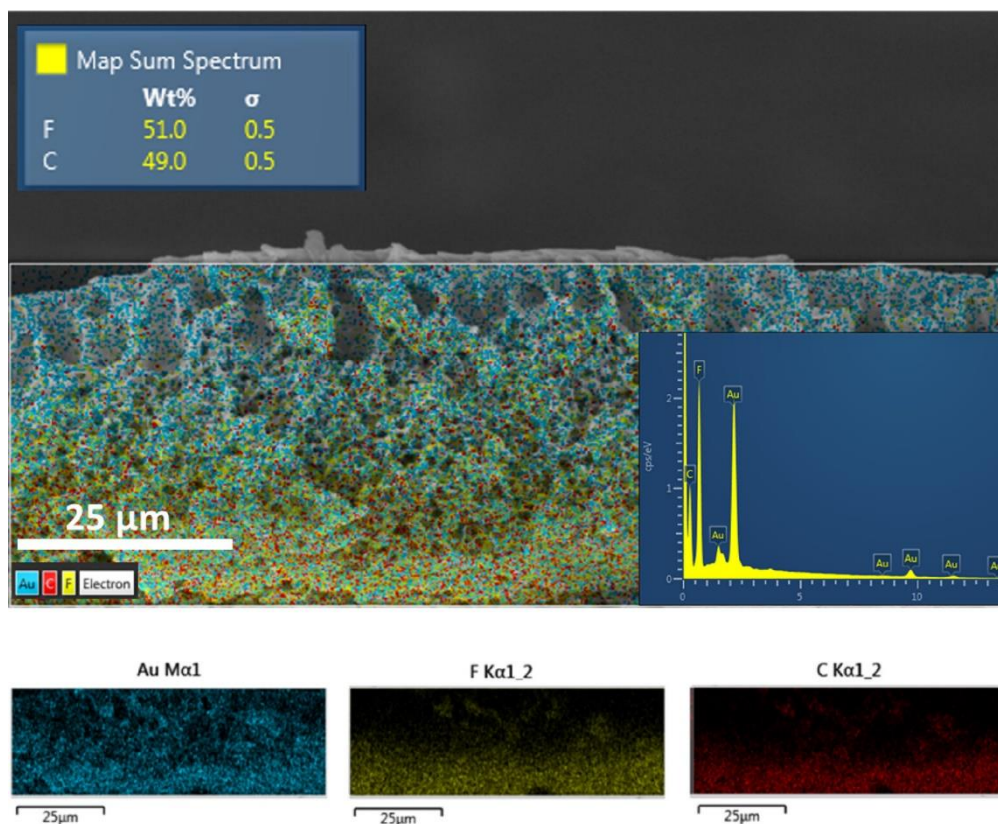


Figure 3.8. Mapping of pristine PVDF membrane and elements distribution

The elemental mapping of M-2 confirmed the presence of Fe, N, O, F, and C. The N, O, and C values proved the presence of quaternary ammonium motifs in the copolymer, catechol-containing DADAHC monomer, and hydrophobic chain of DTDAC monomer, respectively. The Fe is used during the modification of membranes to interact with catecholic motifs. The following findings confirm the presence of the amphiphilic copolymer in the fabricated PDDD-PVDF membrane (**Fig.3.9**).

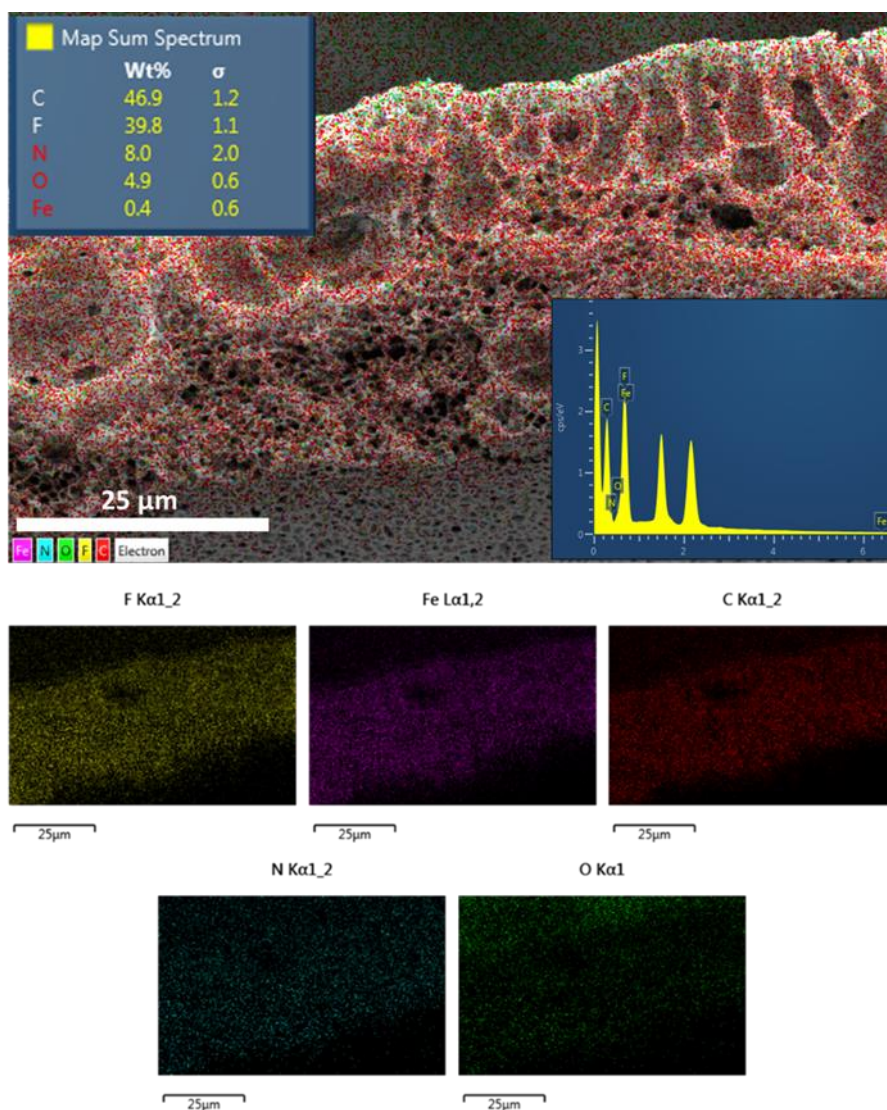


Figure 3.9. Mapping data of M-2 PDDD-PVDF membrane

The surface chemistry and the roughness of the membranes play a critical role in controlling the interaction of the oil with the membrane surface. AFM analysis was performed to determine the three-dimensional morphologies of the pristine and the PDDD-incorporated PVDF membranes. In 3D AFM images, the ridges and the valleys can be recognized by the light and the dark areas, which appeared owing to the roughness of the membrane (**Fig 3.10**). Initially, the roughness of the membranes decreased with the incorporation of the PDDD from 26.6 nm to 17.6 nm. The further increase of the PDDD

membranes increased the surface roughness, and the surface roughness for the M-2 and the M-3 membrane was observed at about 96.8 and 166 nm, respectively. As the roughness directly relates to the surface area and in these membranes later on, more permeation fluxes were observed compared to the M-0 and M-1 membranes.

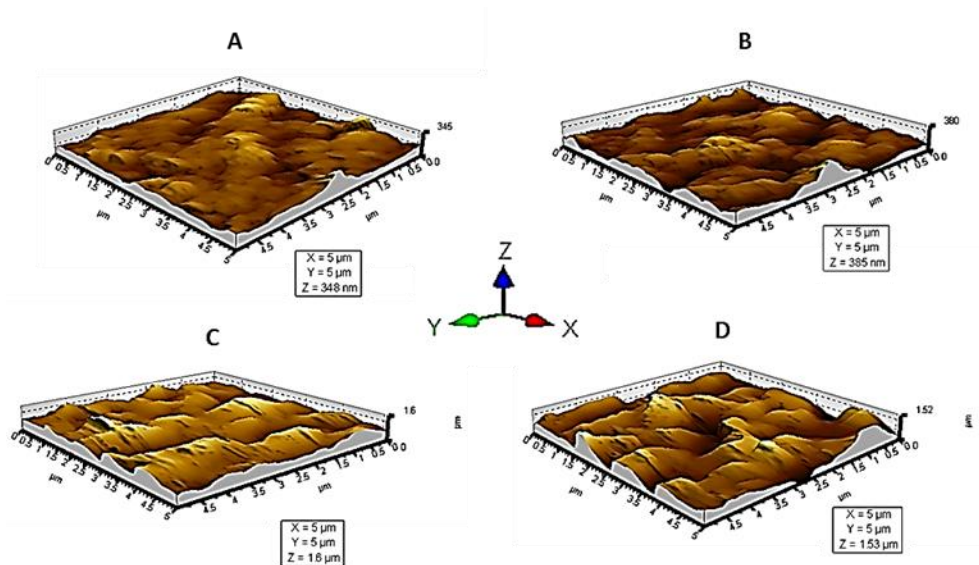


Figure 3.10. AFM analysis of the (A) M-0, (B) M-1, (C) M-2, and (D) M-3 membranes

3.3.4. The hydrophilicity of PVDF membranes

The performance of pristine PVDF membranes for wastewater treatment is hindered due to their hydrophobic nature. In separating the oil-in-water emulsion, two factors play a critical role (a) surface wettability,[176] and (b) suitable pore size; both of these factors work synergetically to provide maximum separation while dealing with the oil-in-water emulsions. The pristine PVDF membrane (M-0) has shown a high water contact angle of 87.6° , showing less affinity towards the water. After the incorporation of PDDD in PVDF membranes, the water affinity of the membranes increased as the PDDD contains the hydrophilic moieties, which contribute to reducing the water contact angle on the

membrane surfaces. The reduction has been consistent with increasing order of PDDD concentration, and the water contact angle is reduced from 87.6° to 54.6° (**Fig. 3.11**). In PDDD polymer, the presence of quaternary ammonium and catecholic motifs triggers a decrease in contact angle, leading to an overall increase in the hydrophilicity of the PVDF membranes that is necessary to improve their performances.

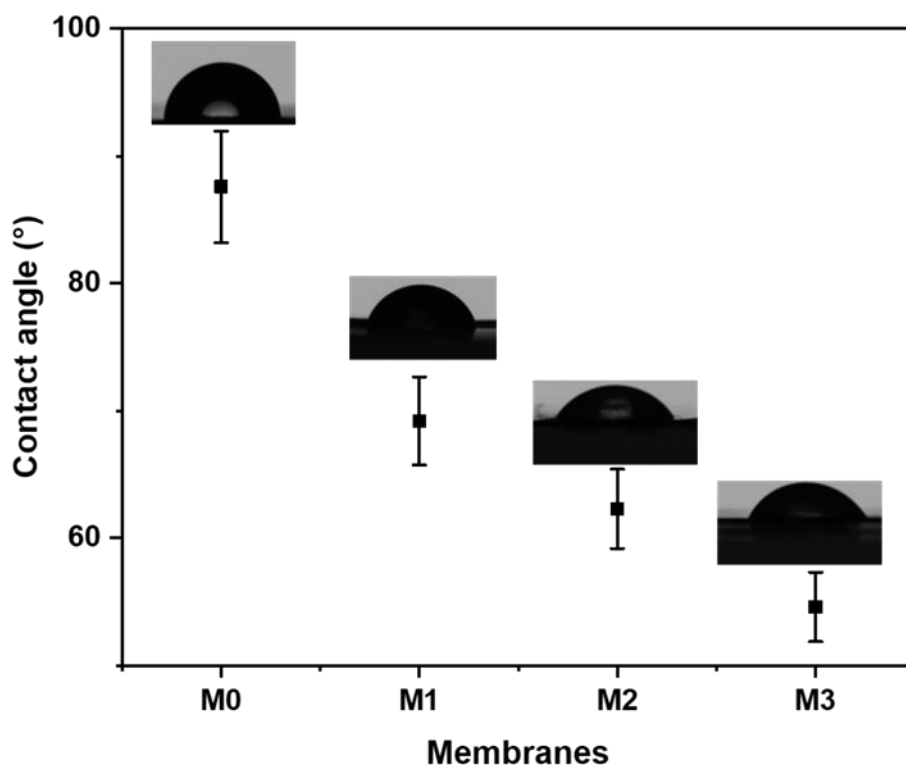


Figure 3.11. Water contact angle on the pristine and PDDD-PVDF membranes surfaces

3.3.5. Separation performance of the pristine and the PDDD-incorporated PVDF membranes

From the water contact angle and the SEM analysis, the PDDD incorporation into the PVDF significantly impacts the membrane hydrophilicity, thereby introducing the finger-like projections into the PVDF membranes. The permeation flux of the feed was measured at a different pressure to see the impact of the transmembrane pressure on the

water permeance through the membranes. The flux (J) of the permeate was calculated according to **Eq. 3.1**, [177]:

$$J = \Delta V / (A \times \Delta t) \quad (3.1)$$

where V (L) is the volume of permeate, A (m^2) is the effective surface area of the membrane, and t (h) is the permeation time. Using 250 ppm of an oil-in-water emulsion, the permeation fluxes of the pristine and the PDDD-incorporated membranes were analyzed. The pressure has a direct impact on the permeation flux; with the increase of the transmembrane pressure from 0.5 bar to 3 bar, the permeation flux of all the membranes improved. However, the PDDD-incorporated membranes have shown a higher permeation flux than the pristine PVDF membranes. At a pressure of 3 bar, the permeation flux of M-1, M-2, and M-3 membranes increased up to 55%, 90%, and 95% compared to the pristine PVDF membrane (M-0). The order of membrane flux was $M-3 > M-2 > M-1 > M-0$ (**Fig. 3.12A**).

The separation efficiency of the pristine and the PDDD-incorporated PVDF membranes was analyzed at the transmembrane pressure of 2 bar. The separation efficiency of the various membranes was calculated according to **Eq. 3.2**, [178]:

$$E (\%) = \left(1 - \frac{C_p}{C_o} \right) \times 100\% \quad (3.2)$$

where E is the percentage of separation efficiency, and C_p and C_o are oil content in permeate and feed, respectively.

The separation efficiency of the pristine and the PDDD-incorporated PVDF membranes revealed that the separation efficiency was significantly impacted by changing the concentration of the PDDD. Incorporating the PDDD improved the separation efficiency

by 99%, whereas, in the absence of the PDDD, the separation efficiency of the pristine PVDF (M-0) membrane was observed at about 92%. The low separation efficiency of the PVDF is due to its high affinity towards oil, which allows the slippage of the oil during the separation of the oil-in-water emulsion. Incorporation of 0.25% and 0.5% of PDDD into the PVDF improved the separation efficiency to 97% and 99%, respectively. However, further incorporation has a negative impact on the separation efficiency of the membranes, and the rejection dropped to 88%. The order of rejection of various membranes was $M-2 > M-1 > M-0 > M-3$. The rejection efficiency of pristine PVDF (M-0) is observed to be around 92%, while for M-1, M-2, and M-3, it was 97%, 99%, and 88%, respectively. From the separation efficiency of the membranes, it is clear that the PDDD incorporation into the PVDF improved the permeation flux and the separation efficiency. The addition of PDDD in pristine PVDF membrane thus enhanced the rejection efficiency for M-1 and M-2 (**Fig. 3.12**).

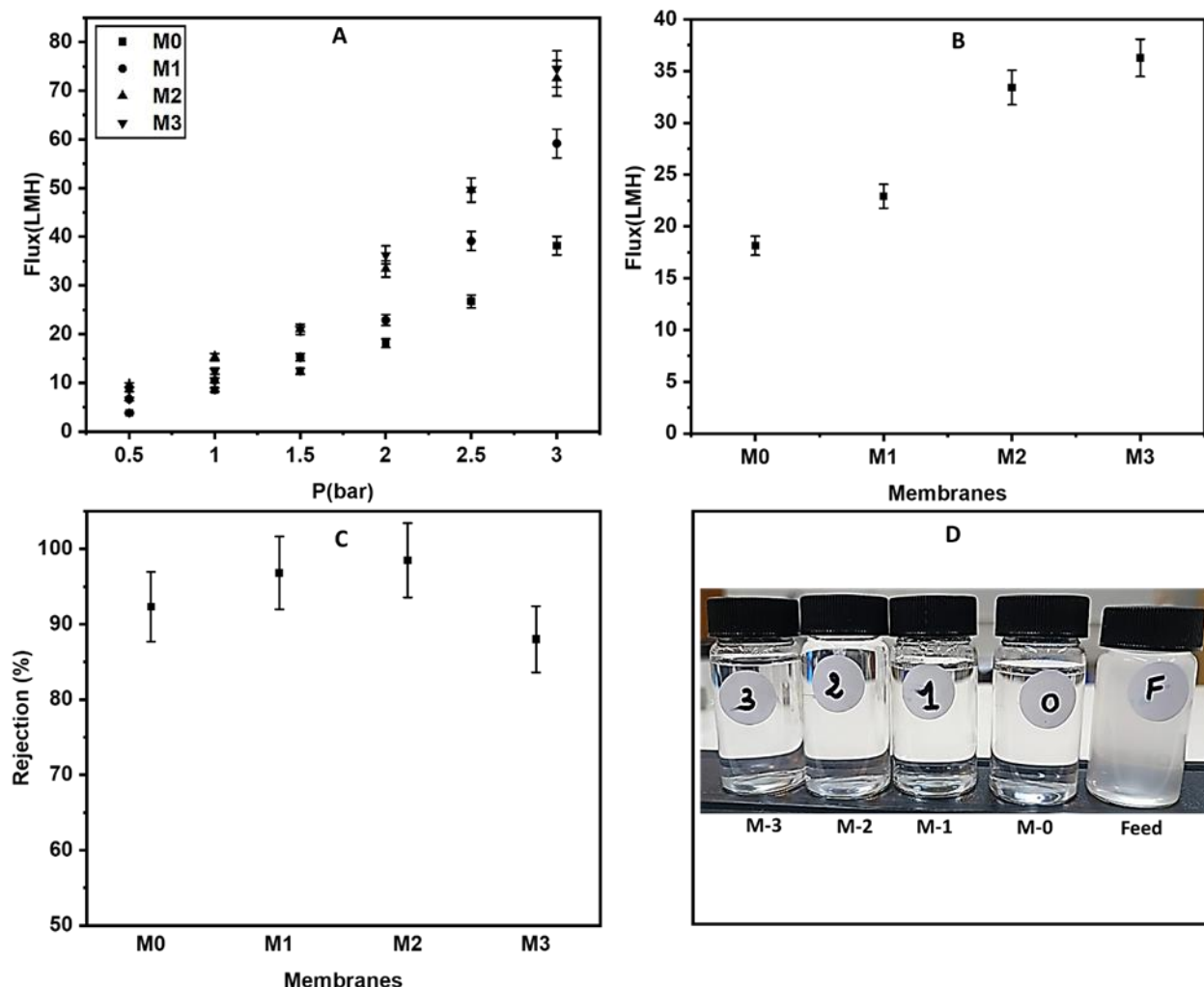


Figure 3.12. (A) Permeation flux of the oil-in-water emulsions at different transmembrane pressure. (B) Permeation flux and (C) Membrane rejection performance at a transmembrane pressure of 2 bar. (D) Photographs of the feed and the permeate of the pristine and the PDDD incorporated membranes

Furthermore, the size distribution of the oil droplets in the oil-in-water emulsions has been shown in **Fig. 3.13**. In **Fig. 3.13A**, it can be seen that the size of the oil droplet varied from 20 to 500 nm. There is an obvious difference in the optical images of the feed and permeate of the various membranes. The optical image of the feed (oil-in-water emulsion) revealed the presence of extensive tiny oil droplets, which were observed all over the image. However, in the optical images (**Fig. 3.13D-F**) of the permeate of the PDDD-incorporated membranes, no oil droplets appeared, which is evidence that the

synthesized PVDF membranes successfully removed the emulsified oil droplets from the oil-in-water emulsions and possessed a great potential to effectively treat the stabilized oil-containing wastewater.

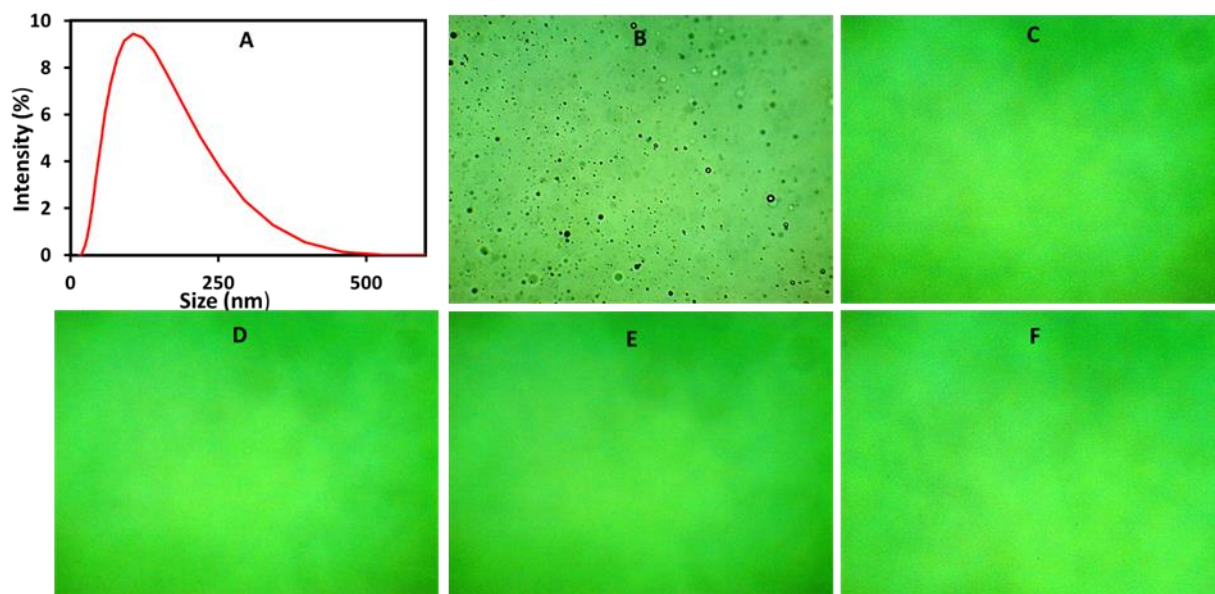


Figure 3.13. (A) Particle size analysis (B) microscopic image of the feed. Microscopic images of the permeate (C) M0, (D) M1, (E) M2, and (F) M3

The anti-fouling characteristics of the PVDF membranes were observed by evaluating the tendency of the membrane to recover their initial flux after a certain duration of the continuous operation of the membranes. The flux recovery ratio (FRR) was calculated using **Eq. 3.3**, [179]:

$$FRR (\%) = \left(\frac{J_{w1}}{J_{w2}} \right) \times 100\% \quad (3.3)$$

where the J_{w1} is the initial permeation flux before fouling, and the J_{w2} is the permeation of the flux restored after the cleaning of the fouled membrane surface. The pristine and the PDDD-incorporated PVDF membrane's flux restoration capability was measured by using the membranes for 6 hours to separate the oil-in-water emulsions, and after every 1

hour, the fresh feed is introduced to avoid a significant change in the concentration of the feed in the dead-end cell. A continuous decline in the flux of the pristine PVDF membrane was observed, and after washing with the deionized water, the flux recovery ratio was only 47% to the initial flux of the pristine membranes, whereas the PDDD-incorporated PVDF membrane showed excellent flux recovery ratios (**Fig. 3.14A**). The M-1 has shown a flux recovery ratio of 81% which was improved to 92% in the case of the M-2 membrane. However, a further increase in the concentration of the PDDD into the membrane (M-3) resulted in a slight decline in the FRR (89%) but significantly higher than the pristine PVDF membrane. A similar trend was observed when the fouling analysis was performed with the CTAB, a positively charged organic model of foulants. The fouling study of the pristine and the PDDD incorporated membranes was continuously performed for 6 hours using the cross-flow system containing the feed consisting of 25 ppm of CTAB. After 6 hours of fouling, all the membranes were washed with double distilled water for 1 hour in the cross-flow system to observe their flux recovery. The least flux recovery was observed in the case of the pristine PVDF membrane, which almost lost more than 50 % of its flux after cleaning, whereas the PDDD-PVDF membranes flux recovery improved as the concentration of the PDDD increased except for M-3 membranes (**Fig. 3.14B**). PDDD produces an electrostatic repulsion towards the CTAB, due to the presence of the quaternary ammonium motifs, thereby reducing the tendency of the CTAB to permanently adhere to the membrane surface. The more higher concentration of the PDDD in the PVDF membrane might lead toward phase separation during the phase inversion process, negatively affecting the membrane, which can result in the lower rejection and anti-fouling characteristics of the

M-3 membrane. The PDDD polymer is equipped with advanced functionalized motifs, which irreversibly prevent the PDDD-incorporated PVDF membrane from fouling.

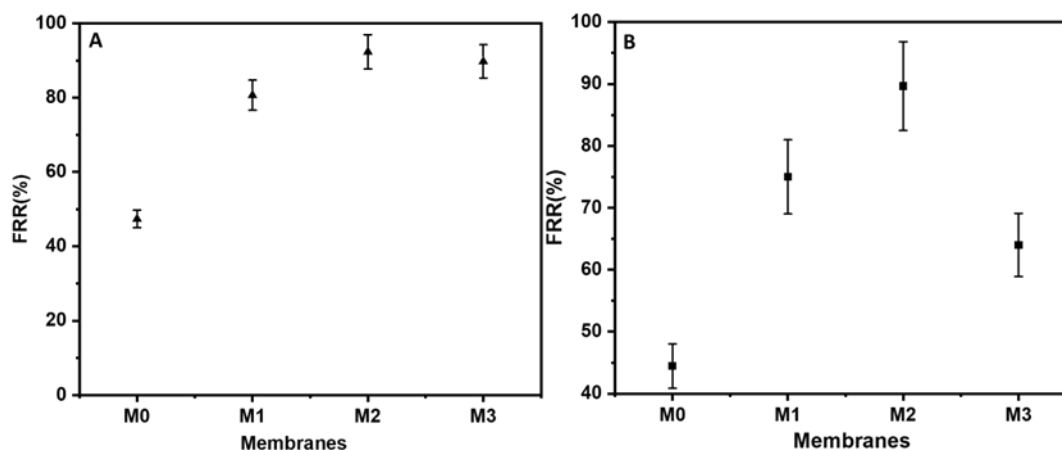


Figure 3.14. Anti-fouling characteristics of the various membranes. Flux recovery of the pristine PVDF and the PDDD-PVDF after 6 hours of fouling of the membranes with (A) oil-in-water emulsions and (B) CTAB foulants in water.

3.3.6. The possible mechanism involved in improved performance of the PDDD-incorporated PVDF membranes.

The PDDD polymer is rationally designed for the successful incorporation into the PVDF polymer materials to develop the PDDD-PVDF membranes. The PVDF membranes are hydrophobic in nature and show less affinity towards the water and more affinity towards the oil, which results in the severe fouling of the membranes during the separation process, and it can be witnessed through the poor flux recovery ratio of the pristine PVDF membranes (**Fig. 3.14**). The poly(DADMAC-co-DTDAC-co-DADAHC) (PDDD) is synthesized from three monomers, and each one has a certain role in the PVDF membrane to improve its performance. The monomer *N,N*-diallyldimethylammonium chloride (DADMAC), is responsible for enhancing the hydrophilicity of the membranes, and it provides better interaction with water and formation of the hydration layer by

interacting with the water through the permanent positive charge and builds strong electrostatic interaction with water. In some studies, it has been reported that the surface containing the positive charge performs better in the demulsification of oil-in-water emulsions.[180] The hydration layer provides a facile opportunity for the permeation of the water and rejects the oil, which results in the demulsification of the oil-in-water emulsion. The PVDF is a hydrophobic polymer, and the addition of hydrophilic polymers usually results in phase separation during the phase inversion process, which may result in severe defects in the membrane, negatively impacting the separation efficiency of the membranes. In the designing of the PDDD polymer, a *N,N*-diallyltetradecan-1-ammonium chloride (DTDAC) monomer is used to enhance the polymer stability in the PVDF membrane. The DTDAC monomer carries hydrophobic motifs, which help the PDDD polymer to be compatible with the hydrophobic PVDF. The third muscle-inspired monomer, *N,N*-diallyldopamine hydrochloride (DADAHC), incorporated into the PDDD polymer, tends to form a coordinated complex with the Fe^{3+} , thereby further contributing to ensuring the stability and hydrophilicity of the permeation channels of the PVDF membrane (**Fig. 3.15**).

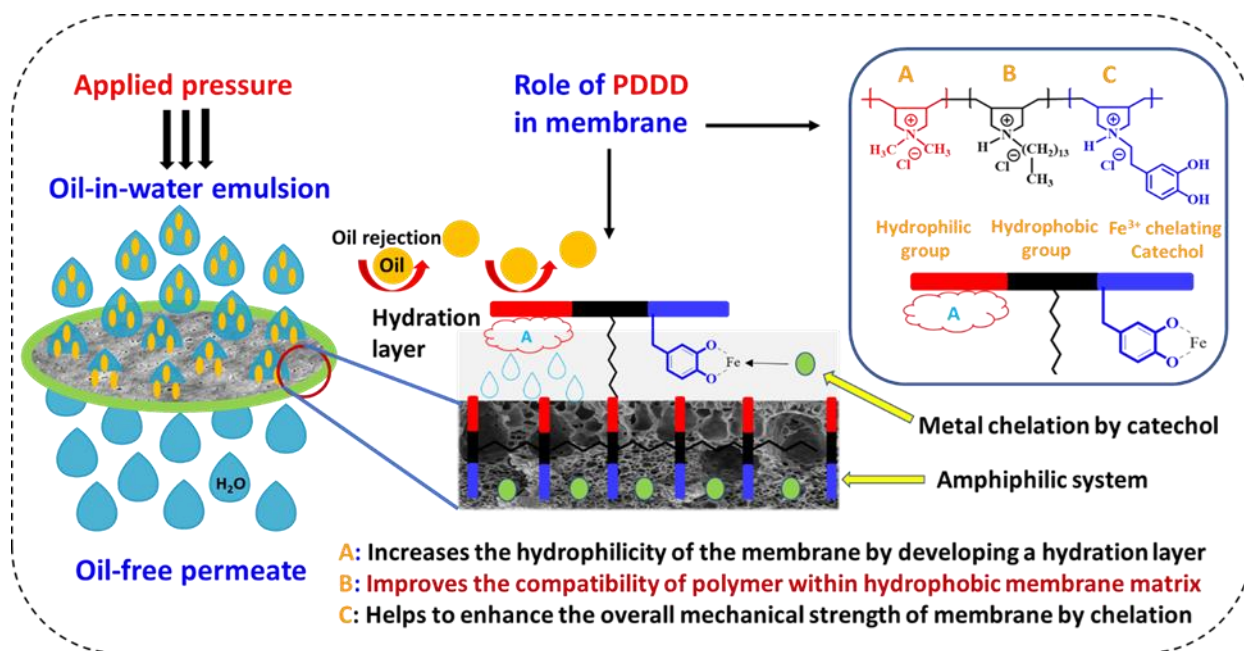


Figure 3.15. Mechanism and role of various components of the PDDD polymer in PDDD-PVDF membrane

The interaction of iron with catechol and its derivatives is very common. The complex formation was confirmed by finding out their $\lambda_{\max}$ with the help of UV-Vis spectrometry. The developed complex has shown a prominent absorbance band in the range of 385-800 nm,[181][182] because of the ligand-to-metal charge transfer event. At different pH, the iron forms different complexes with the catechol group, which display different complex states with different colors depending on the availability of the deprotonated catechol groups. In this work, as DADAHC contains a catechol group, the iron added during the coagulation process of the modified membranes leads to this complexation. The model experiment was conducted with DADAHC and ferric ions solutions to observe the Fe^{3+} chelation. The mono complex was immediately formed when the pH was less than 4, which gave dark green color, while when the pH was adjusted to more than 9, a reddish tris complex was observed. The $\lambda_{\max}$ for the acidic solution complex was 681 nm, and for

the basic solution, it was 490 nm (**Fig. 3.16**). This absorbance band at different pH was according to the precedent literature.[183][184]

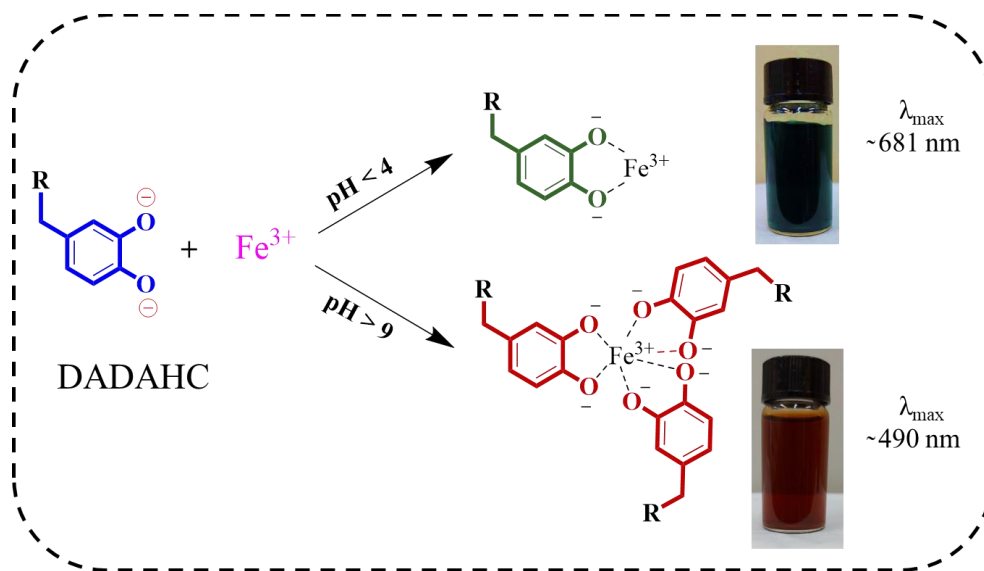


Figure 3.16. Complexation of the N,N-diallyldopamine hydrochloride (DADAHC) with the Fe^{3+}

The Fe^{3+} was introduced in the phase inversion process through the coagulation bath,[185] the Fe^{3+} moved along with the non-solvent during the solidification of the membranes. The migrated Fe^{3+} into the PDDD-PVDF matrix can be coordinated with the catechol-containing motifs, which enhances the hydrophilicity of the PDDD-PVDF membrane channels. Thus, the designed PDDD polymers consist of advanced motifs responsible for enhanced separation performance and anti-fouling characteristics of the membranes.

3.4. Conclusion

The stabilized oil-in-water emulsion is considered highly toxic for aquatic life. Membrane-based technologies are considered effective in eliminating the oil from industrial wastewater. Still, the rapid fouling and low permeation flux are considered the

major hurdles in the scale-up of these technologies. Herein, an advanced terpolymer, PDDD, is introduced to improve the efficiency of the PVDF membranes. The designed polymer was equipped with three kinds of motifs: (a) quaternary ammonium groups to enhance the membrane affinity towards water, (b) hydrophobic motif to improve the compatibility of the PDDD polymer with the PVDF membrane, and (c) muscle-inspired catechol motifs which provide the hydrophilicity to permeation channels by coordinating with the Fe^{3+} during the coagulation process. After incorporating the PDDD polymer, the hydrophilicity of the membranes was improved, and the water contact angle reduced significantly from 87.6° to 54.6° . PDDD substantially enhanced the membranes' separation efficiency, reaching more than 99% while treating the oil-in-water emulsions. The flux recovery ratio of the PVDF membrane was considerably improved from 47% to 92%. The FRR was calculated after 6 h of separating the oil-in-water emulsions. The pristine PVDF membrane has a strong affinity towards oil which result in the formation of the compact cake layer, whereas the synergy of the DADMAC, DTDAC, and DADAHC prevents the permanent fouling of the surface during the oil-in-water emulsion separation.

CHAPTER 4

β -Cyclodextrin-derived diallylamine salt: Synthesis and its Copolymerizations

Zeeshan Arshad, Shaikh A. Ali, β -Cyclodextrin-derived diallylamine salt: Synthesis and its Copolymerizations, *Carbohydrate Polymers*, Submitted.

Abstract

A diallyl amine salt monomer bearing β -CD substituent has been cyclopolymerized for the first time. Thus, 6-O-toluenesulfonyl- β -cyclodextrin $-\text{[(C}_6\text{H}_{10}\text{O}_5)_6\text{-(C}_5\text{H}_7\text{)]-CH}_2\text{OTs}$ upon reaction with diallylamine followed by protonation afforded diallylamine salt monomer $-\text{[(C}_6\text{H}_{10}\text{O}_5)_6\text{-(C}_5\text{H}_7\text{)]-CH}_2\text{NH}^+(\text{CH}_2\text{CH=CH}_2)_2 \text{Cl}^-$ (**I**). Cyclopolymerization of monomer **I** and its copolymerization with monomers $[\text{Me}_2\text{N}^+(\text{CH}_2\text{CH=CH}_2)_2 \text{Cl}^-]$ (**II**) or $[\text{O}_2\text{CCH}_2\text{NH}^+(\text{CH}_2\text{CH=CH}_2)_2]$ (**III**) or $[\text{H}_2\text{O}_3\text{PCH}_2\text{NH}^+(\text{CH}_2\text{CH=CH}_2)_2 \text{Cl}^-]$ (**IV**) or $[\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{NH}^+(\text{CH}_2\text{CH=CH}_2)_2 \text{Cl}^-]$ (**V**) gave a series of copolymers having residues of β -CD and glycine or methyl phosphonate or aspartic acid. Terpolymerization in the presence of SO_2 afforded polymers with alternate placement of the SO_2 units. Solution properties of the pH-responsive polyzwitterions including viscosity have been examined. Water-insoluble terpolymer **I/V/SO**₂ having 20 mol% β -CD residues has been shown to remove organic micropollutant 2-naphthol by host/guest complexation. The work has paved the way for possible synthesis of cross-linked polymers that would simultaneously remove organic micropollutants and toxic metal ions (by complexing with chelating ligands of glycine, aspartic acid, aminomethyl phosphonate) from contaminated aqueous bodies.

Keywords

Diallylamine salts, β -Cyclodextrin, Cyclopolymerization, Micropollutants, Polyzwitterions, Ionic polymers

4.1. Introduction

Cyclic oligosaccharide β -Cyclodextrin (β -CD), composed of seven glucopyranose units bonded by α -1,4 glycosidic linkage, takes the shape of a truncated cone where the apex is replaced by a plane parallel to the base (**Scheme 4.1**) [186]. The secondary OH groups remain in the bigger cavity while the primary OH groups stay in the smaller cavity (**Scheme 4.1**, inset). U.S. FDA considers the cyclodextrin as safe [187,188]. β -CD, produced by enzymatic degradation of starch, has an inner lipophilic cavity having a diameter of 0.60-0.65 nm wrapped up by hydrophilic peripheral [188,189]. The hydrophilic nature of the exterior of cyclodextrin or its complexes imparts water-solubility and insolubility in typical organic solvents.

Easy availability and applications in the fields of drug delivery, pharmaceutical industry, biosensors, tissue engineering, water treatment, etc. make β -CD an attractive natural material [186]. β -CD is used as a stationary phase in HPLC chromatography [190]. In drug delivery, the cyclodextrins confer solubility and stability to a variety of hydrophobic drugs in the process of formation of inclusion compounds, which are then able to penetrate body tissues to deliver biologically active functional groups [191,192]. β -CD forms intramolecular H-bonds involving secondary OH groups owing to which it has poor water-solubility [32,193]. Each glucopyranose unit has sterically crowded two

secondary OH groups, while the primary OH at C-6 faces less steric encumbrance. Chemical modification of cyclodextrins via methylation, tosylation, etc. helps to manipulate their host-guest behavior [34,191]. The water-soluble inclusion complexes were made by β -CD with cholesterol to manufacture cholesterol-free products. The cholesterol moiety (hydrophobic) does go into the interior of the cyclodextrin [194]. A book chapter describes the emerging usage of cyclodextrin systems in the food industry [195]. Host-guest inclusion complexes of β -CD with several vitamins have been explored [196]. The use of cyclodextrins primarily as a reliable and powerful mode of transport for drug delivery has been reviewed [197].

Water resources are under threat owing to the presence of micropollutants (organic moieties in low concentration). A porous polymer based on cyclodextrins has been demonstrated to have a high affinity towards micropollutants resulting in high uptake of them [198]. A mesoporous polymer of high surface area having stiff aromatic groups has been generated by crosslinking β -CD [199]. The encapsulation and removal of micropollutants from the water *via* adsorption method have been reported for the polymer.

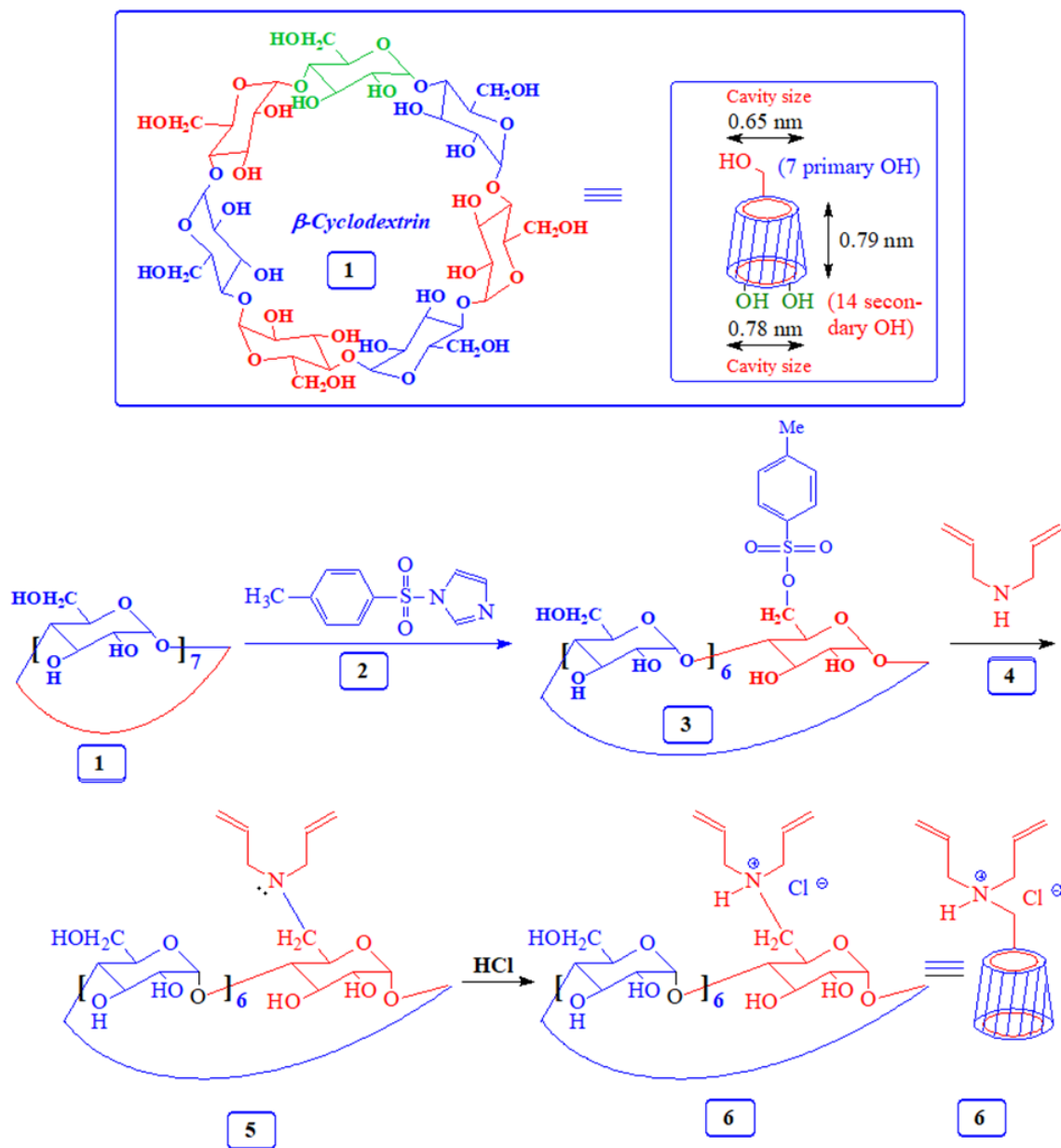
Crosslinked hydrogels of β -CD and poly β -CDs have been synthesized *via* reaction of -OH groups with -COOH, -COCl, epoxides, and -NCO [200–202]. Modification of hydroxyl groups of β -CD to accommodate vinyl motifs and their free radical polymerization (FRP) leads to poly(β -CDs) bearing CD motifs as pendants [203–205]. ‘Click’ reaction involving azide/alkyne cycloaddition has been explored for the probable formation of a thermoresponsive hydrogel [206]. The inner hydrophobic cavity of the β -CD in CD-based polymers can play host to numerous organic compounds [207]. The -OH

of β -CD groups has been modified using common organic reagents [208]. A methyl methacrylate monoester of β -CD has been copolymerized with *N*-isopropyl acrylamide via FRP [209]. A bis-acrylate ester of β -CD upon polymerization with acrylic acid and *N*-isopropyl acrylamide led to the formation of thermo and pH-responsive hydrogels [210].

FRP of *N*, *N*-diallyl quaternary ammonium salts, known as Butler cyclopolymerization protocol, afforded numerous industrially important ionic polymers [211–216]. The cyclopolymerization in the presence of cross-linker leads to the generation of a multitude of resins, which were found to be efficient for the remediation of priority metal ions and dyes [217]. The objective of this work is to synthesize a β -cyclodextrin-based diallyl amine salt monomer **6** (**Scheme 4.1**) and its scope of copolymerization with other diallyl amine salt monomers as well as terpolymerization with SO₂. The incorporation of SO₂ radical (i.e. sulfonyl radical) during the chain propagation reduces the rigidity and increases the solubility of the propagating chain resulting in increased polymer yields [218]. The novelty of the work would include the synthesis of the novel β -CD-based monomer and its polymerization will represent the first example of FRP using Butler cyclopolymerization protocol. Unlike β -cyclodextrin-based acrylic monomers, which are labile to undergo hydrolysis under alkaline pH, monomer **6** being attached to β -cyclodextrin through a robust C-N bond at C-6 is expected to be stable.

Butler cyclopolymerization protocol has etched a place of distinction to generate the eighth most important architecture of industrially important synthetic polymers whose backbones are embedded with five-membered pyrrolidine ring [219,220]. We hypothesize that the synthesis of new β -CD-based monomer **6** and its

cyclopolymerization and copolymerization with several hydrophilic monomers having chelating motifs could generate a multitude of cyclopolymers with improved hydrophilicity. Incorporation of β -CD motifs and metal-ion chelating ligands in the same polymer backbone would pave the way to develop cross-linked resins for simultaneous remediation of organic contaminants as well as priority metal ions.



Scheme 4.1. Generation of β-cyclodextrin-derived diallyl amine salt

4.2. Experimental

4.2.1. Materials

Azoisobutyronitrile (AIBN) (crystallized from chloroform-ethanol) and imidazole were purchased from Fluka Chemie AG. β -Cyclodextrin (β -CD), p-toluenesulfonyl chloride, diallylamine, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPD), ammonium persulfate (APS), diallyldimethylammonium chloride **7**, and dimethylsulfoxide (DMSO) ($\geq 99.5\%$) were purchased from Sigma-Aldrich. Membranes having molecular weight cut-off (MWCO) of 3500 and 6000-8000 were purchased from Spectra/Por (Spectrum Lab., Inc.) and used for dialysis against distilled water. Monomers diallylaminomethylphosphonic acid (**12**) [221], *N*, *N*-diallylaspartic acid hydrochloride (**15**), [222] and diallylammonioethanoate (**10**) [223] were synthesized as described. Tosyl imidazole **2** was prepared as described [88] in 90% yield (mp 78-79 °C, lit. [88] 78.0-79.0°C).

4.2.2. Physical methods

Perkin Elmer instrument (Series II Model 2400) was utilized to record FTIR spectra. Elemental analyses were carried out in a Perkin Elmer (16F PC) spectrometer. The samples for elemental analysis were dried in vacuo at 60 °C for 6 h. An SDT analyzer (Q600: TA Instruments) was used under a flow of N₂ for Thermogravimetric analysis (TGA). NMR spectra were measured in A Bruker AvanceIII 400 MHz spectrometer using signal of HOD protons at δ 4.65 and ¹³C dioxane signal at δ 67.4 ppm as internal standards. ³¹P was referenced with 85% H₃PO₄ in DMSO. An Ubbelohde viscometer

(Constant = 0.005 cSt/s) under N₂ was used to measure viscosity at 30.0±0.1°C. The temperature was controlled by a CT72/P (SI Analytics, Germany) water bath. Viscosity measurements were at least triplicated to obtain time with an average error of <0.2%. CO₂-free distilled water was used for viscosity measurements.

4.2.3. Synthesis of 6-O-toluenesulfonyl-β-CD 3

A modified procedure [88] is described. In a RB flask (2 L), β-CD **1** (40 g, containing ≤ 14 % water, 30.3 mmol) was dissolved in water (900 mL) by stirring at 60 °C. When the temperature was brought down to 45 °C, tosyl imidazole **2** (31.3 g, 141 mmol) in powder form was added to the stirring solution. After 2 h, NaOH (18 g, 0.45mol) in water (50 mL) was poured slowly into the reaction mixture in 20 min. After an additional 10 min, the unreacted tosyl imidazole was removed by filtration. To quench the reaction, 48.2 g ammonium chloride was added resulting in a clear solution for a while. A milky suspension was obtained after 5 min; thereafter during 3 h at 5 °C, the product started precipitating, which was then filtered, washed with ice-cold water (200 mL), and cold acetone (200 mL). The white powder of tosylate **3** was dried in vacuo at 50 °C (16 g, 41%). The reaction was repeated to obtain more of the tosyl derivative **3**.

4.2.4. Synthesis of diallylamine derivative bearing residue of β-Cyclodextrin

Tosylate **3** (20.0 g, 15.5 mmol), dissolved in DMSO (35 g) at 50 °C, was treated with excess diallylamine **4** (14.6 g, 150 mmol). The homogeneous solution was stirred under N₂ at 70 °C for 48 h to complete the reaction as confirmed by ¹H NMR. The reaction mixture was washed with ether (3×50 mL) and the supernatant ether layers were

decanted. After dissolving the residual sticky material in water (50 mL) and treating it with K_2CO_3 (7 g), a gentle stream of N_2 at 50 °C was passed through the solution to remove any remaining diallylamine. The mixture was cooled to 5 °C, the precipitated diallylamine derivative was filtered, and washed with cold water (20 mL) and acetone (50 mL). The compound was dried in vacuo to obtain water-insoluble **5** as a white powder (14.7 g, 78%). Mp: The compound did not melt up to 290 °C as it was decomposed to a black material. [Found: C, 46.6; H, 6.8; N, 1.0%. $\text{C}_{48}\text{H}_{79}\text{NO}_{34}$ requires C, 47.48; H, 6.56; N, 1.15%]. ν_{max} (KBr): 3310, 2922, 2884, 1367, 1153, 1077, 1024, 936, 859, 754, and 583 cm^{-1} .

4.2.5. Synthesis of β -CD-derived monomer 6

To an ice-cold a heterogeneous mixture of diallyl amine derivative **5** (13.5 g, 11.1 mmol) in water (25 mL) was added dropwise under stirring concentrated HCl (1.2 g, 37% HCl, 12.2 mmol). The homogeneous solution upon immediate freeze-drying afforded a white solid of **6** (13.8 g, 99%). [Found: C, 45.0; H, 6.7; N, 1.0%. $\text{C}_{48}\text{H}_{80}\text{ClNO}_{34}$ requires C, 46.10; H, 6.45; N, 1.12%]. ν_{max} (KBr): 3392, 2927, 1643, 1452, 1342, 1158, 1029, 939, 853, 760, 706 and 585 cm^{-1} .

4.2.6. Cyclopolymerization of monomers 6 and 7

4.2.6.1 Copolymerization of 7 and 6 in an 85:15 mol ratio to obtain 8b

A solution of monomer **7** (810 mg, 5 mmol) and **6** (1.10 g, 0.88 mmol) in water (1.03 g), containing initiator AMPD (50 mg) was stirred under N_2 at 75 °C in the closed flask for 24 h. The thick solution was dialyzed using dialysis tube of 6000 MWCO followed by

freeze drying to obtain **8b** as a white solid (1.63 g, 85%). [Found: C, 50.5; H, 8.2; N, 4.1%. Incorporation of monomers **7/6** in a mol ratio of 85:15 requires C, 51.73; H, 7.94; N, 4.31%]. ^1H NMR analysis revealed that while the feed ratio was 85:15, the incorporation was determined to be 87:13. ν_{max} (KBr): 3314, 2980, 2930, 2890, 1642, 1471, 1392, 1250, 1151, 1079, 1028, 944, 753, 709, and 586 cm^{-1} .

4.2.6.2 Homopolymerization of **6** to obtain **8c**

A solution of monomer **6** (1.25 g, 1.0 mmol) in water (1.25 g) containing AMPD (15 mg) under N_2 was stirred at $75\text{ }^\circ\text{C}$ in a closed flask for 24 h. After adding additional water (0.9 g) and AMPD (15 mg), the mixture was stirred further at $75\text{ }^\circ\text{C}$ for 24 h and then dialyzed using dialysis tube of 6000 MWCO. The resultant solution was freeze-dried to obtain white solid **8c** (0.64 g, 51%). [Found: C, 45.6; H, 6.7; N, 1.0%. $\text{C}_{48}\text{H}_{80}\text{ClNO}_{34}$ requires C, 46.10; H, 6.45; N, 1.12%]. ν_{max} (KBr): 3310, 2924, 2850, 1643, 1454, 1414, 1334, 1151, 1077, 1021, 944, 845, 753, 709, 652, and 602 cm^{-1} .

4.2.6.3 Copolymerization of **7**, **6**, and SO_2 in an 80:20:100 mol ratio to obtain **9b**

To a solution of **7** (405 mg, 2.5 mmol) and **6** (782 mg, 0.625 mmol) in DMSO (1.6 g) was absorbed SO_2 (368 mg, 5.7 mmol). After adding AIBN (60 mg) and stirring at $70\text{ }^\circ\text{C}$ for 24 h, the thickened mixture upon dialysis (3500 MWCO) and freeze-drying afforded **9b** (1.3 g, 94%). [Found: C, 44.1; H, 6.8; N, 3.0; S, 6.9%. Incorporation of monomers **7/6/SO₂** in a 80:20:100 mol ratio requires C, 43.33; H, 6.55; N, 3.16; S, 7.23%]. ^1H NMR analysis revealed that while the feed ratio was 80:20, the incorporation was determined to

be 83:17. $\nu_{\max}$ (KBr): 3334, 2980, 2933, 2886, 1649, 1473, 1417, 1396, 1299, 1126, 1079, 1028, 945, 753, 650, and 605 cm^{-1} .

4.2.6.4 Copolymerization of **6** and SO_2 to obtain **9c**

SO_2 (115 mg, 1.8 mmol) was absorbed on a solution of **6** (1.25 g, 1.0 mmol) in DMSO (1.33 g). AIBN (20 mg) was added to the homogeneous solution, which was stirred under N_2 at 70 $^\circ\text{C}$ for 48 h. After adding more AIBN (20 mg), the heating was continued for a further 48 h. The mixture upon dialysis using dialysis tube of 3500 MWCO followed by freeze-drying afforded **9c** (0.72 g, 55%). [Found: C, 44.9; H, 6.4; N, 1.0; S, 2.2%. $\text{C}_{48}\text{H}_{80}\text{ClNO}_{36}\text{S}$ requires C, 43.85; H, 6.13; N, 1.07; S, 2.44%]. $\nu_{\max}$ (KBr): 3332, 2980, 2885, 1642, 1460, 1382, 1303, 1252, 1151, 1126, 1078, 1027, 940, 758, 706, and 588 cm^{-1} .

4.2.6.5 Copolymerization of **10** and **6** in an 80:20 mol ratio to obtain **11b**

To a solution of monomer **10** (388 mg, 2.5 mmol), **6** (782 mg, 0.625 mmol), and NaCl (55 mg, 945 mmol) in water (0.63 g), initiator AMPD (25 mg) was added under N_2 and stirred at 75 $^\circ\text{C}$ for 24 h. NaCl was added to make its concentration 1.5 M. After adding water (0.25 g) and AMPD (15 mg), stirring was continued for an additional 30 h at 75 $^\circ\text{C}$. The thickened gel was dialyzed against distilled water using dialysis tube of 6000 MWCO and then freeze-dried to obtain **11b** as a white solid (0.87 g, 74%). [Found: C, 50.4; H, 7.3; N, 3.6%. Incorporation of monomers **10/6** in an 80:20 mol ratio requires C, 51.34; H, 7.11; N, 3.74%]. ^1H NMR analysis revealed that while the feed ratio was 80:20, the incorporation was determined to be 82:18. $\nu_{\max}$ (KBr): 3660, 3350, 2980, 2888, 1619, 1461, 1393, 1252, 1153, 1081, 1031, 955, and 612 cm^{-1} .

4.2.6.6 Copolymerization of **12**, **6**, and SO₂ in an 80:20:100 mol ratio to obtain **13b**

To a solution of **12** (570 mg, 2.5 mmol) and **6** (782 mg, 0.625 mmol) in DMSO (1.6 g) was absorbed SO₂ (340 mg, 5.3 mmol) and added AIBN (60 mg). The homogeneous solution in a closed flask was stirred at 70 °C for 24 h. The resultant mixture upon dialysis using a dialysis tube of 6000 MWCO led to the separation of polymer **13b** as a gelly liquid. The whole mixture containing insoluble polymer as well as the aqueous layer upon freeze-drying gave white powder of **13b** (1.23 g, 84%). [Found: C, 38.0; H, 6.0; N, 2.8; S, 6.5%. Incorporation of monomers **12/6/SO₂** in an 80:20:100 mol ratio requires C, 39.08; H, 5.87; N, 3.00; S, 6.86%]. ¹H NMR (D₂O + NaHCO₃) analysis revealed that while the feed ratio was 80:20, the incorporation was determined to be 84:16. $\nu_{\max}$ (KBr): 3274, 2980, 2920, 1647, 1418, 1298, 1123, 1024, 912, and 753 cm⁻¹.

4.2.6.7 Synthesis of zwitterionic *N, N*-diallylaspartic acid (**14**)

The treatment of disodium *N, N*-diallylaspartate, prepared as described [222] with 2 equivalents of HCl gave **14** as a crystalline monomer in 95% yield. Mp. 67-68 °C; [Found: C, 56.1; H, 7.2; N, 6.4%. C₁₀H₁₅NO₄ requires C, 56.33; H, 7.09; N, 6.57%]. $\nu_{\max}$ (KBr): 3350, 2982, 2864, 1713, 1614, 1377, 1227, 1187, 1093, 993, 941, 859, 767, and 644 cm⁻¹; δ_{H} (D₂O) 2.85 (2H, d, *J* 6.4 Hz), 3.62 (2H, dd, *J* 7.7, 13.5 Hz); 3.80 (2H, dd, *J* 6.6, 13.5 Hz), 4.18 (1H, t, *J* 6.4 Hz); 5.48 (4H, m), 5.82 (2H, m); δ_{C} (D₂O) 31.53 (1C), 55.54 (2C), 61.85 (1C), 127.12 (2C), 127.29 (2C), 172.16 (1C), 174.54 (1C), (dioxane: 67.41).

4.2.6.8 Copolymerization of **6** and **14** to obtain **16b** and **16c**

A solution of monomer **14** (533 mg, 2.5 mmol), **6** (348 mg, 0.278 mmol), and NaCl (42 mg, 0.718 mmol; NaCl was added to make its concentration 1.5 M.) in water (475 mg) in an RB flask (5 mL) was heated quickly under N₂ to 100 °C. To this stirred homogeneous mixture, initiator APS was added in portions of 50 mg, 50 mg, 25 mg, and 25 mg with intervals of 2 min in between the addition of each portion. After heating further for 5 min at 100 °C, the thickened mixture was dialyzed using dialysis tube of 3500 MWCO. The polymer started settling down (24 h). The whole mixture upon freeze-drying gave **16b** (655 mg, 74%). [Found: C, 51.4; H, 7.1; N, 4.2%. Incorporation of monomers **10/6** in a 90:10 mol ratio requires C, 52.29; H, 6.84; N, 4.42%]. ¹H NMR analysis revealed that while the feed ratio was 90:10, the incorporation was determined to be 92:8. ν_{max} (KBr): 3345, 2930, 2864, 1714, 1614, 1457, 1372, 1235, 1153, 1080, 1028, 1003, 940, 857, 647, and 604 cm⁻¹.

The above polymerization with a feed ratio of 90:10 was repeated using AMPD as an initiator (25 mg) while keeping all other materials the same. Initially, the mixture was stirred at 75 °C for 24 h; then additional AMPD (25 mg) and water (172 mg) were added and heated at 75 °C a further 24 h. Dialysis as above afforded polymer **16b** in 45% yield. ¹H NMR analysis revealed that while the feed ratio was 90:10, the incorporation was determined to be 90.3:9.7.

The above polymerization was repeated using APS as the initiator and **10/6** in a mol ratio of 80:20 to obtain **16c** in 70% yield.

4.2.6.9 Copolymerization of **15**, **6**, and SO₂ in an 80:20:100 mol ratio to obtain **17b**

SO₂ (372 mg, 5.8 mmol) was absorbed on to a solution of **15** (625 mg, 2.5 mmol) and **6** (782 mg, 0.625 mmol) in DMSO (1.6 g). After adding AIBN (60 mg) and purging with N₂, the homogeneous solution was stirred at 70 °C for 24 h. The content in the flask upon dialysis using dialysis tube of 6000 MWCO followed by freeze-drying gave **17b** (1.3 g, 86%). [Found: C, 40.0; H, 5.7; N, 2.6; S, 6.0%. Incorporation of monomers **7/6/SO₂** in an 80:20:100 mol ratio requires C, 41.13; H, 5.65; N, 2.73; S, 6.24%]. ¹H NMR (D₂O + NaHCO₃) analysis revealed that while the feed ratio was 80:20, the incorporation was determined to be 83:17.

The above polymerization was repeated using **15/6** in a 60:40 mol ratio using **15** (1.25 mmol), **6** (0.833 mmol), SO₂ (3.5 mmol), and AIBN (60 mg) in DMSO (1.2 g). During dialysis, the homogeneous solution became turbid, which was freeze-dried to give **17c** (1.15 g, 77%). $\nu_{\max}$ (KBr): 3310, 2980, 2927, 2889, 1716, 1622, 1457, 1374, 1298, 1123, 1078, 1022, 943, 850, 753, 649, and 604 cm⁻¹.

4.2.7 Removal of organic micropollutant 2-naphthol (2-NO)

The water solubility of **17b** (50 mg) having 20 mol% CD residues was tested using water (5 mL). After stirring (3 h) followed by filtration and drying, 93% of the polymer was recovered. A stock solution of 0.25 mM of 2-naphthol (2-NO) analyte was prepared. For the adsorption isotherm, experiments were carried out by the addition of polymer (50 mg) into analyte solution (9 mL) of 0.05, 0.1, 0.15, 0.2, and 0.25 mM taken in screw cap glass vials with constant stirring (500 rpm) at 298 K for 1 h. The suspension passed through the

0.22 μm inorganic membrane filter and filtrate was analyzed by UV–vis spectroscopy (Genesys 10S, Thermo Scientific). The calibration curve using analyte concentration of 0.0125 – 0.25 mM was plotted for the analyte and then from the slope equation, the unknown concentration of the analyte after adsorption was calculated.

The amount of analytes adsorbed by the polymer, q_e (mg g^{-1}) was calculated using **Eq 4.1**:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (4.1)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and final concentration of 2-NO, while m (g) and V (L) represent the mass of polymer and volume of aqueous solution.

The percent removal (R) was calculated using **Eq.4.2**:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4.2)$$

The kinetics study was performed by the addition of the polymer (222.2 mg) into the 0.100 mM analyte solution (40 mL) taken in screw cap glass vial with constant stirring (500 rpm) at 298 K. The specified amount (2 mL) of the suspension was taken out by syringe from the mixture after certain intervals and filtered by 0.22 μm inorganic membrane filter and immediately analyzed by UV-vis spectroscopy to find out the residual concentration of the pollutant.

4.3. Results & Discussion

4.3.1. Synthesis and spectral analyses of monomer

6-O-toluenesulfonyl- β -cyclodextrin **3** upon reaction with excess diallylamine **4** afforded tertiary amine **5**, which was converted cleanly to its hydrochloride salt **6** (**Scheme 4.1**). While β -CD **1** is sparingly soluble in water (18.5 mg mL⁻¹), its tosyl derivative **3** and tertiary amine **5** were found to be insoluble in water. Interestingly, diallylammonium monomer **6** is very soluble in water. To confirm the structure and integrity of the CD motifs, NMR spectra of **1**, **3**, **5**, and **6** were recorded and displayed in **Figs. 4.1** and **4.2**. The carbons are marked **a-f** as shown in the structure of **1** (**Scheme 4.1**). The proton marked 'a' at C1 appeared at δ 4.8 ppm in all the spectra, while alkene protons marked 'h' and 'i' of **5** and **6** are displayed around δ 5.5 ppm as expected (**Fig. 4.1d**, **4.1e**, **4.1f**). Note that the spectra in D₂O are simpler than in DMSO-d₆, because in the latter solvent, the OH signals appear at different chemical shifts (*cf.* **Figs. 4.1a** vs. **4.1b** and **4.1e** vs. **4.1f**).

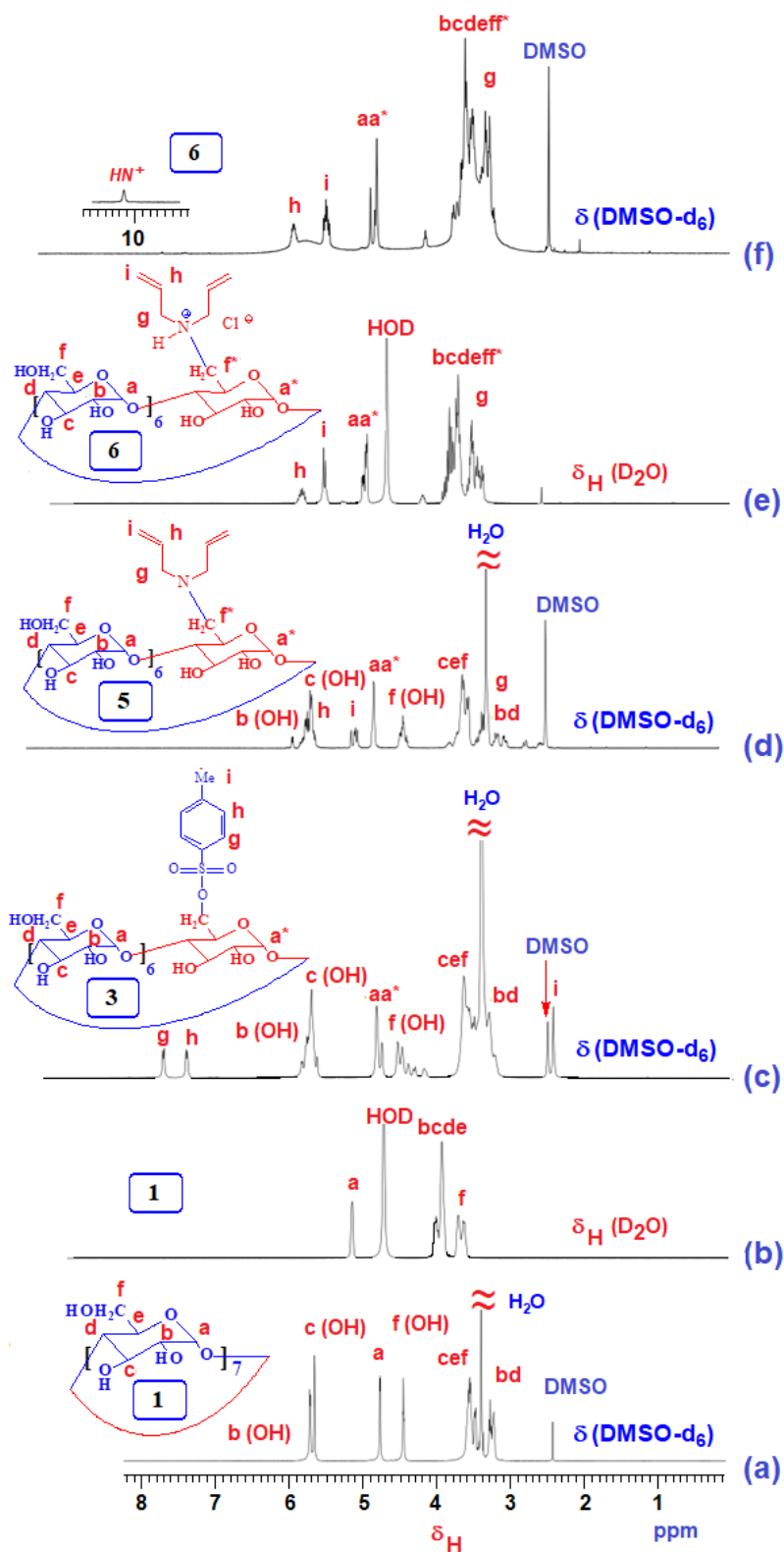


Figure 4.1. ^1H NMR spectra of (a) β -Cyclodextrin (1) in DMSO- d_6 , (b) 1 in D₂O, (c) 3 in DMSO- d_6 , (d) 5 in DMSO- d_6 , (e) 6 in D₂O, and (f) in DMSO- d_6

^{13}C NMR spectra of β -CD **1** display six signals in DMSO- d_6 confirming the equivalent nature of all the seven cyclic skeletons (**Fig. 4.2a, b**). However, in the tosyl **3** and diallylamine derivatives **5**, the cyclic rings become nonequivalent and as such display more signals (**Fig. 4.2c, d**). The alkene carbons marked 'h' and 'i' of **5** appeared in their expected chemical shifts (**Fig. 4.2d**). Note each alkene carbon around $\delta 127$ ppm is split into a doublet of equal intensity because of their diastereotopic nature (**Fig. 4.2f**). 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*).

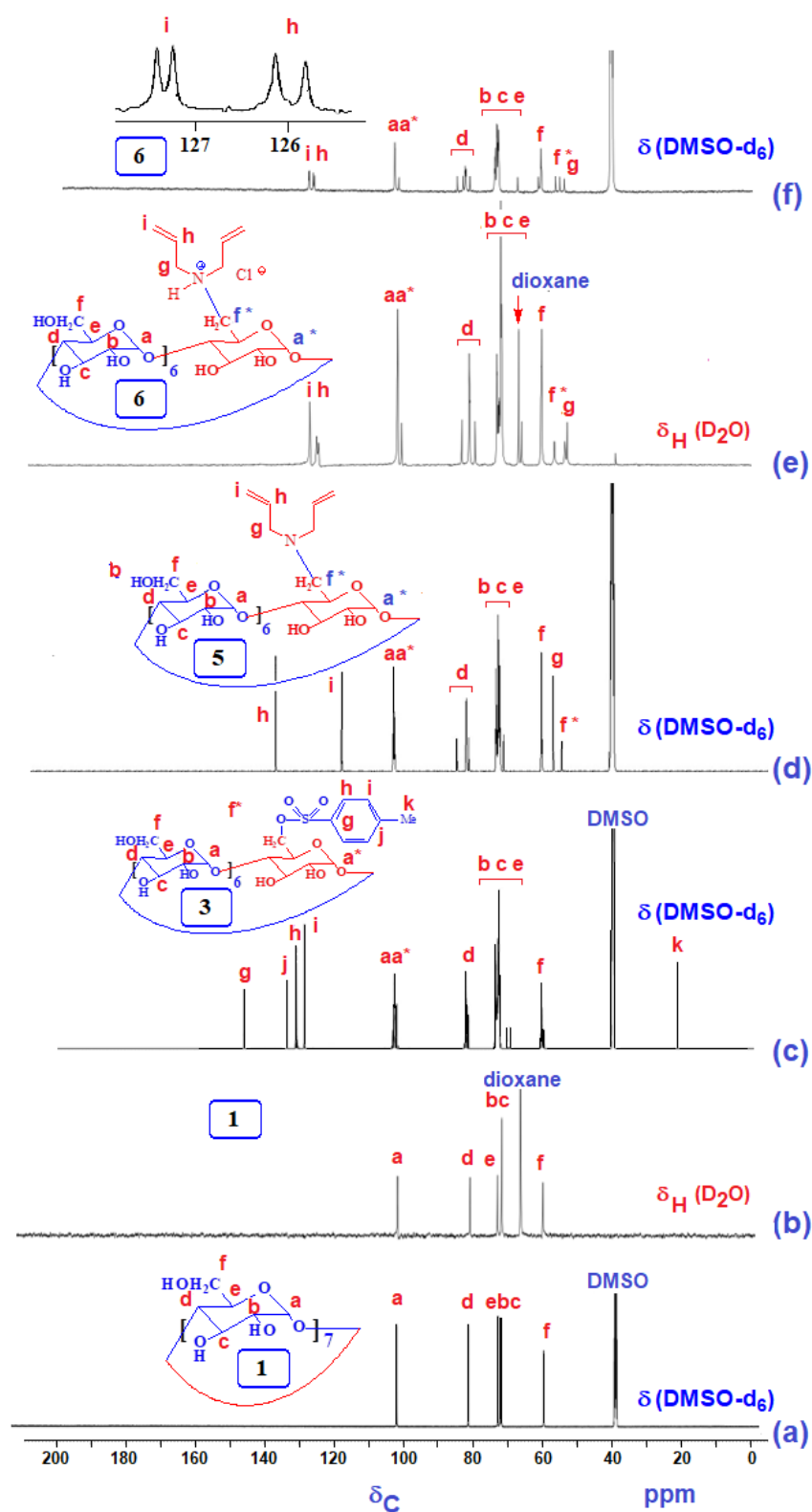
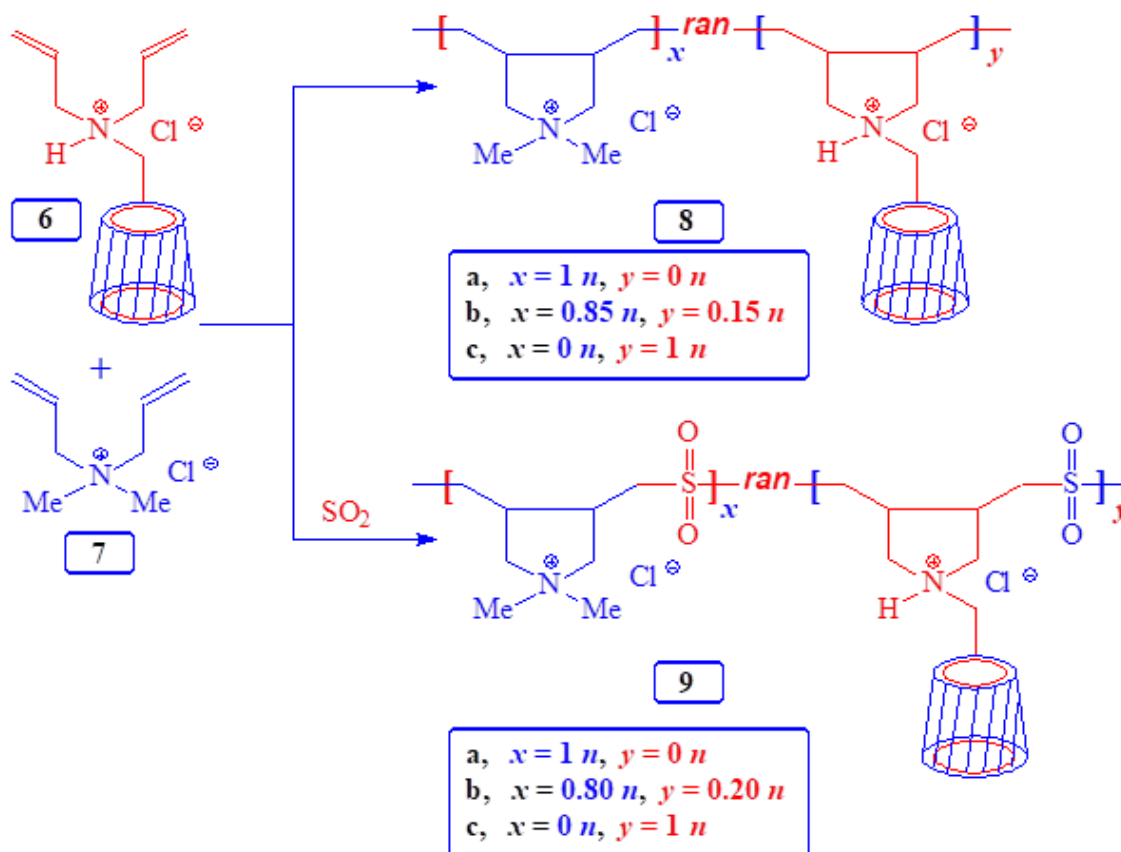


Figure 4.2. ^{13}C NMR spectra of (a) β -Cyclodextrin (1) in DMSO-d_6 , (b) 1 in D_2O , (c) 3 in DMSO-d_6 , (d) 5 in DMSO-d_6 , (e) 6 in D_2O , and (f) in DMSO-d_6

4.3.2. Synthesis and spectral analyses of cyclopolymers

Monomers **7** and **6** underwent AMPD-initiated cyclopolymerization in aqueous systems to generate the corresponding water-soluble homopolymers **8a** [224] and **8c** respectively, while **7/6** in a feed ratio of 85:15 afforded copolymer **8b** (Scheme 4.2). ^1H NMR analysis revealed the monomer incorporation **7/6** as 87:13.



Scheme 4.2. Cyclopolymerization of monomers **6** and **7** and their alternate copolymerization with SO_2

The AIBN-initiated co- and ter-polymerizations of **6**, **7**, and SO_2 in solvent DMSO led to polymers **9a**, [224] **9b**, and **9c** (Scheme 4.2). Almost zero reactivity ratios ($r_1 \approx r_2 \approx 0$) of diallyl monomers (M_1) and SO_2 (M_2) ensured the alternating placement of SO_2 [225]. Monomers' feed ratio almost matched the incorporation ratio in the polymer **9b**.

NMR spectral analyses of **8** can decipher the incorporation of β -CD-derived monomer **6** into the polymers. **Fig. 4.3a,b** reveals the ^1H spectra of monomer **7** and its homopolymer **8a**, while the corresponding ^{13}C spectra are displayed in **Figs. 4.4a,b, 4.3c,d**, and **4.4c,d** show the NMR spectra of monomer **6** and its homopolymer **8c**. Note the signals of the alkene Hs and Cs marked 'a' and 'b' of **7** (**Figs. 4.3a** and **4.4a**) disappeared in the spectra of homopolymer **8a** (**Figs. 4.3b** and **4.4b**), thereby implying the successful cyclopolymerization leading to a five-membered ring embedded polymer backbone. Similar disappearance of alkene signals (marked 'h', 'i') happened involving conversion of monomer **6** to its homopolymer **8c** (*cf.* **Figs. 4.3c** vs **4.3d** and **4.4c** vs **4.4d**). The chemical shifts of the acetal H and C marked a/a* of monomer **6** and polymers **8b, c** appeared at δ 5 ppm (**Fig. 4.3c, d, e**) and 100 ppm (**Fig. 4.4c, d, e**), thereby ensuring the incorporation of cyclodextrin residues into the polymer backbone. Copolymer composition of polymer **8b** (**Fig. 4.3e**) was calculated using area integration of proton marked a/a* at δ 5 ppm and rest of the signals.

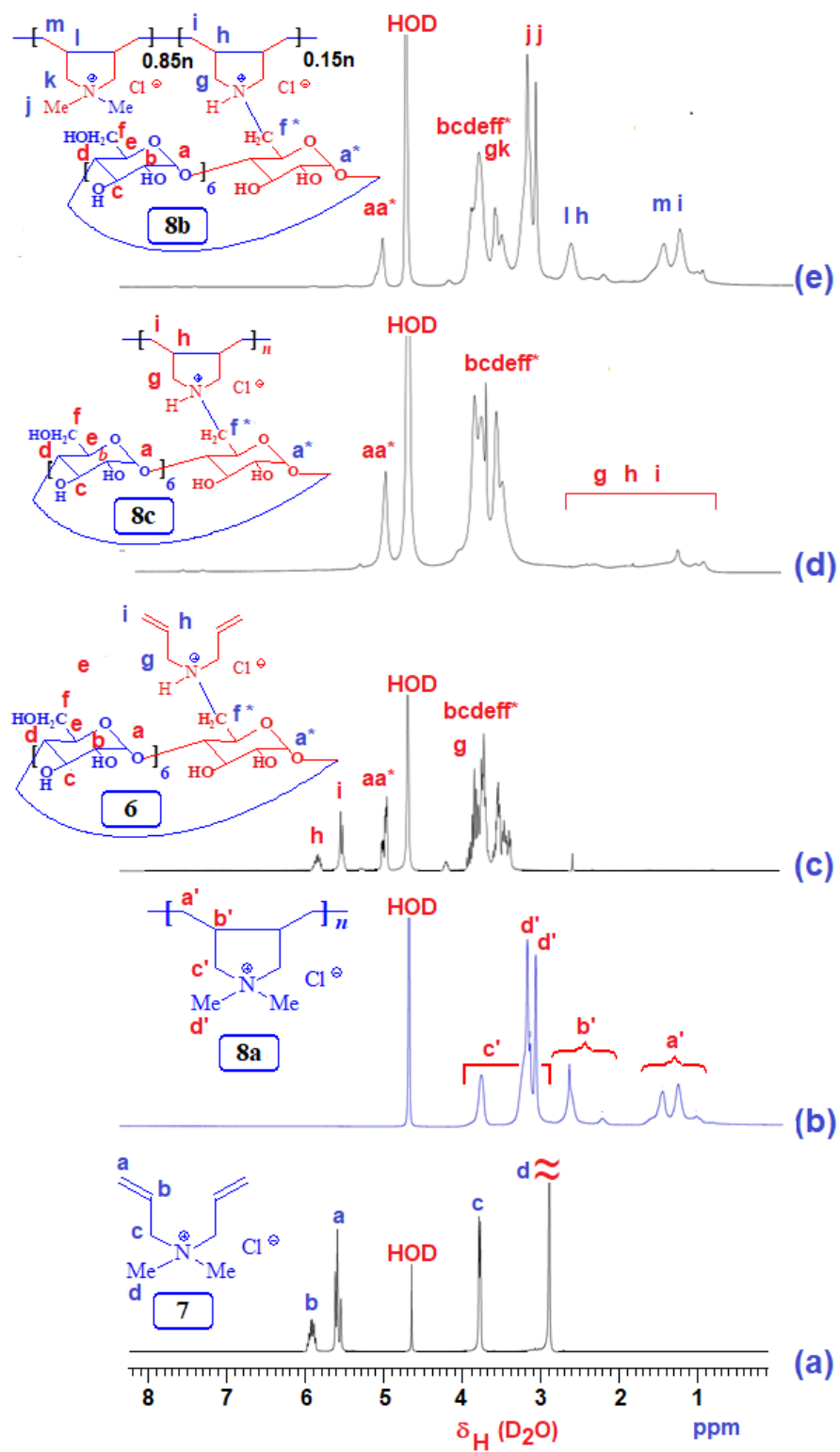


Figure 4.3. ^1H NMR spectra in D_2O of (a) 7, (b) 8a, (c) 6, (d) 8c, and (e) 8b

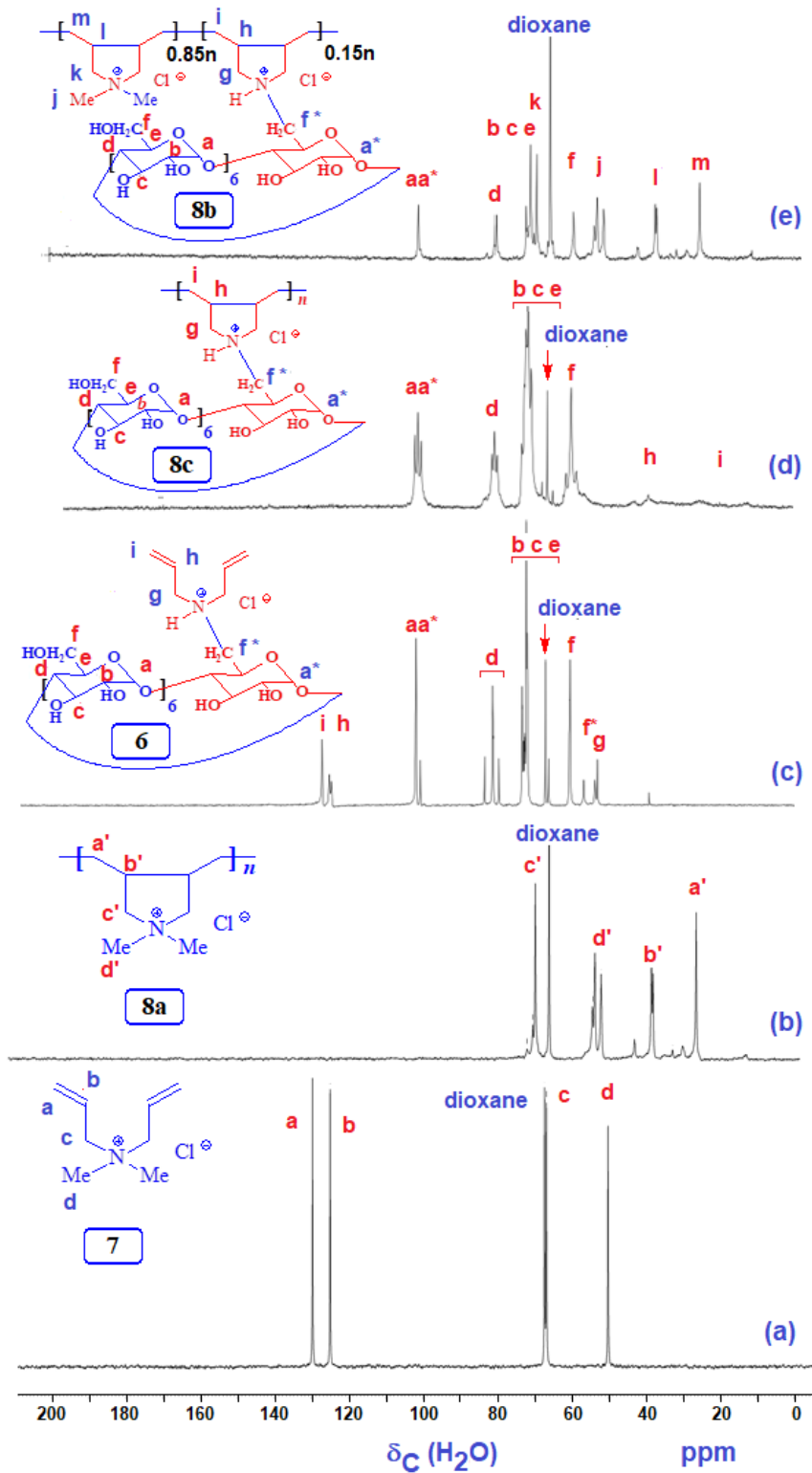


Figure 4.4. ^1H NMR spectra in D_2O of (a) monomer 7, (b) polymer 8a, (c) monomer 6, (d) polymer 8c, and (e) polymer 8b.

FTIR spectrum of **9b** revealed the presence of bands at 1299 and 1126 cm^{-1} owing to the vibrations of SO_2 unit [226]. ^1H and ^{13}C NMR spectra of SO_2 copolymers **9a, b** (**Scheme 4.2**) are shown in **Figs. 4.5** and **4.6**, respectively. An 80:20 copolymer confirms the incorporation of β -CD residues in **9b** as revealed by the presence of protons and carbons marked aa* at $\delta 5$ ppm (**Fig. 4.5b**) and $\delta 100$ ppm (**Fig. 4.6b**), respectively. Spectra also revealed the successful cyclopolymerization owing to the disappearance of signals for the alkene protons and carbons.

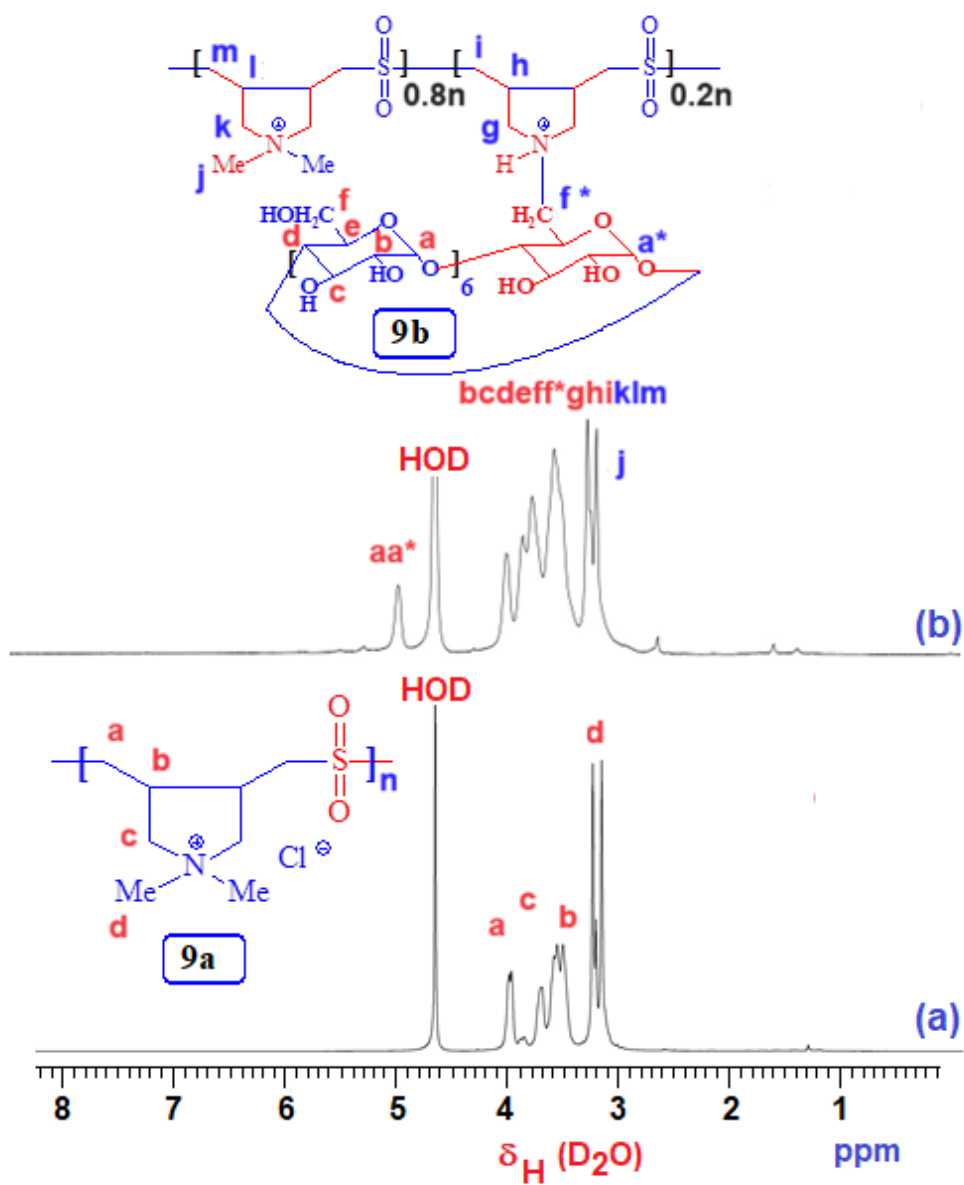


Figure 4.5. ^1H NMR spectra in D_2O of (a) 9a and (b) 9b

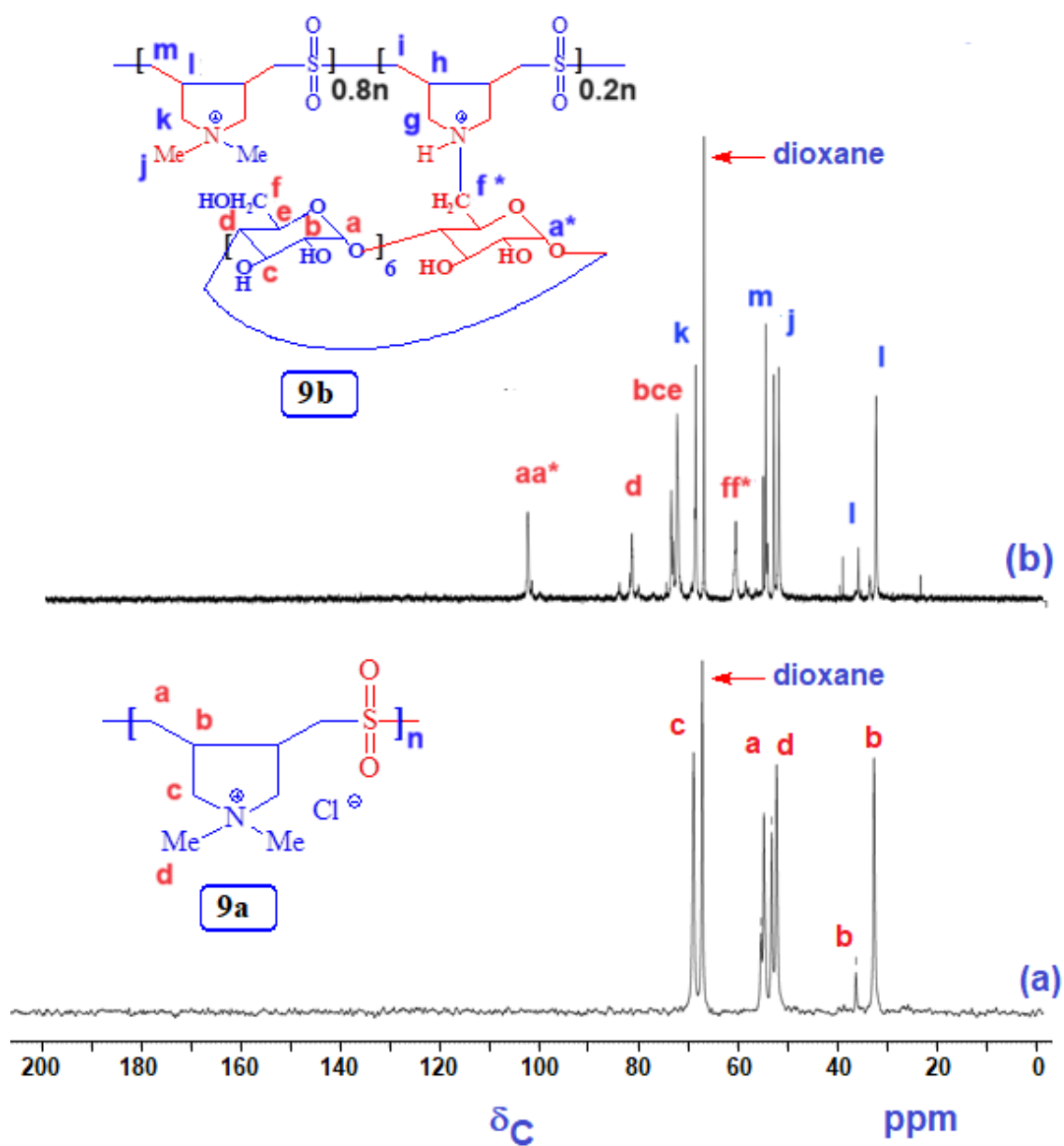
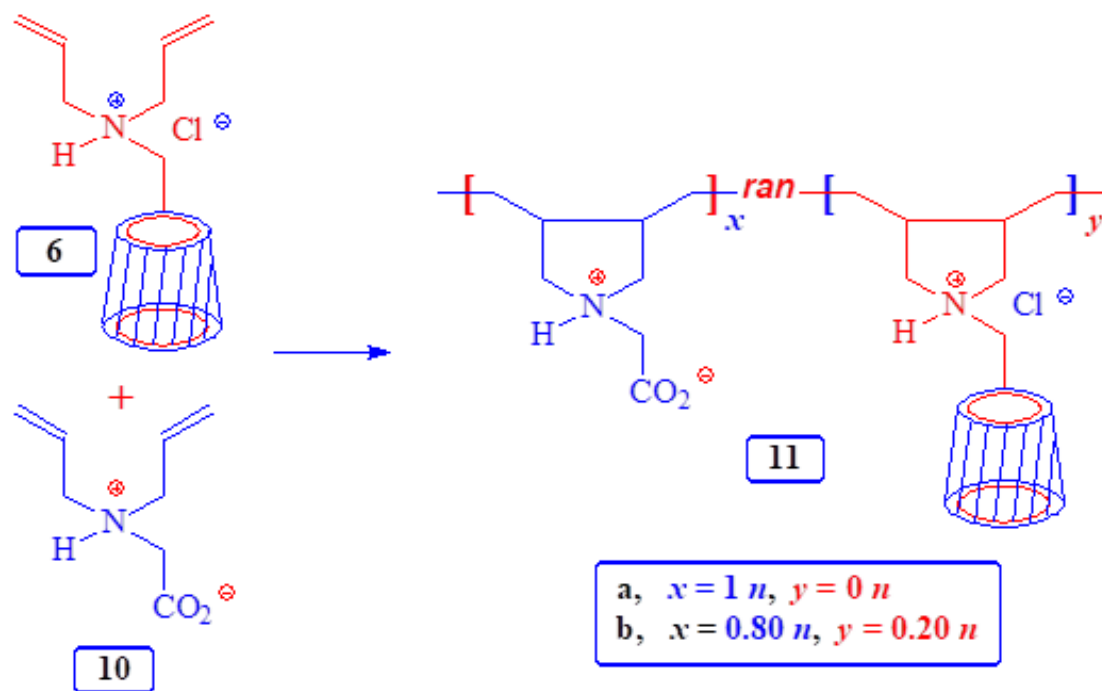


Figure 4.6. ^{13}C NMR spectra in D_2O of (a) **9a** and (b) **9b**

The protocol for the synthesis [227] of homopolymer **11a** was followed to generate copolymer **11b**. Thus, monomers **10** (containing residue of amino acid glycine) and **6** in an 80:20 feed ratio afforded copolymer **11b** with **10/6** incorporation ratio of 82:18 as

determined by the area integration of proton signals (*vide supra*) (**Scheme 4.3**). The absorption bands of COO^- (a part of the zwitterionic motifs) of **11b** appeared at 1393 and 1619 cm^{-1} in the IR spectrum[228]. ^1H and ^{13}C spectra (**Figs. 4.7** and **4.8**) confirmed the presence of carboxyl carbon (marked 'n') at $\delta 170\text{ ppm}$ and aa* carbon at $\approx \delta 100\text{ ppm}$ [**Fig. 4.8** (c)]. β -CD protons (marked 'aa*') appeared at $\delta 5\text{ ppm}$ [**Fig. 4.7** (c)]. The spectral analysis thus ensured the incorporation of monomers **6** and **10** into the polymer backbone.



Scheme 4.3. Cyclopolymerization of monomers **6** and **10**

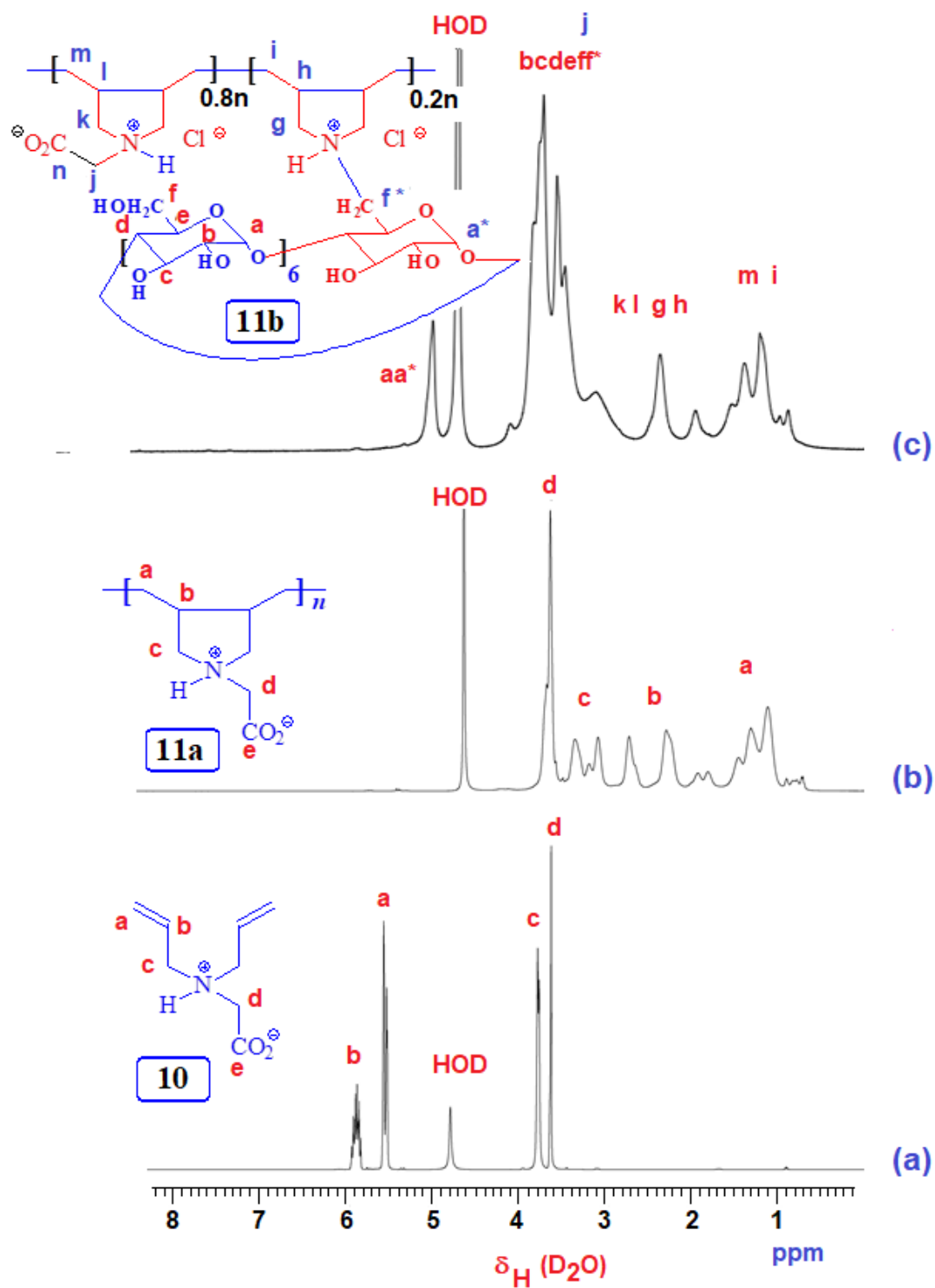


Figure 4.7. ^1H NMR spectra in D_2O of (a) polymer 10, (b) 11a and (c) 11c

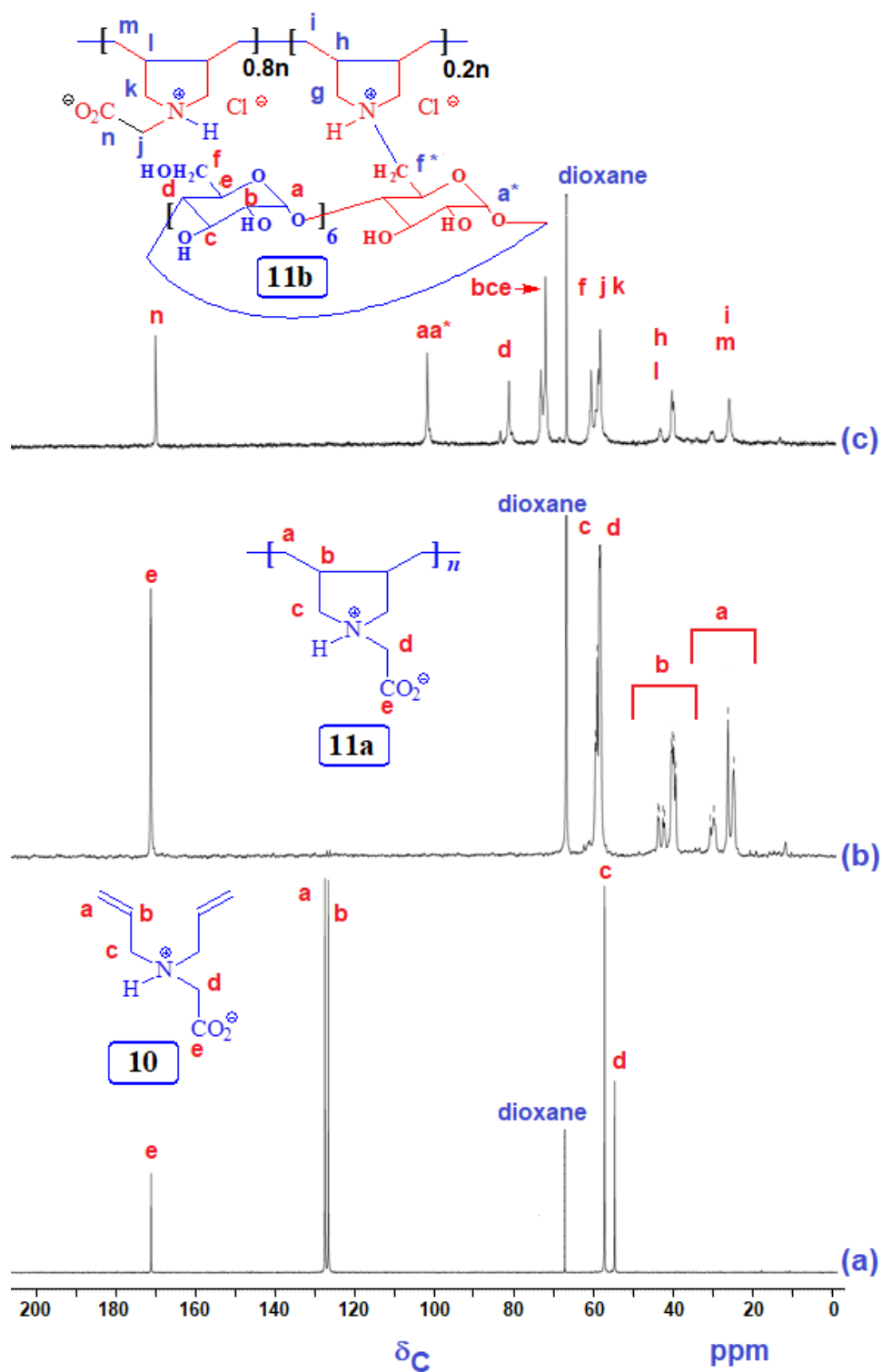
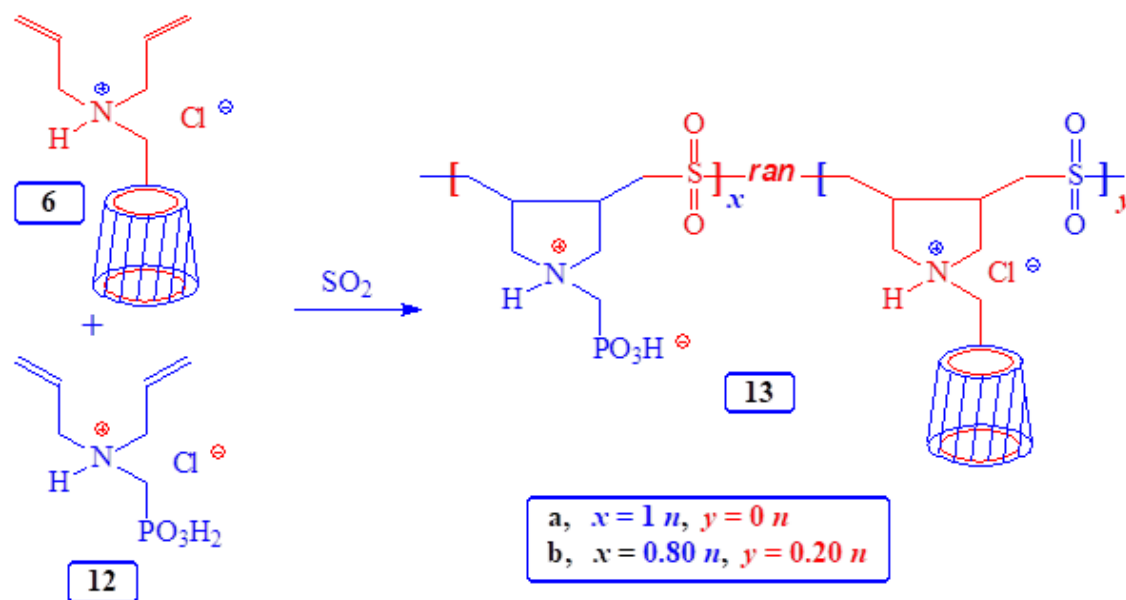


Figure 4.8. ^{13}C NMR spectra in D_2O of (a) polymer 10, (b) 11a and (c) 11c

Phosphonic acid monomers **12** and **12/6** in a feed ratio of 80:20 underwent cyclopolymerization in the presence of SO_2 gave copolymer **13a** [227] and terpolymer

13b, respectively (**Scheme 4.4**). The IR absorption at 1275 cm^{-1} **13b** was assigned to the P-O stretch [229]. The two strong bands at 1298 and 1123 cm^{-1} were assigned to vibrations of SO_2 units. ^1H , ^{13}C (**Figs. 4.9 and 4.10**), and ^{31}P spectral analyses confirmed the structure of the polymer backbone. ^{31}P signal appearing at $\delta 5.64\text{ ppm}$ confirmed the incorporation of monomer **12** into the terpolymer **13b**. As described earlier the presence of protons and carbons marked 'aa*' at $\delta 5\text{ ppm}$ (**Fig. 4.3c**) and $\delta 100\text{ ppm}$ (**Fig. 4.4c**), respectively, ensures the incorporation of monomer **6**.



Scheme 4.4. Terpolymerization of monomers 6, 12, and SO_2

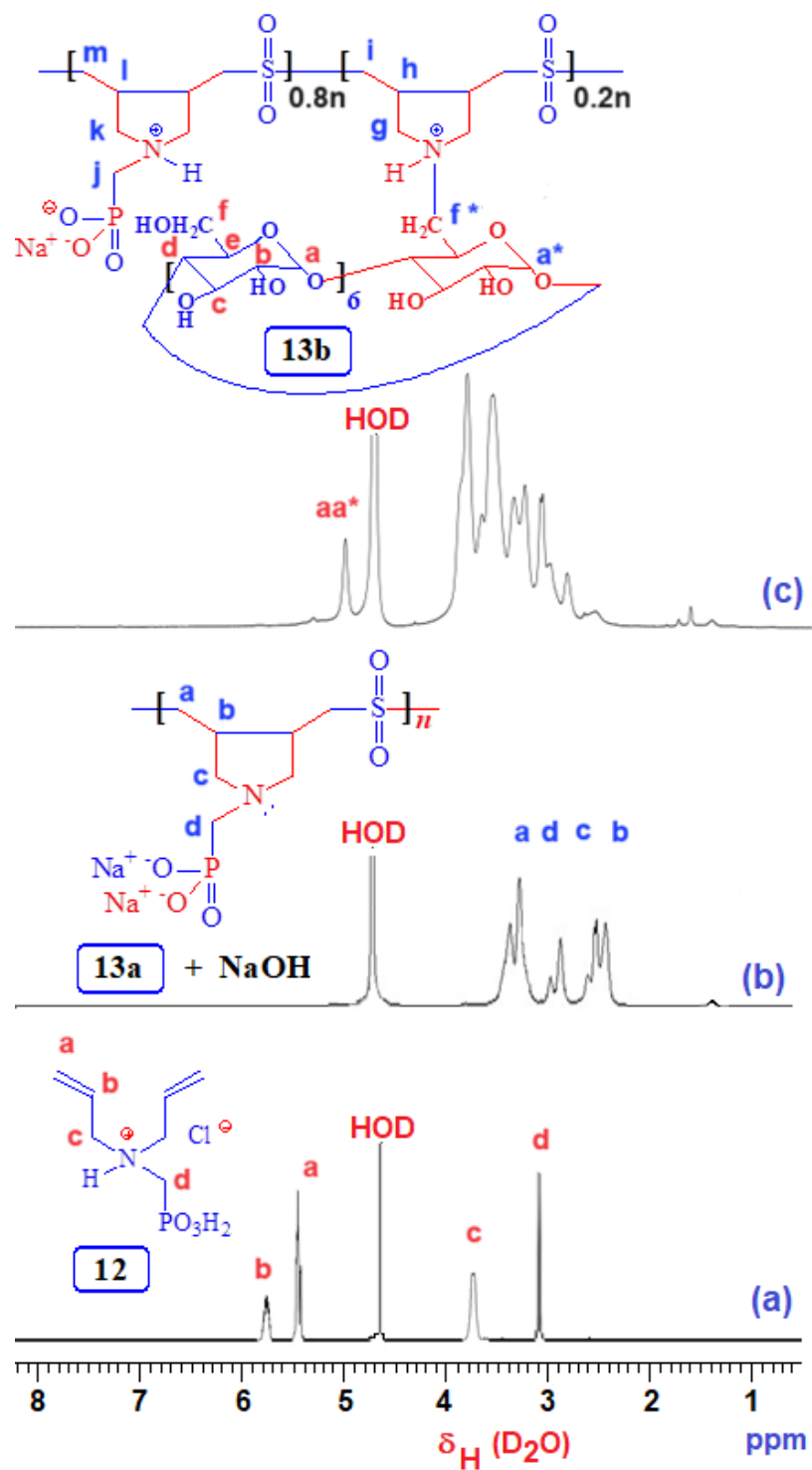


Figure 4.9. ^1H NMR spectra in D_2O of (a) 12, (b) 13a + NaOH, (c) 13b + NaHCO_3

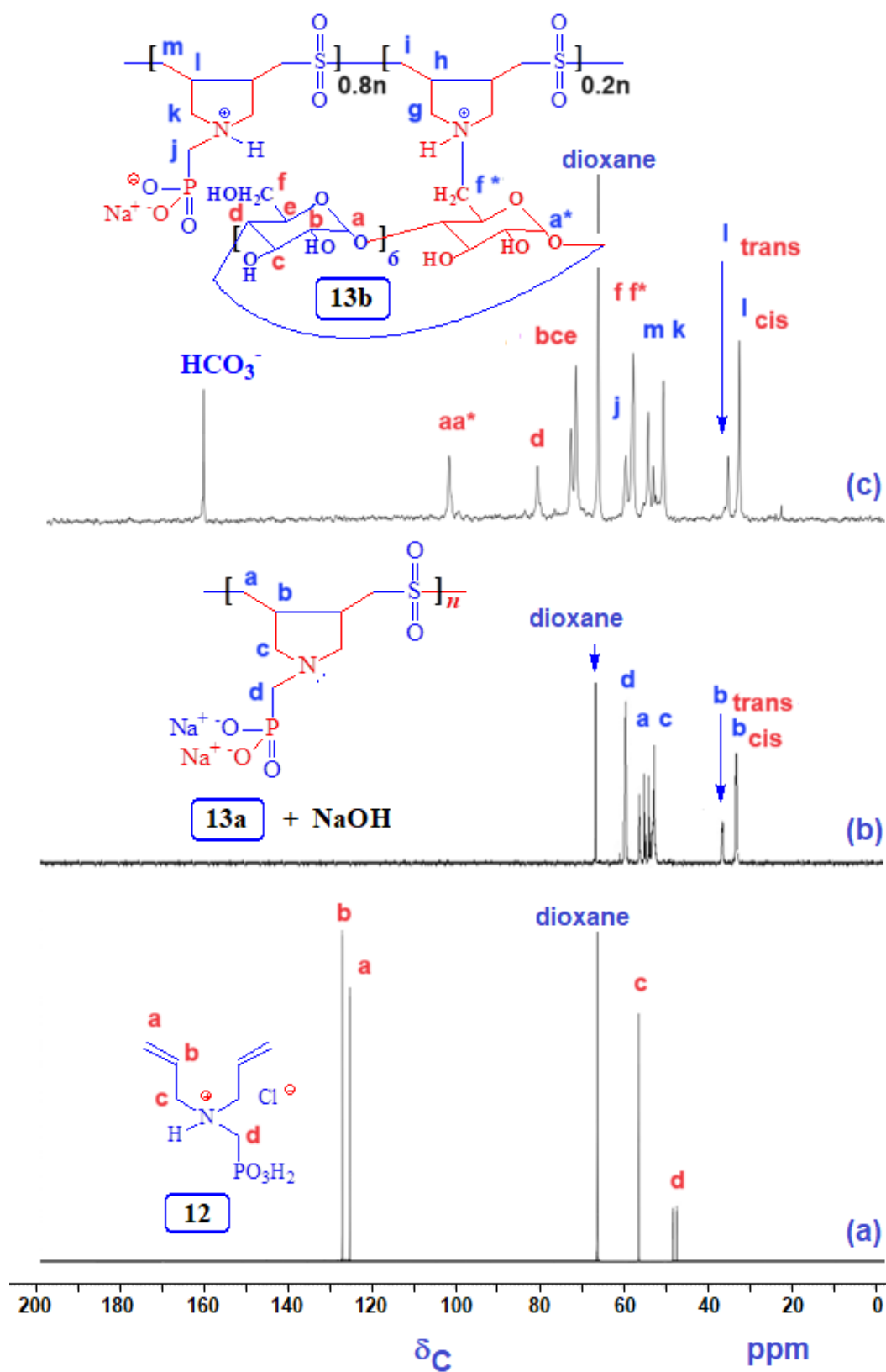
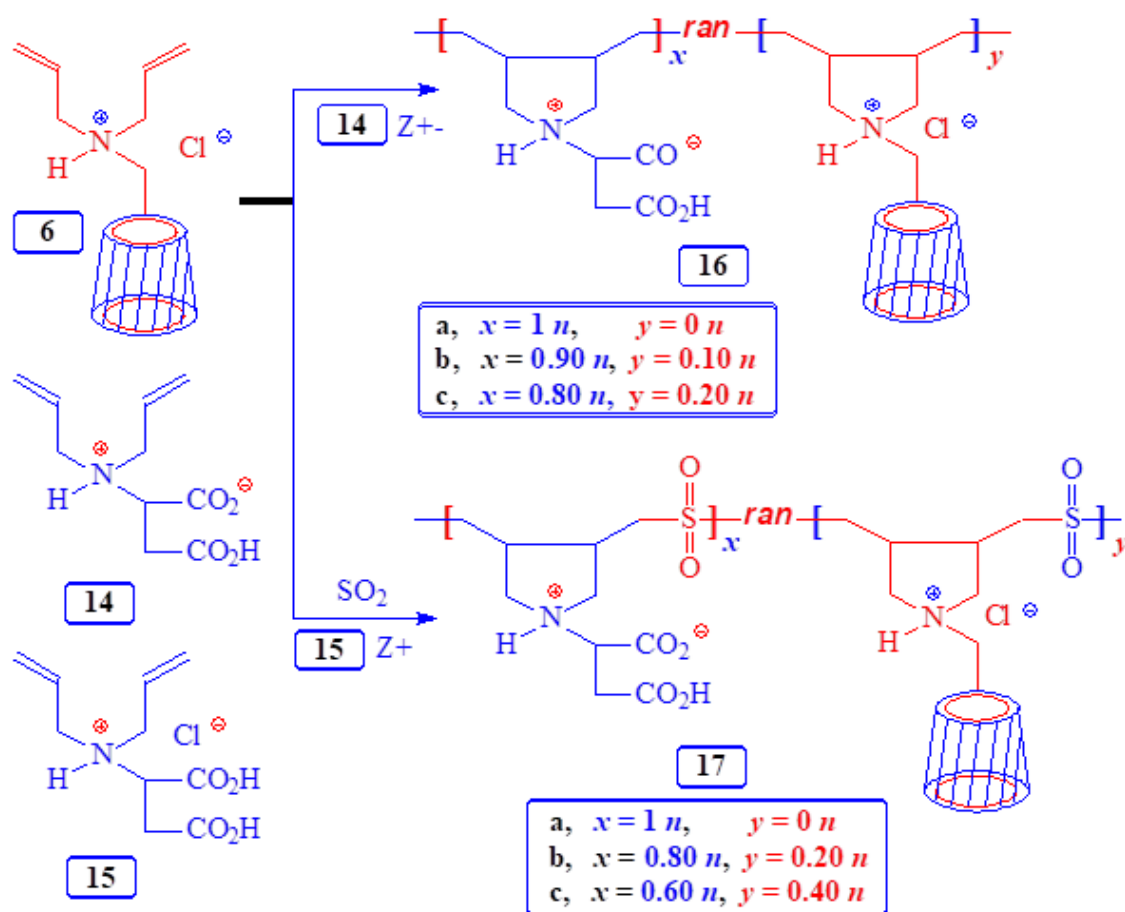


Figure 4.10. ^{13}C NMR spectra in D_2O of (a) 12, (b) 13a + NaOH, (c) 13b + NaHCO_3

Finally, monomer **14** having residue of aspartic acid and **6** in various proportions underwent copolymerization to give polymers **16**, while in the presence of SO₂ the co- and terpolymers **17** are generated (**Scheme 4.5**). The synthesis of β -CD-free polymers **16a** and **17a** were reported before [222,225]. The stretching of COO⁻ in **16b** appeared at 1457 and 1634 cm⁻¹, [222,228] whereas the absorption at 1714 cm⁻¹ to the C=O stretch of COOH. Absorption bands at 1298 and 1123 cm⁻¹ were assigned to the vibrations of the SO₂ unit in **17c**. The stretching of COO⁻ appeared at 1374 and 1622 cm⁻¹ respectively, [225,228] while the C=O stretch appeared at 1716 cm⁻¹.



Scheme 4.5. Cyclopolymerization of monomers **6** and **14** (or **15**) and their alternate copolymerization with SO₂

NMR spectra of **16** and **17** are shown in (**Figs. 4.11** and **4.12**) and (**Figs. 4.13** and **4.14**). As analyzed earlier, the spectral analyses revealed the incorporation of the monomers in the co- and ter-polymers. Note the appearance of protons marked 'aa*' at δ 5 ppm (**Figs. 5.11** (c), d and **4.13** (b) and carbons marked 'aa*' at δ 100 ppm (**Figs. 4.12** (c) and **4.14** (b) ensure the presence of β -CD residues. The appearance of two signals for C=O carbons at $\approx \delta$ 175 ppm (**Figs. 4.12** (c) and **4.14** (b) confirm the presence of aspartic acid residues.

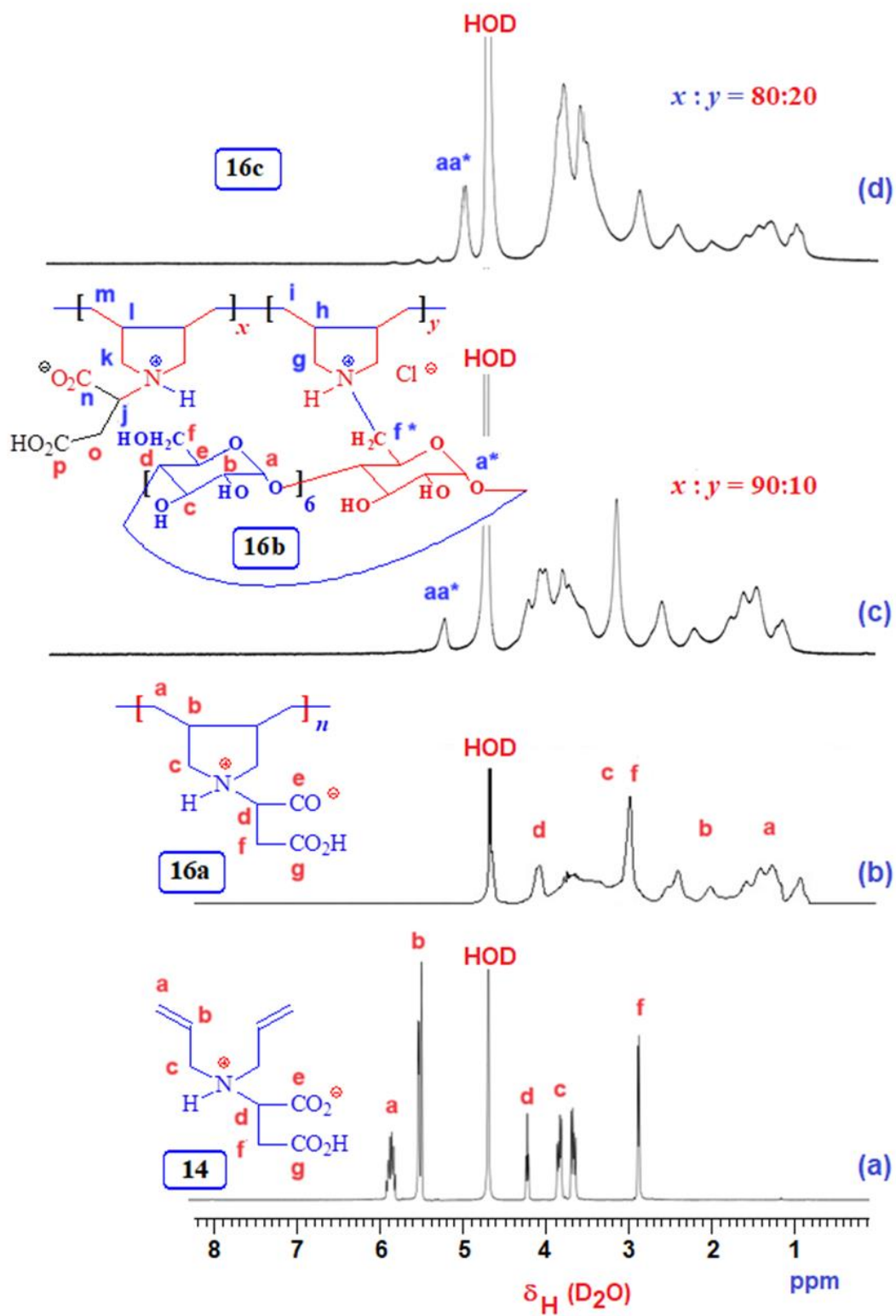


Figure 4.11. ^1H NMR spectra of (a) 14 (in D_2O), (b) 16a (in $\text{D}_2\text{O} + \text{NaCl}$), (c) 16b (in $\text{D}_2\text{O} + \text{NaCl}$), and (d) 16c (in $\text{D}_2\text{O} + \text{NaCl}$)

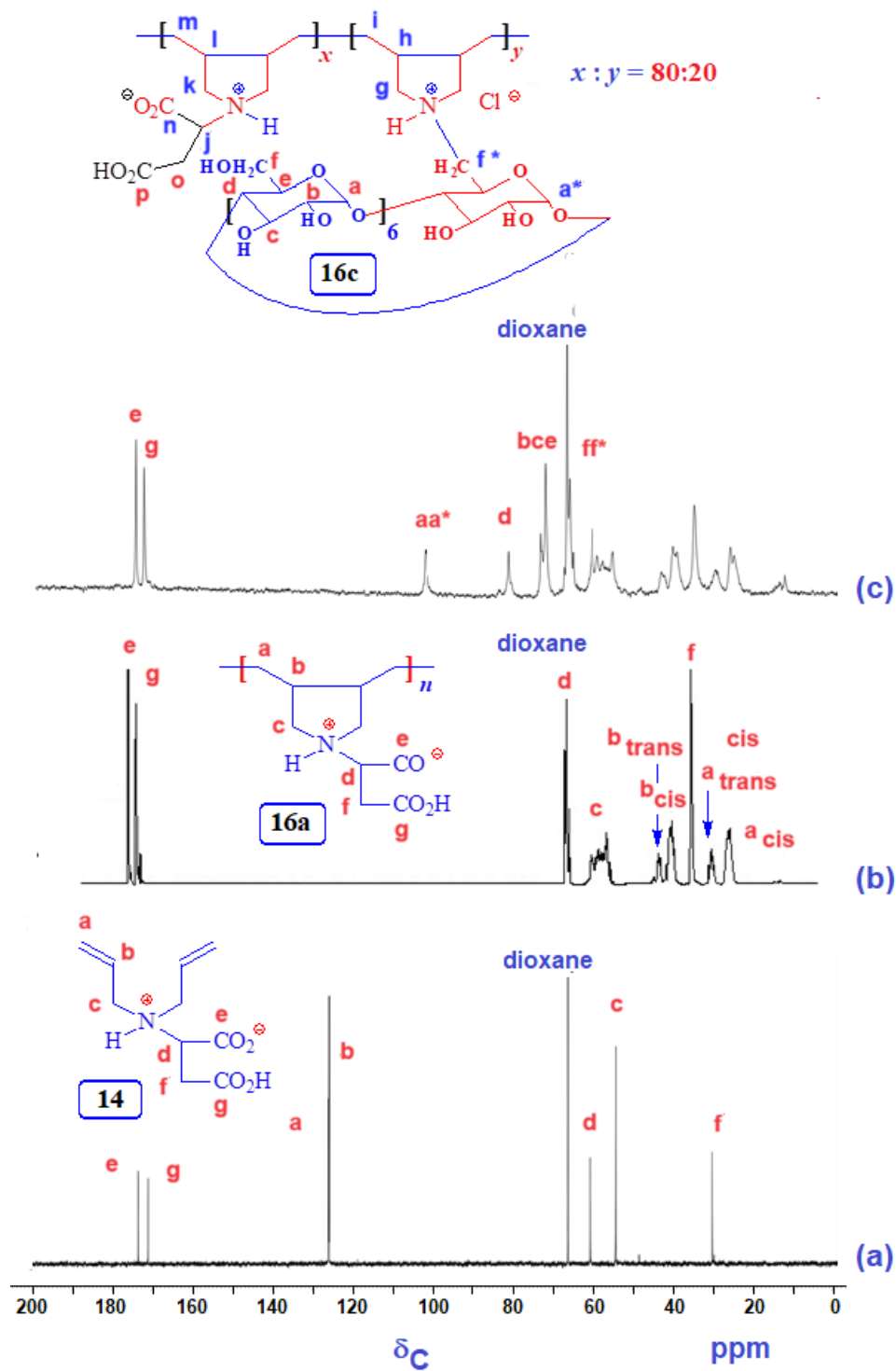


Figure 4.12. ^{13}C NMR spectra of (a) 14 (in D_2O), (b) 16a (in $\text{D}_2\text{O} + \text{NaCl}$), (c) 16b (in $\text{D}_2\text{O} + \text{NaCl}$), and (d) 16c (in $\text{D}_2\text{O} + \text{NaCl}$)

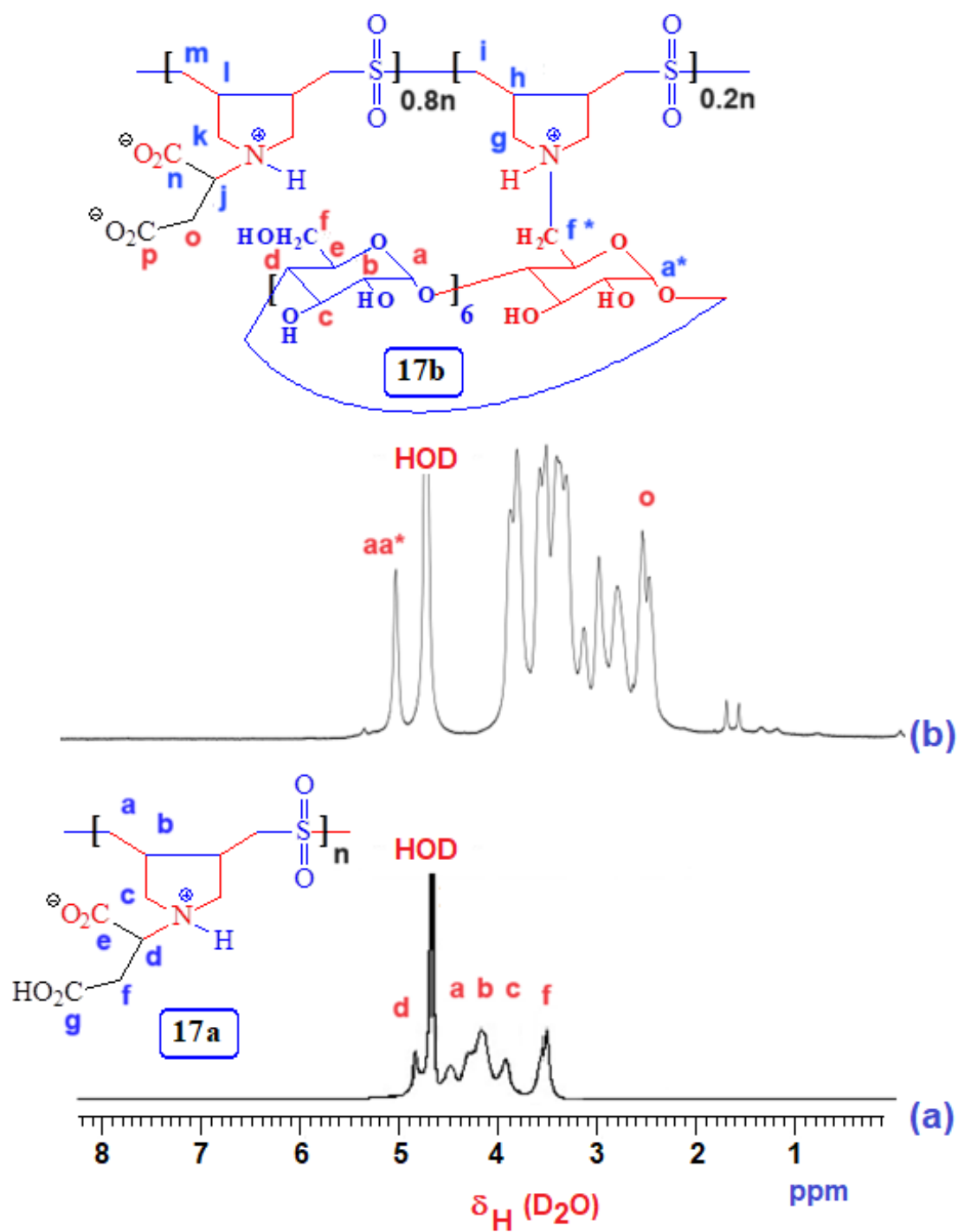


Figure 4.13. ^1H NMR spectra of (a) 17a in the presence of KI in D_2O ; (b) 17b in the presence of NaHCO_3 in D_2O

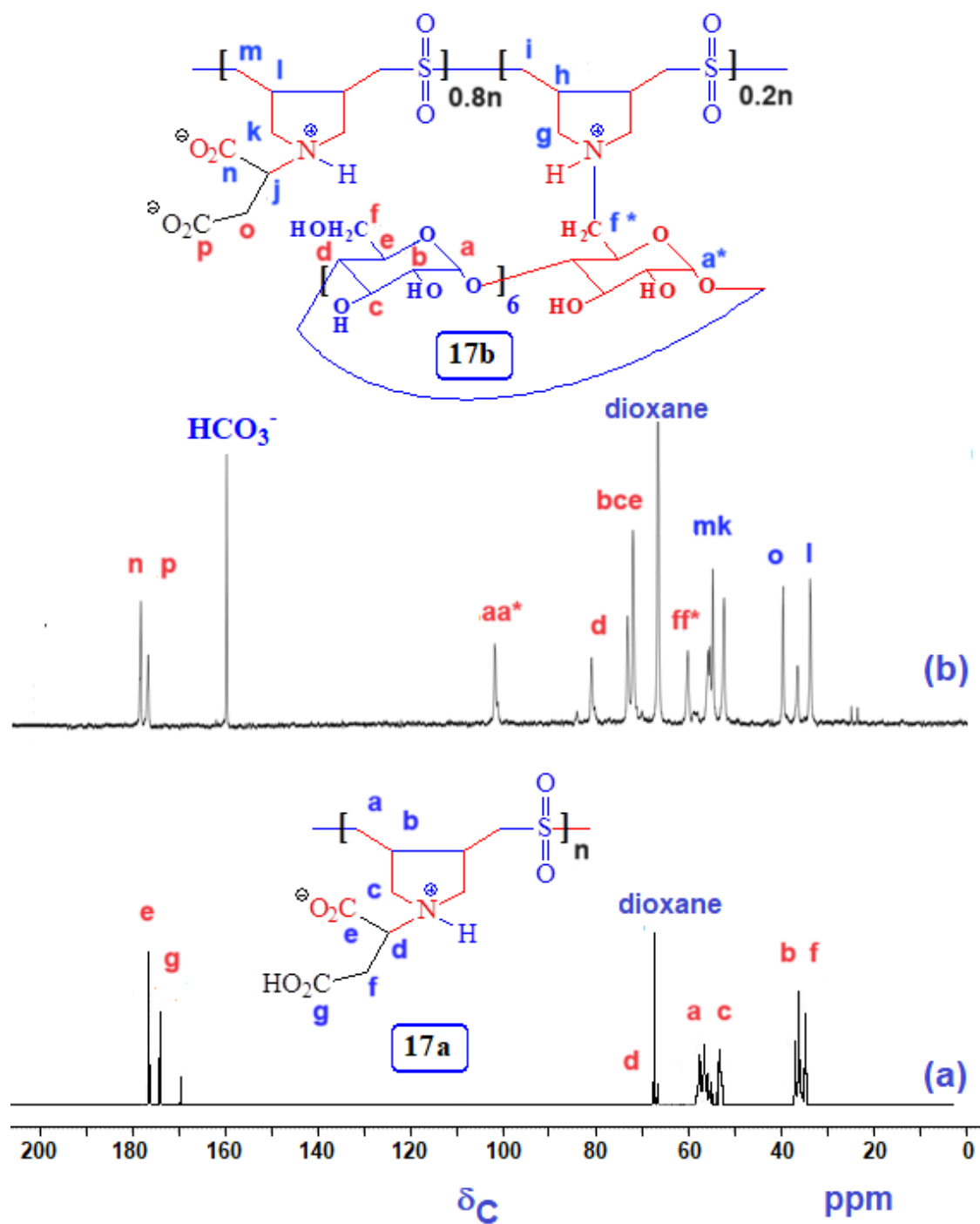
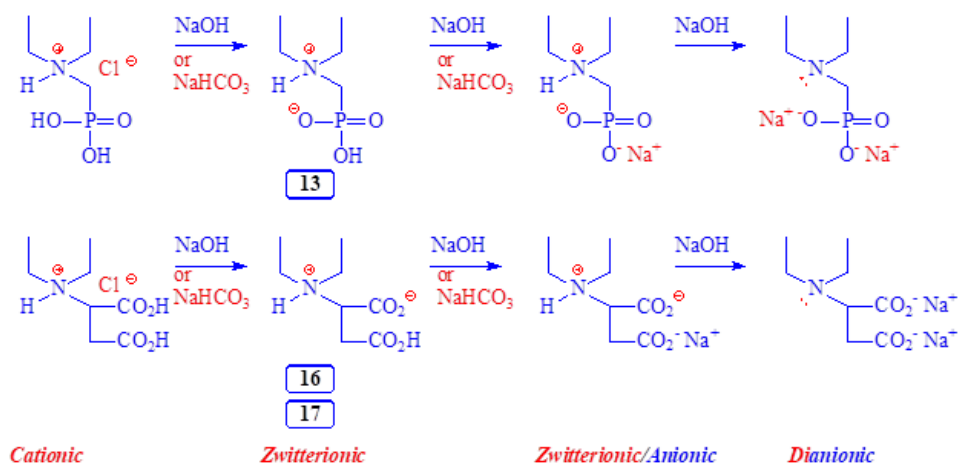


Figure 4.14. ^{13}C NMR spectra of (a) 17a in the presence of KI in D_2O ; (b) 17b in the presence of NaHCO_3 in D_2O

4.3.3. Solubility behavior

The cyclopolymerization details are included in **Table 4.1**. The feed ratio of (M_1/M_2) monomers matches with the incorporation ratio in the polymers, thereby implying the equal reactivity of the monomers. The yields remain in the range 45-94%. Polymers **8**, **9**, and **11** are water-soluble, while zwitterionic/cationic **13**, **16**, and **17** are insoluble in water, however, become water-soluble in the presence of NaHCO_3 or NaOH . In the presence of a base, the zwitterionic motifs become zwitterionic/anionic (by abstraction of proton in CO_2H) which imparts water-solubility (**Scheme 4.6**). Polymers **13**, **16**, and **17** having dominant electroneutral ($\pm$) motifs were found to be water-insoluble like many polyzwitterions [230–234]. A salt like NaCl disrupts the zwitterionic interactions thereby facilitating the solubility of **13a**, [229] **16a**, [222] and **17a** [225]. It is worth noting that **16b** containing 10 mol% β -CD was soluble in salt (NaCl)-added water, while **16c** having 20 mol% β -CD residues was soluble in salt-free water owing to the presence of higher percentage of CD residues. All the polymers in series **17** were found to be water-insoluble but soluble in the presence of NaHCO_3 or NaOH .



Scheme 4.6. pH-induced transformation of functional motifs

Table 4.1 Polymerization of monomers **M₁, **6** (**M**₂) and SO₂**

Polymerization of monomers M ₁ , 6 (M ₂) and SO ₂ .									
Entry	M ₁ (mmol)	M ₂ (6) (mmol)	SO ₂ (mmol)	M ₁ / M ₂ feed	Initiator ^a (mg)	Yield ^b Polymer (%)	M ₁ / M ₂ polymer	Intrinsic Viscosity ^c (dL g ⁻¹)	$\overline{M}_v^d$ & $\overline{M}_n^e$
1 ^f	7 (10)	–	–	100:0	AMPD (75)	8a (86)	100:0	0.787	28800 ^{d, f}
2	7 (5)	0.88	–	85:15	AMPD (50)	8b (85)	87:13	0.232	–
3	–	1.00	–	0:100	AMPD (30)	8c (51)	0:100	0.0317	–
4 ^f	7 (10)	–	11.5	100:0	AIBN (100)	9a (93)	100:0	0.297	11500 ^{e, f}
5	7 (2.5)	0.625	5.7	80:20	AIBN (60)	9b (94)	83:17	0.110	13700 ^e
6	–	1.00	1.8	0:100	AIBN (40)	9c (55)	0:100	0.0749	–
7 ^g	10 (25)	–	–	100:0	APS (545)	11a (89)	100:0	0.0642	4600 ^{e, g}
8	10 (2.5)	0.625	–	80:20	AMPD (40)	11b (74)	82:18	0.0693	–
9 ^h	12 (10)	–	10	100:0	AIBN (200)	13a (80)	100:0	0.100 ⁱ	–
10	12 (2.5)	0.625	5.3	80:20	AIBN (60)	13b (84)	84:16	0.230 ⁱ	16900 ^e 11600 ^j
11 ^k	14 (30)	–	–	100:0	APS (900)	16a (74)	100:0	0.0401 ⁱ	–
12	14 (2.5)	0.278	–	90:10	APS (150)	16b (74)	92:8	0.0674 ⁱ	–
13	14 (2.5)	0.278	–	90:10	AMPD (50)	16b (45)	90:10	0.0985 ⁱ	–
14	14 (2.5)	0.625	–	80:20	APS (150)	16c (70)	83:17	0.0553 ⁱ	–
15 ^l	15 (20)	–	20	100:0	AIBN (100)	17a (73)	100:0	0.573 ⁱ	–
16	15 (2.5)	0.625	5.8	80:20	AIBN (60)	17b (86)	83:17	0.455 ⁱ	24650 ^e
17	15 (1.25)	0.833	3.5	60:40	AIBN (60)	17c (77)	63:37	0.228 ⁱ	31500 ^e

^aAMPD = 2,2'-azobis(2-methylpropionamidine) dihydrochloride, AIBN = 2,2'-Azobisisobutyronitrile, APS = Ammonium persulfate; ^byields are written under parentheses.; ^cViscosity of 1-0.125% in 0.1 M NaCl at 30 °C
^dViscosity average molar mass; ^e $\overline{M}_n$ calculated by end group analysis; ^f[224]; ^g[227]; ^h [229]; ⁱ + 1 equiv. NaHCO₃(or NaOH); ^j(by GPC, MW, PDI:2.5) ^k[222]; ^l[225].

The intrinsic viscosity $[\eta]$ of the polymers **8** in 0.1 M NaCl is included in **Table 4.1**. The incorporation of M_2 having residues of β -CD leads to a decrease in viscosity (entries 1-3). A similar trend is observed for SO_2 -incorporated alternating polymers **9** (entries 4-6). The zwitterionic polymers **11** having residues of glycine were found to have low viscosities (entries 7,8). Polyphosphonate **13b** having β -CD residues is found to have higher $[\eta]$ than **13a** (entries 9,10). Polymers **16** containing residues of aspartic acid (**16a**) as well as β -CD residues (**16b,c**) were found to have low $[\eta]$ values (entries 11-14), while the corresponding SO_2 alternate polymers **17a,b,c** obtained in very good yields have higher viscosity values (entries 15-17). In this series increasing incorporation of β -CD residues leads to a decrease in $[\eta]$. Note that the viscosities of **13**, **16**, and **17** belong to the zwitterionic/anionic family obtained by treating pH-responsive zwitterionic form with one equivalent NaOH.

Attempts to analyze the molar masses of the synthesized polymers by GPC gave erratic results, presumably owing to the strong adsorption of amine, phosphonate, or carboxy motifs to the column materials as reported for similar polymers [235]. However, for some of the SO_2 polymers, the $\overline{M}_n$ values (Table 1) were calculated using end group analysis as reported before [224]. The initiator fragment $(CH_3)_2C(CN)$ representing the end group appeared as a minor signal at δ 1.30 ppm. It is expected that each polymer chain will have one initiator fragment since the termination process is suggested to proceed through abstraction of the allylic proton of the monomers to yield unreactive allylic radicals [236].

4.3.4. Thermogravimetric Analysis

The TGA curves for some polymers, shown in **Fig. 4.15**, reveal their stability up to ≈ 250 °C with $\approx 5\%$ weight-loss accounted for the removal of H₂O/moisture. A major steep loss at ≈ 250 °C is accounted for the loss of β -CD residues along with SO₂ units (in some polymers).

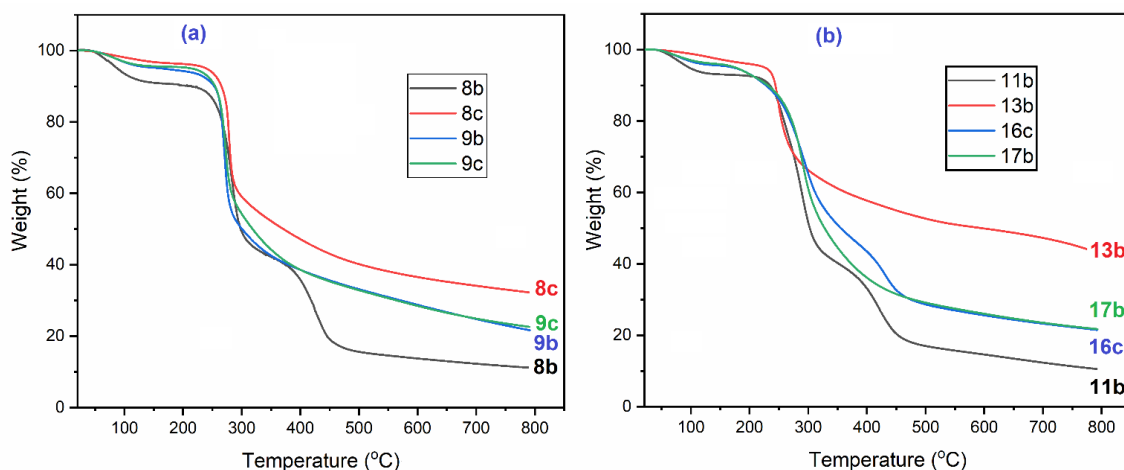


Figure 4.15. TGA curves for (a) 8b, 8c, 9b, 9c and (b) 11b, 13b, 16c, 17b

4.3.5. Removal of an organic micropollutant: Adsorption and kinetic 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 [237,238]. Insoluble polymers containing motifs of β -cyclodextrin (β -CD), can remove these anthropogenic organic chemicals from contaminated water by adsorption method. The hydrophobic cavity of β -CD formed host-guest complexes with many organic compounds [239,240]. 2-naphthol (2-NO), a naphthol-based pollutant [241], was used in this study.

Water-insoluble polymer **17b** was selected for the adsorptive removal of organic pollutants. The polymer is water-soluble to the extent of $\approx 7\%$. The $\lambda_{\max}$ for 2-NO was found to be 274 nm (**Fig. 4.16**). The polymer showed promising adsorption behavior resulting in the removal of 88% 2-NO (**Fig. 4.16b**). The results paved the way to synthesize cross-linked polymers to eliminate the problem associated with partial water-solubility of linear polymers like **17b**. Another difficulty faced with **17b** is that it is not swellable in water. We expect the water-swellability to increase in cross-linked resins, which is anticipated to improve the efficiency of the adsorptive removal of organic contaminants.

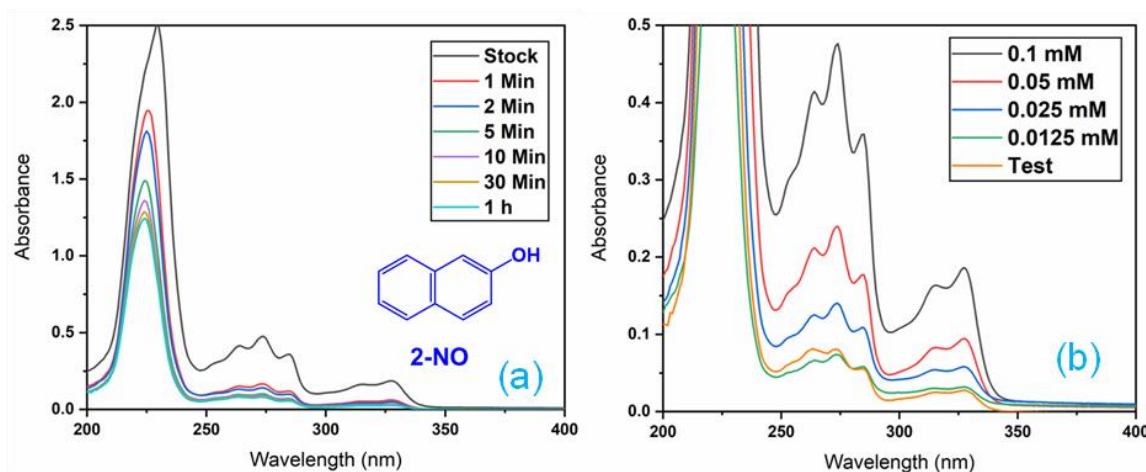


Figure 4.16. UV spectra for (a) Kinetic analysis of 2-NO sample (C_0 : 0.1 mM) and (b) 2-NO samples with C_0 of 0.0125, 0.025, 0.05, and 0.1 mM along with residual C_e (Test) from a C_0 solution of 0.1 mM after polymer treatment

Real time concentrations (C_t) can be used to calculate real-time q_t . Linear pseudo-first and pseudo-second order **Eq. 4.3** and **4.4** were used to investigate the kinetic behavior (**Fig. 4.16a**) of the adsorption of 2-NO onto the polymer [242]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4.3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.4)$$

where k_1 (1/min) and k_2 (g mg⁻¹ min⁻¹) are the corresponding first and second order rate constants.

The adsorption of 2-NO by the polymer was described by linear Langmuir **Eq. 4.5** [242]:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}} \quad (4.5)$$

where C_e (mmol L⁻¹), q_e (mg g⁻¹), maximum adsorption capacity, $q_{\max}$ (mg g⁻¹), and Langmuir isotherm constant, K_L (L mmol⁻¹) are the parameters used with units written in parentheses.

Fig. 4.17a ensures the fast removal of the micropollutant; within 5 min most of the pollutant is removed. Square of correlation (R^2) values confirms the better fitting of the data for the pseudo-second order kinetic model (**Fig. 4.17c**) as compared to first-order kinetic fit (**Fig. 4.17b**). From the plot, the second order rate constant (k_2) was calculated to be 1.218 g mg⁻¹ min⁻¹. From the Langmuir adsorption isotherm (**Fig. 4.17d**), $q_{\max}$ and K_L were found to be 63.7 mg g⁻¹, 2962 L mol⁻¹.

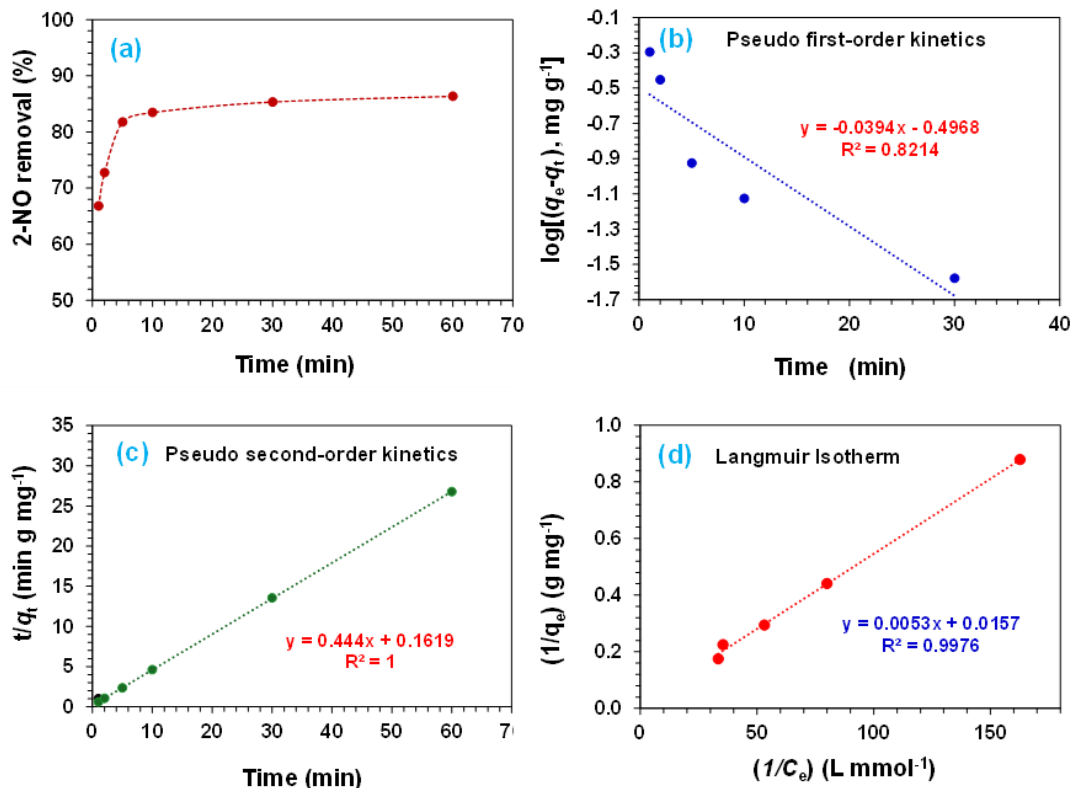


Figure 4.17. For adsorption of 2-NO on polymer 17b at 298 K: (a) using C_o of 0.1 mM, percent removal versus time plot, (b) pseudo first-order kinetic plot, (c) Pseudo second-order kinetic plot, and (d) Langmuir adsorption isotherm

4.4. Conclusion

For the first time, a diallyl amine salt 6 bearing β -CD substituent has been synthesized. A plethora of copolymers as well as alternately placed SO_2 polymers have been synthesized in good yields using 6 and a variety of diallyl amine salts bearing pH-responsive motifs of aspartic acid, glycine, and methylenephosphonate. pH-dependent solution behavior of the stimuli-responsive polymers has been examined.

Note that the β -CD has been bonded to the polymer backbone through a robust C-N bond. Polymers having ester-linked β -CD units (through OH group) are labile owing to

the hydrolyzability of ester motifs, but the current polymers are expected to be stable under alkaline conditions.

As a test case, water-insoluble polymer 17b has been tested for the removal of organic micropollutants. The experimental results confirmed the previous hypothesis that β -CD-based monomer 6 can effectively undergo polymerization and copolymerization to generate polymers with improved water-solubility as compared to pristine β -CD. Copolymers bearing residues of β -CD along with chelating motifs of glycine, phosphonate, and aspartic acid have been synthesized as hypothesized. Work is underway in our laboratory to synthesize cross-linked polymers that can simultaneously remove organic micropollutants as well as priority metal ions from contaminated aqueous bodies.

CHAPTER 5

A Dual-purpose Sorbent containing residues of β -Cyclodextrin, aminomethyl phosphonate, and aspartic acid for Removal of Polyaromatic hydrocarbons and Toxic metal ions

Abstract

The occurrence of poly aromatic hydrocarbons (PAHs) and heavy metals (HMs) in aqueous bodies posed a serious environmental threat to humans and wildlife. A cross-linked terpolymer (CLTP) having β -CD (for PAHs extraction) and HMs (Pb^{2+} & Hg^{2+}) scavenger (aspartic acid and methylenephosphonate) motifs was synthesized. The CLTP was used in a stir bar-supported micro-solid-phase extraction (SB- μ -SPE) technique for extraction of PAHs from aqueous samples and analyzed by gas chromatography – mass spectrometry (GC-MS). A wide number of parameters were studied in the method optimization. The HMs removal study was conducted in ppm to ppb level concentration (1ppm – 200 ppb). The CLTP extract PAHs and adsorb the HMs with excellent efficiency. The synthesized CLTP can be used to simultaneously remove the PAHs and HMs from the contaminated water source.

Keywords

Polyaromatic hydrocarbons, Heavy metals, Extraction, Adsorption, Beta Cyclodextrin
Cross linked diallyl amine polymers

5.1. Introduction

Human and animal habitats are always exposed to different classes of environmental contaminants (ECs) from a variety of sources via different routes, both sequentially and simultaneously [243]. This leads to the presence of numerous toxic compounds in the water cycle, which is one of most serious environmental issues [244]. Environmental toxicants such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) have been frequently found in contaminated water and have attracted great concerns in recent years due to their persistent toxicological risk to humans and wildlife. Recent studies have stated the occurrence of organic pollutants, such as PAHs, and inorganic HMs in various aquatic systems such as influent and effluent from wastewater treatment plants, groundwater, surface waters or seawater [245]. The bioaccumulation of PAHs and HMs in living systems is of great concern. The carcinogenic and mutagenic effects of PAHs have been documented in several studies, and the exposure to HMs contaminates is associated with cardiovascular disorder and cancer [246,247]. There are several methods such as biodegradation, chemical precipitation, photocatalysis oxidation, adsorption, electrochemical techniques, and membrane filtration for the removal of these pollutants from water [248–253]. From these methods, adsorption is the most simple, efficient, and flexible method. Furthermore, there is minimum chemical waste in this process, as well the adsorbent can be reused to make this process even more cost-effective.

In the past most of the research focused on individual removal of PAHs or HMs, but both are present in water sources. Currently, researchers are interested in simultaneous removal of organic pollutants and heavy metals due to their adverse effects on the environment, humans, and wildlife. The co-existence of PAHs and HMs in water is a

prevalent problem. It is important to decontaminate both from water sources and the possibility to remove them simultaneously is highly desirable and interesting. These contaminants have different properties and compositions that make it even more difficult to remove with the use of conventional procedures.

Among various kinds of methods, the one of the quickest, simplest, broadly applicable and most effective one is adsorption [254]. This method can be applied to remove different pollutants such as HMs and organic compounds. The elimination of the PAHs is reported using different adsorbents such as bentonite [255], chitosan [256], peat moss [257], activated rice husk [257], nanotubes [258], activated carbon [259], zeolite [260], biochar [261], and graphene [262].

Cyclodextrins (CDs) can form host-guest complex by inclusion of various molecules into the cavity with compatible dimension and polarity [263]. Thus, the adsorption of the hydrophobic PAHs in aqueous medium can be enhanced by CDs. However, CDs cannot remove the HMs due to inability to make complexes with metal ions. The modified CDs were designed having the ability to make complex with HMs, for example carboxymethyl- β -cyclodextrin can make complex with mercury, cadmium, strontium, and nickel in the presence of several organic pollutants [264–266]. The CDs are also biocompatible and non-toxic [264]. A CDs based porous polymer has been reported with high uptake of organic micropollutants [198]. A crosslinked mesoporous β -cyclodextrin polymer was synthesized using stiff aromatic groups as linkers that demonstrated high surface area for microorganic pollutants [199]. For removing both PAHs and HMs from water, a new adsorbent is designed in this work. A novel cross-linked resin has been synthesized, in which β -cyclodextrin and metal chelating motifs (aspartic acid and

aminophosphonate) are incorporated in a polymer network via Butler's cyclopolymerization [219]. The diallyl quaternary ammonium (DQA) salts are polymerized via cyclopolymerization protocol to yield different homo and co polymers having five membered ring backbone, which is considered an important architecture [220]. Among those salts Diallyl dimethylammonium chloride (DADMAC) is one of the salts that discussed in more than one thousand patents and research articles and extensively used for water decontamination applications [216]. Three DQA monomers diallylaminomethyl- β -cyclodextrin hydrochloride (DMCDH), diallylaspartic acid hydrochloride (DASAH), and diallylaminomethylphosphonic acid (DMPSA) were synthesized. Sulfur dioxide (SO_2) as fourth monomer was included and then using a cross linker tetra allylhexane-1,6-diamine (TAHDM) a new cross-linked tetrapolymer (CLTP) was obtained via cyclopolymerization. The β -cyclodextrin was incorporated to adsorb the PAHs (**Fig. 5.1**), while DASAH and DMPSA used as HMs (Pb^{2+} , Hg^{2+}) scavengers.

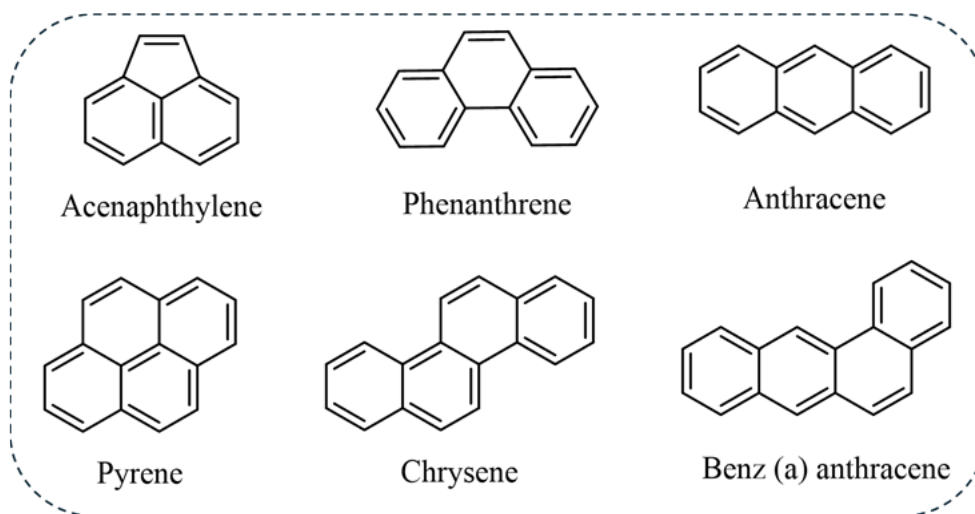


Figure 5.1. Structures of tested PAHs

5.2. Materials and Methods

5.2.1. Chemicals and materials

Imidazole and 2,2'-Azobisisobutyronitrile (AIBN) were purchased from Fluka Chemie AG (Buchs, Switzerland). Dimethylsulfoxide (DMSO), *p*-toluenesulfonyl chloride, β -Cyclodextrin and diallylamine, were purchased from Sigma-Aldrich. Monomers *N,N*-diallylaspartic acid hydrochloride [267], diallylaminomethylphosphonic acid [268] and cross linker tetra allylhexane-1,6-diamine (TAHDM) [269] were synthesized as described. The polyaromatic hydrocarbon standards (Isophorone, phthalic acid bis methyl ester, acenaphthylene, phenanthrene, anthracene, pyrene, chrysene, and Benz (a) anthracene) were purchased from SUPELCO Analytical, Germany. Analytical grade solvents (toluene, methanol (METH), dichloromethane (DCM), hexane (HEX), acetone (ACE), and acetonitrile (ACNT) were ordered from Fisher (Loughborough, UK).

5.2.2. Physical Methods

Field Emission Scanning Electron Microscope was used to analyze the morphology of the resin, and elemental analysis was done by EDS detector. Fourier Transform Infrared (FTIR) spectra of sorbent was taken by Nicolet 6700 spectrometer (Thermo Scientific). The thermogravimetric analyses (TGA) were performed using SDT analyzer (Q600: TA Instruments) under nitrogen flow.

5.2.3. Adsorption of Pb(II) and Hg(II)

A number of concentrations ppm to ppb level were prepared from Pb(II) and Hg(II) stock solutions (1000 ppm) and adsorption capacities (q_e) (mg g^{-1}) of the concentrations were

calculated by following **Eq. 5.1** where C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}) of the Pb(II) and Hg(II) respectively, V is volume (L) of Pb(II) and Hg(II) solution and m is the mass of the resin (g).

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (5.1)$$

The percent metal removal (R) was calculated using **Eq. 5.2**.

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (5.2)$$

The adsorption studies were carried out by the addition of resin (50 mg) into 0.2 – 1 ppm Pb(II) and Hg(II) solutions (20 mL) taken in screw cap glass vials with constant stirring (300 rpm) at 298 K for 3 h and maintaining the pH 6.0 for Pb(II) and pH 5.2 for Hg(II) using 0.1 M NaOH and/or 0.1 M HNO₃ solution. The solution were filtered and ICP-OES (Perk Elmer) analysis was performed to measure Pb(II) concentration while mercury analyzer (Lumex instrument) was used to determine Hg(II) concentration. Statistical analysis and isotherm fitting were done on the MATLAB program.

5.2.4. Analytical method for PAHs

To measure the PAHs level in aqueous media chromatography technique was applied as it is an established method and gas chromatography (GC)/ mass spectrometry (MS) has been widely used for this purpose. For the analysis of PAHs, GC has many advantages such as less solvent demand, automated processing, and simple operational conditions [270].

5.2.5. GC-MS conditions and configuration

The GC-MS configuration and conditions for the separation and quantification of target PAHs are the same as reported [271]. The temperature in the oven was adjusted as follows: initially, it was held at 50 °C for 1 minute then increased 6 °C min⁻¹ to 180 °C and then further ramped to 230 °C at 10 °C min⁻¹ and kept for 1.0 min for a total run time of 28.667 min. During the analysis, 1.0 µL of analyte was injected in the GC column by Splitless injection mode. The retention times were confirmed after running the scan mode for the identification of the analyte's peaks. For the quantitative analysis, the selective ion monitoring mode (SIM) was applied by selecting the ions of the respective PAHs as shown in **Table 5.1**.

Table 5.1. Target compounds, their retention time, and selected target ions for SIM mode

Retention time (min) ± SD	Target compounds	Abbreviation	Selected target ions
13.138 ± 0.021	Acenaphthylene	ACPH	152
17.066 ± 0.015	Phenanthrene	PHEN	178
17.14 ± 0.018	Anthracene	ANTH	178
20.447 ± 0.022	Pyrene	PYRE	202
24.000 ± 0.021	Chrysene	CHRY	208
24.144 ± 0.019	Benz (a) anthracene	BE(a)AN	228

5.2.6. Stir bar-supported micro-solid-phase extraction (SB- μ -SPE) procedure and optimization

SB- μ -SPE device was developed inside a bag of (polypropylene) PP sheets, 20 mg of the sorbent was taken as the optimum amount along with a stir-bar having a dimension of 7 mm x 2 mm, and the bag opening was heat sealed. It is important to make sure that the bag is properly sealed to avoid leakage during extraction. The device was sonicated for 5 minutes in toluene, then air-dried and enclosed in a glass vial with the sample solution and sodium chloride (0.5 g). The stirring was done for 15 minutes at 600 rpm and then the device was removed, cleaned with water, and dried with lint-free tissue. A microcentrifuge vial having 200 μ L methanol (as desorption solvent) was taken and the device was transferred to it and sonicated for 10 minutes. The solvent was removed for GC-MS analysis after the desorption was done. All the steps of extraction were optimized in deionized water by keeping the concentration of analyte at 5 ng mL⁻¹. The tests were performed in triplicates where peak area was used as a measuring factor for the study. The optimized factors included desorption solvent, sorbent dosage, extraction time, salt effect, solvent volume, and desorption time.

5.2.7. Analytical parameters and real sample analysis

The determination of limit of detections (LODs), linearity, relative recoveries, and repeatability was done with optimized experimental settings to assess the technique. To plot the target analytes, a five-points calibration curve was developed by taking known concentrations of PAHs ranging between 1-50 ng mL⁻¹ using ultrapure water. To calculate the LODs, the signal-to-noise (S/N = 3) ratio method was used. For the

evaluation of analysis reproducibility, three concentrations (1, 5, and 20 ng mL⁻¹) were selected from the linear range of the analyte. Three trials were conducted for each concentration. The optimized method was administrated for the analysis of PAHs in wastewater samples. The wastewater sample was collected from the domestic wastewater treatment plant prior to its discharge into large water bodies. For real sample analysis, a 10 mL unspiked sample was extracted using CLTP packed in SB- μ -SPE device and investigated using the GC-MS method. Real sample analysis was tested by spiking three concentrations (1, 5, 20 ng mL⁻¹) into the wastewater matrix. Relative recoveries were also tested in the wastewater.

5.2.8. Synthesis

(a) Preparation of Tosyl imidazole

Tosyl imidazole was synthesized as described [88]. 65 g of imidazole was dissolved in 250 ml dichloromethane (DCM) then the solution kept at 0 °C. 80 g of p-toluenesulfonyl chloride was dissolved in 250 ml of DCM then dropwise added onto the imidazole solution over the period of 90 minutes. The reaction mixture was allowed to come on room temperature followed by stirring for 2 hours. The resulting mixture was filtered by silica gel and washed with hexane-ethyl acetate (500 mL) in ratio of 1:1. The filtrate became residue under low pressure after addition of ethyl acetate (50 mL) and hexane (500 mL). Further filtration of this suspension was done to obtain white solid tosyl imidazole (84 g).

(b) Synthesis of 6-O-toluenesulfonyl- β -CD

A modified procedure is described [88]. In a 500 ml round bottom flask, 12.5 g of β -Cyclodextrin is dissolved in 255 ml of water by heating to 60 °C with vigorous stirring. When solution came to 45 °C, 8.9 g tosyl imidazole powder form added into it. After 2 hours, NaOH solution (5.22 g dissolved in 14 ml of water) was added dropwise into to the reaction mixture over the period of 20 minutes. After 10 minutes, reaction mixture was filtered to remove the unreacted tosyl imidazole. To quench the reaction, 13.7 g ammonium chloride was added resulting in a clear solution for a while. A milky suspension was obtained after 5 minutes. The reaction mixture was kept under stream of air overnight. For the workup, the product was mixed in 140 ml double distilled water. The water was separated by centrifugation. The reaction mixture was washed two times with ice-water and acetone respectively then dried (5 g, 40%). The reaction was repeated to obtain more tosyl containing β -CD derivative.

(c) Synthesis of diallyl amine monomer containing β -Cyclodextrin

10.0 g of diallylamine was added into the solution of 2 (9.0 g of 2 dissolved in 15 g of DMSO). At room temperature a clear solution was obtained. At 70 °C the homogenous solution was stirred under N₂ for 48 hours to get white solid. The reaction mixture was washed with ether (250 ml) and supernatant was decanted off. To this mixture, water (30 ml) was added and neutralized with 2.0 g potassium carbonate. The reaction mixture was slightly heated to facilitate acid-base reaction. Nitrogen gas was blown to remove unreacted diallylamine. The mixture was cooled to 5 °C, the precipitated diallylamine derivative was filtered, and washed with cold water (25 mL) and acetone (50 mL) and

dried under vacuum (7 g, 78%). The compound did not melt up to 290 °C as it was decomposed to a black material. [Found: C, 46.6; H, 6.8; N, 1.0%. C₄₈H₇₉NO₃₄ requires C, 47.48; H, 6.56; N, 1.15%]. ν_{max} (KBr): 3310, 2922, 2884, 1367, 1153, 1077, 1024, 936, 859, 754, and 583 cm⁻¹.

(d) Synthesis of 4 (diallyl amine salt containing β -Cyclodextrin)

4.88 g of diallyl amine containing β -Cyclodextrin **3** was added into 11.2 ml distilled water (heterogeneous solution) after that 400 mg of 37 % HCl added into it, the reaction mixture was soluble upon adding HCl. After keeping it in refrigerator for 15 minutes, freeze dried for 24 hours. White crystal of **4** was obtained (4.83 g, 99%). [Found: C, 45.0; H, 6.7; N, 1.0%. C₄₈H₈₀ClNO₃₄ requires C, 46.10; H, 6.45; N, 1.12%]. ν_{max} (KBr): 3392, 2927, 1643, 1452, 1342, 1158, 1029, 939, 853, 760, 706 and 585 cm⁻¹.

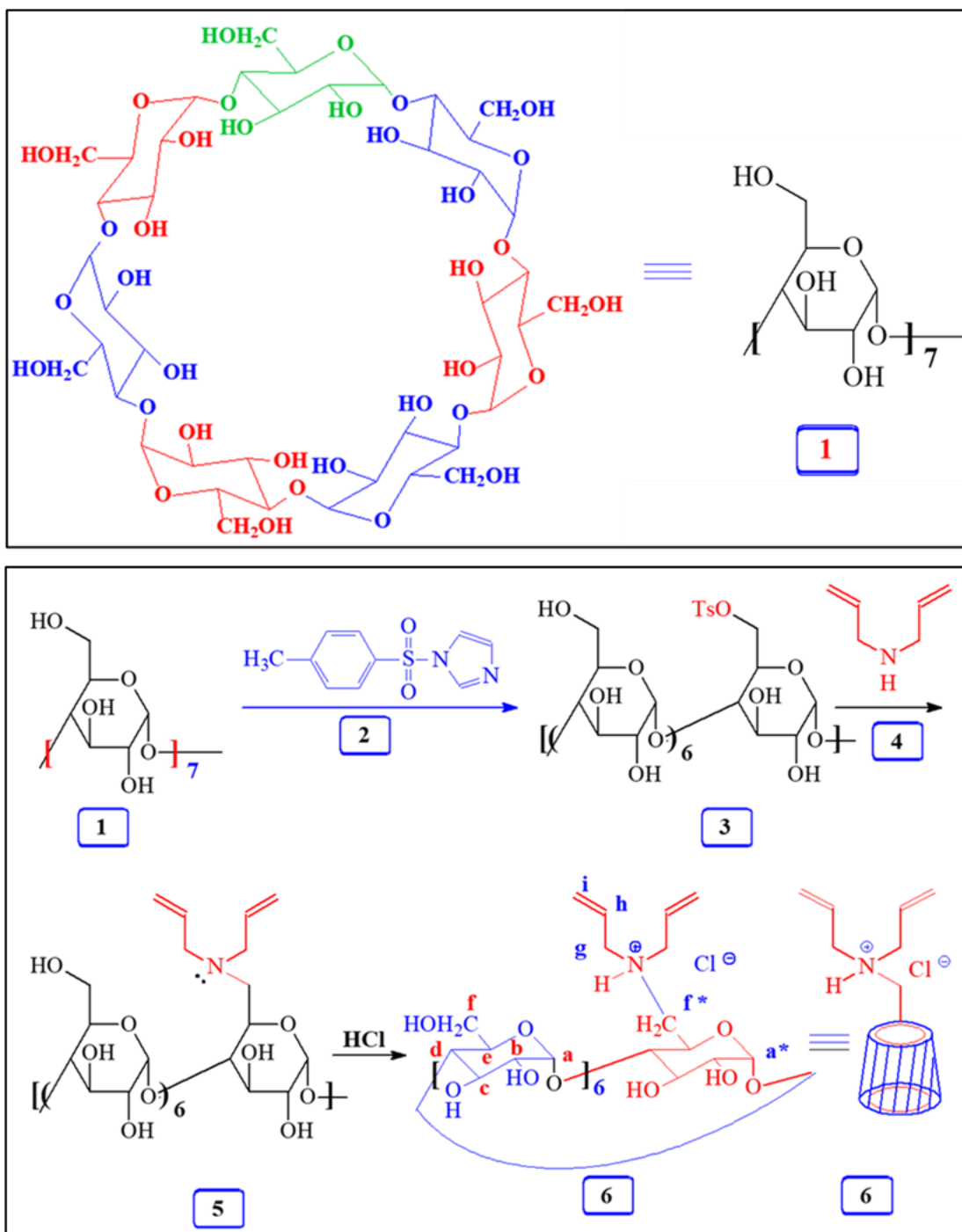
5.2.9. Synthesis of CLTP (DASAH - DMPSA - DMCDH)

A solution of monomer DASAH (0.86 g, 3.69 mmol), DMPSA (0.92 g, 3.69 mmol), DMCDH (4.00 g, 3.17 mmol) and cross-linker TAHDM (0.59 g, 1.70 mmol) in DMSO (10.2 g) was prepared in round bottom flask (50 mL). After purging the reaction mixture with SO₂ (1.1 g, 17 mmol) AIBN (295 mg) was added, and the mixture was stirred in a closed flask at 65 °C for 24 h. The reaction mixture became thick resulting in immobilization of stir-bar; DMSO (5.0 g) was added to the thickened mixture followed by addition of AIBN (55 mg), and the polymerization was continued at 75 °C for a further 22 h. The solidified material was soaked in water for 6 h, then washed with water and acetone. The resin was vacuum dried at 70 °C (5.3 g, 78%).

5.3. Results & Discussion

5.3.1. Synthesis of monomer

6-O-toluenesulfonyl- β -cyclodextrin **3** upon reaction with excess diallylamine **4** afforded tertiary amine **5**, which was converted cleanly to its hydrochloride salt **6** (**Scheme 5.1**). While β -CD **1** is sparingly soluble in water (18.5 mg mL⁻¹), its tosyl derivative **3** and tertiary amine **5** were found to be insoluble in water. Interestingly, diallylammonium monomer **6** is very soluble in water.



Scheme 5.1. Synthesis of β -cyclodextrin-derived diallyl amine salt

To confirm the structure and integrity of the CD motifs, NMR spectra of **1**, **3**, **5**, and **6** were recorded and displayed in **Figs. 5.2** and **5.3**. The carbons are marked **a-f** as shown in

the structure of **1** (**Scheme 5.1**). The proton marked 'a' at C1 appeared at δ 4.8 ppm in all the spectra, while alkene protons marked 'h' and 'i' of **5** and **6** are displayed around δ 5.5 ppm as expected (**Fig. 5.2d, 5.2e, 5.2f**). Note that the spectra in D₂O are simpler than in DMSO-d₆, because in the latter solvent the OH signals appear at different chemical shifts (*cf.* **Figs. 5.2a vs. 5.2b and 5.2e vs. 5.2f**).

¹³C NMR spectra of β -CD **1** display six signals in DMSO-d₆ confirming the equivalent nature of all the seven cyclic skeletons (**Fig. 5.3a, b**). However, in the tosyl **3** and diallylamine derivatives **5**, the cyclic rings become nonequivalent and as such display more signals (**Fig. 5.3c, d**). The alkene carbons marked 'h' and 'i' of **5** appeared in their expected chemical shifts (**Fig. 5.3d**). Note each alkene carbon around δ 127 ppm is split into a doublet of equal intensity because of their diastereotopic nature (**Fig. 5.3f**). 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*).

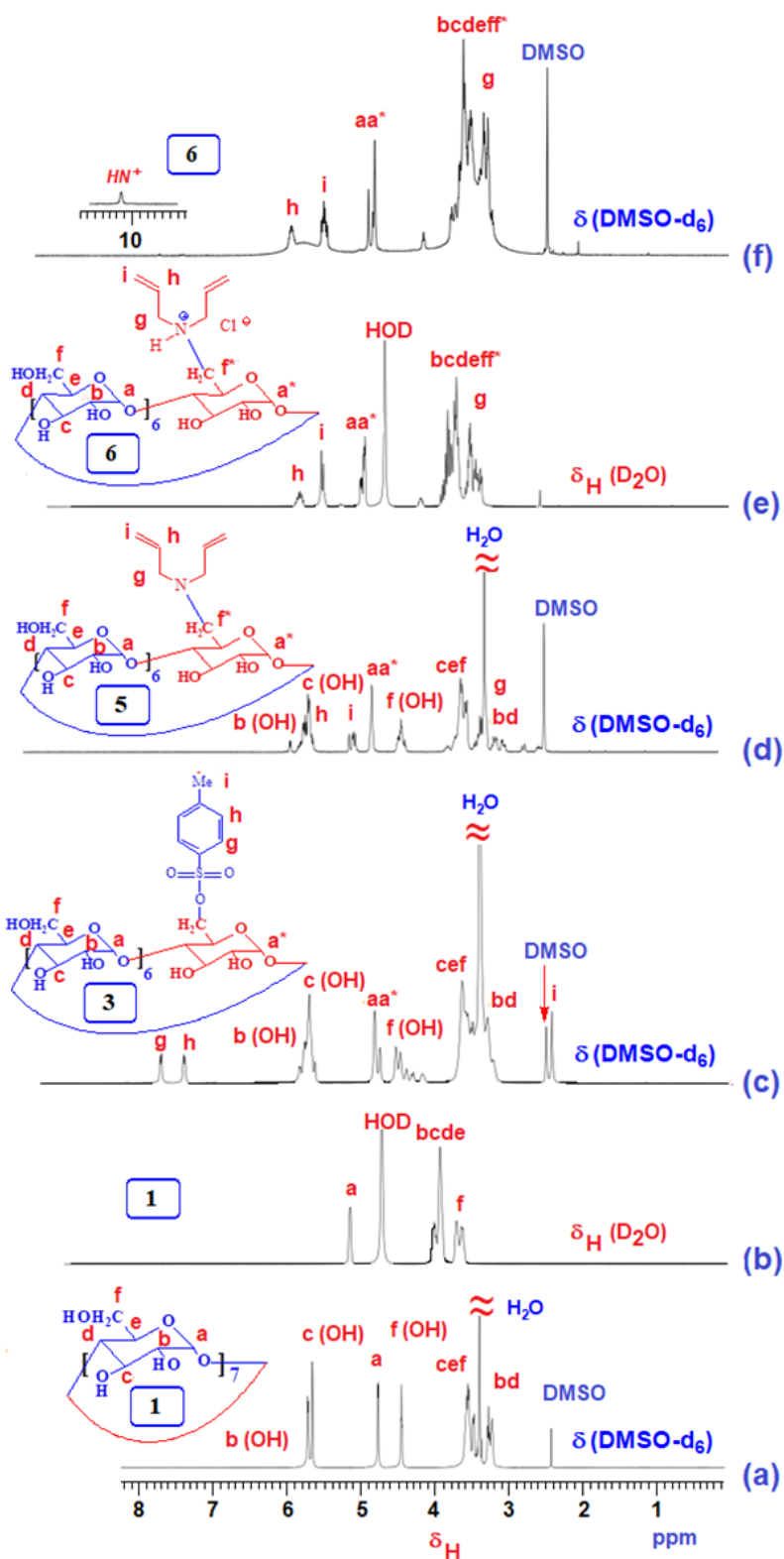


Figure 5.2. ^1H NMR spectra of (a) b-Cyclodextrin (1) in DMSO-d_6 , (b) 1 in D_2O , (c) 3 in DMSO-d_6 , (d) 5 in DMSO-d_6 , (e) 6 in D_2O , and (f) in DMSO-d_6

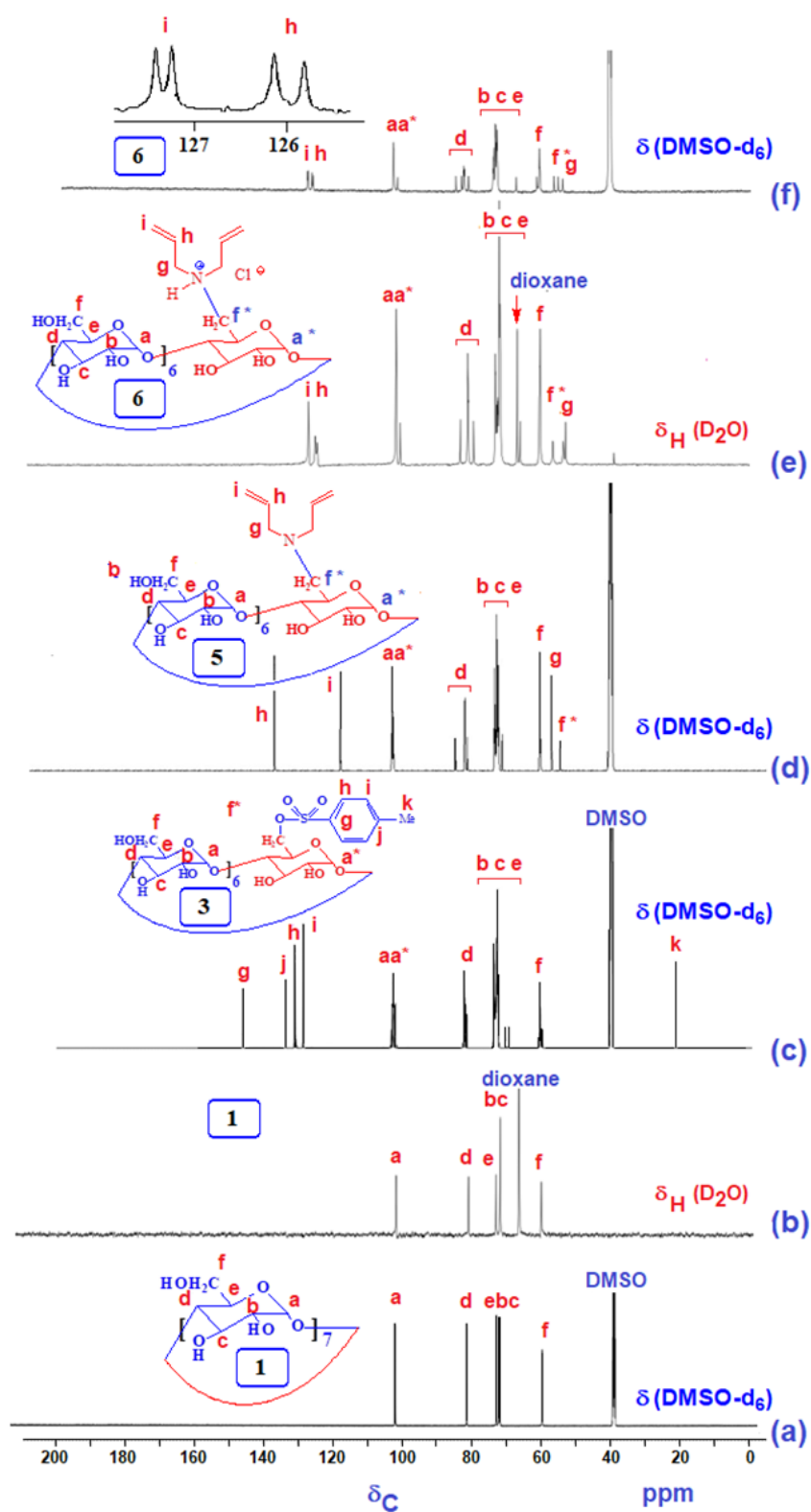
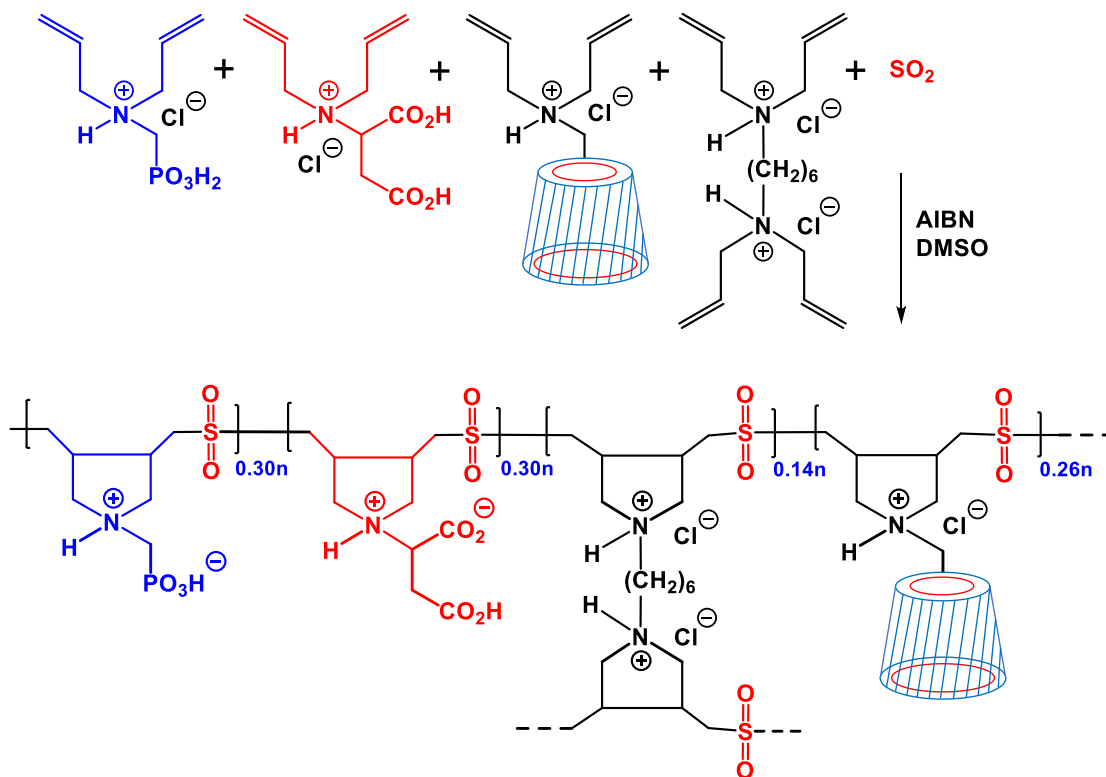


Figure 5.3. ^{13}C NMR spectra of (a) b-Cyclodextrin (1) in DMSO- d_6 , (b) 1 in D_2O , (c) 3 in DMSO- d_6 , (d) 5 in DMSO- d_6 , (e) 6 in D_2O , and (f) 6 in DMSO- d_6

5.3.2. Adsorbent (CLTP) synthesis

The CLTP was synthesized (78 %) via AIBN initiated copolymerization of monomers DASAH (30 mol%), DMPSA (30 mol%), and DMCDH (26 mol%) using cross linker TAHDM (14 mol%) (**Scheme 5.2**). The =C–H and C=C stretching of diallyl motifs in the monomers normally appears at $\approx 3080\text{ cm}^{-1}$, and $\approx 1640\text{ cm}^{-1}$ respectively [267,272]. The absence of these vibrations in the FTIR spectra of CLTP confirmed that all alkenes' motifs are consumed for the formation of cyclic rings present in the resin backbone. ν_{max} (KBr): 3363, 2924, 1701, 1627, 1411, 1299, 1155, 1122, 1078, 1024, 995 and 853 cm^{-1} .



Scheme 5.2. Synthesis of CLTP

5.3.3. TGA of CLTP

The TGA analysis showed a gradual weight loss that started from 38 °C. The continuous decrease observed till 240 °C with 11% weight loss that is attributed to moisture escape. A sharp weight loss of 11% in the 241 – 260 °C range is attributed to degradation of some organic fractions present in the CLTP. A gradual loss of 38% in the 261–793 °C range is due to the loss of pyrrolidine rings. The TGA curve shows that the CLTP is stable up to 200 °C (Fig. 5.4)

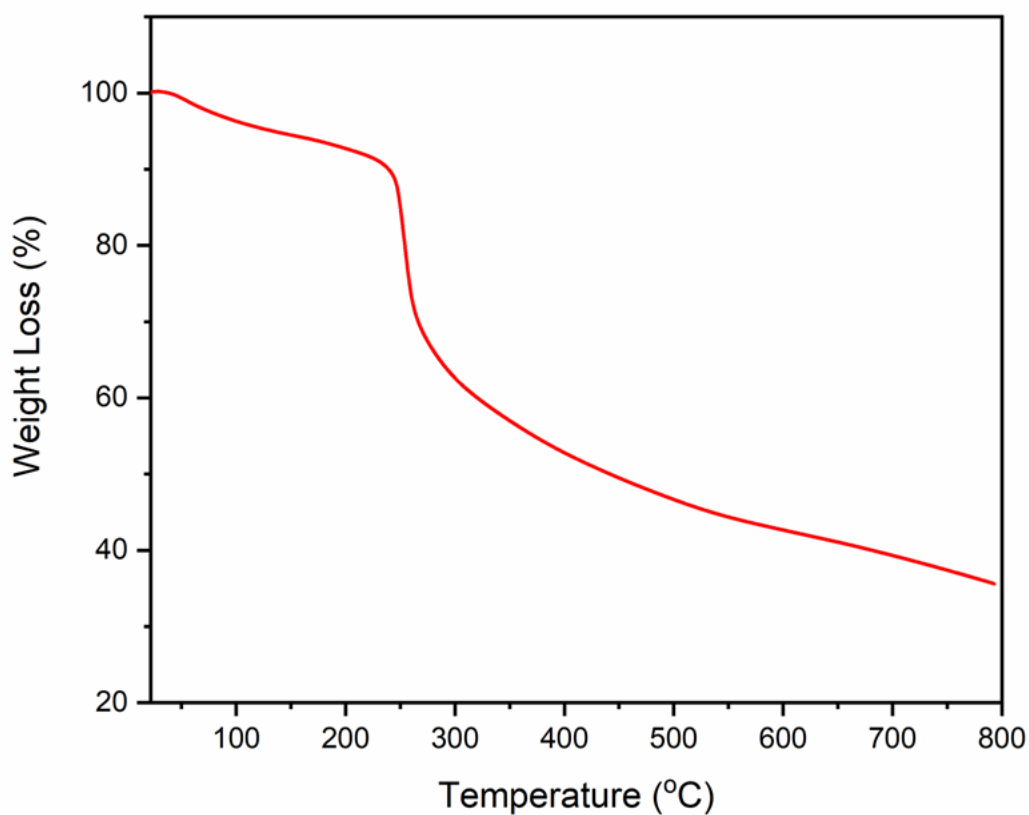


Figure 5.4. TGA graph of CLTP

5.3.4. FTIR Analysis

The FTIR analysis was done for the CLTP, Pb^{2+} loaded CLTP and Hg^{2+} loaded CLTP (**Fig. 5.5**) The characteristic peaks of β -CD motifs were observed at 3363 and 2924 cm^{-1} that attributed to the O-H and C-H stretching vibrations. Moreover, the peaks at 1627, 1155, 1024, and 853 cm^{-1} correspond to glucose units (H-O-H, C-O, C-O-C) and rings (C-O-C) of CD, respectively [273]. The absorptions at 1411 and 1627 cm^{-1} were recognized as the symmetric and asymmetric stretching of COO^- present in the aspartic acid motif in the dipolar form, respectively [274]. The presence of CO_2H was confirmed by the peak at 1701 cm^{-1} that was due to the C=O vibration. The two peaks at 995 and 1078 cm^{-1} were attributed to P-O stretching vibrations of the phosphonate motif. The Vibrations of SO_2 moiety were observed at 1122 and 1299 cm^{-1} [275]. In the Pb^{2+} loaded CLTP, the changes in the stretching vibrations for P-O peaks observed due to the complex formation between the phosphonate group and the Pb^{+2} ions [275]. Additionally, the change in broadness and intensity of these peaks justify the Pb^{2+} presence [276]. Similarly in the case of Hg^{2+} loaded CLTP, a visible change was observed in the strength of the peaks ranging between 600 – 1500 cm^{-1} due to the presence of Hg^{2+} [277].

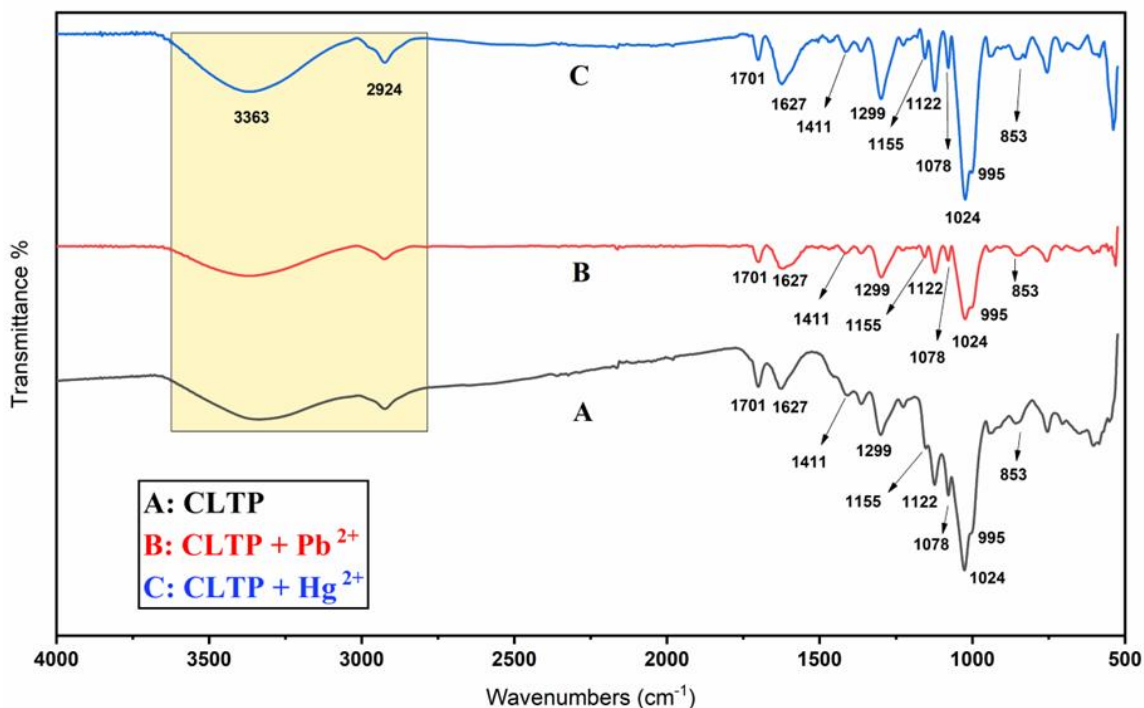


Figure 5.5. FTIR spectra of CLTP (A), Pb²⁺ loaded CLTP (B) and Hg²⁺ loaded CLTP (C)

5.3.5. SEM and EDX analysis

The morphological analysis of the surface was conducted for loaded and unloaded CLTP by SEM after coating with gold. The surface of the unloaded resin showed smooth surface with plane crystals, while in case of loaded resin a change in surface roughness and morphology can be seen where metal ions are deposited. The EDX of the resins was also done to check the elemental composition of the surface. The presence of C, O, S, N, P, and Cl confirmed as expected for CLTP. The EDX spectrum of CLTP + Pb²⁺ showed the presence of Pd along with C, O, S, N, and P, while the CLTP + Hg²⁺ spectrum showed the presence of Hg addition to the C, O, S, N and P. The EDX analysis and change in surface morphology confirm the adsorption of the metal ions on CLTP (**Fig. 5.6**).

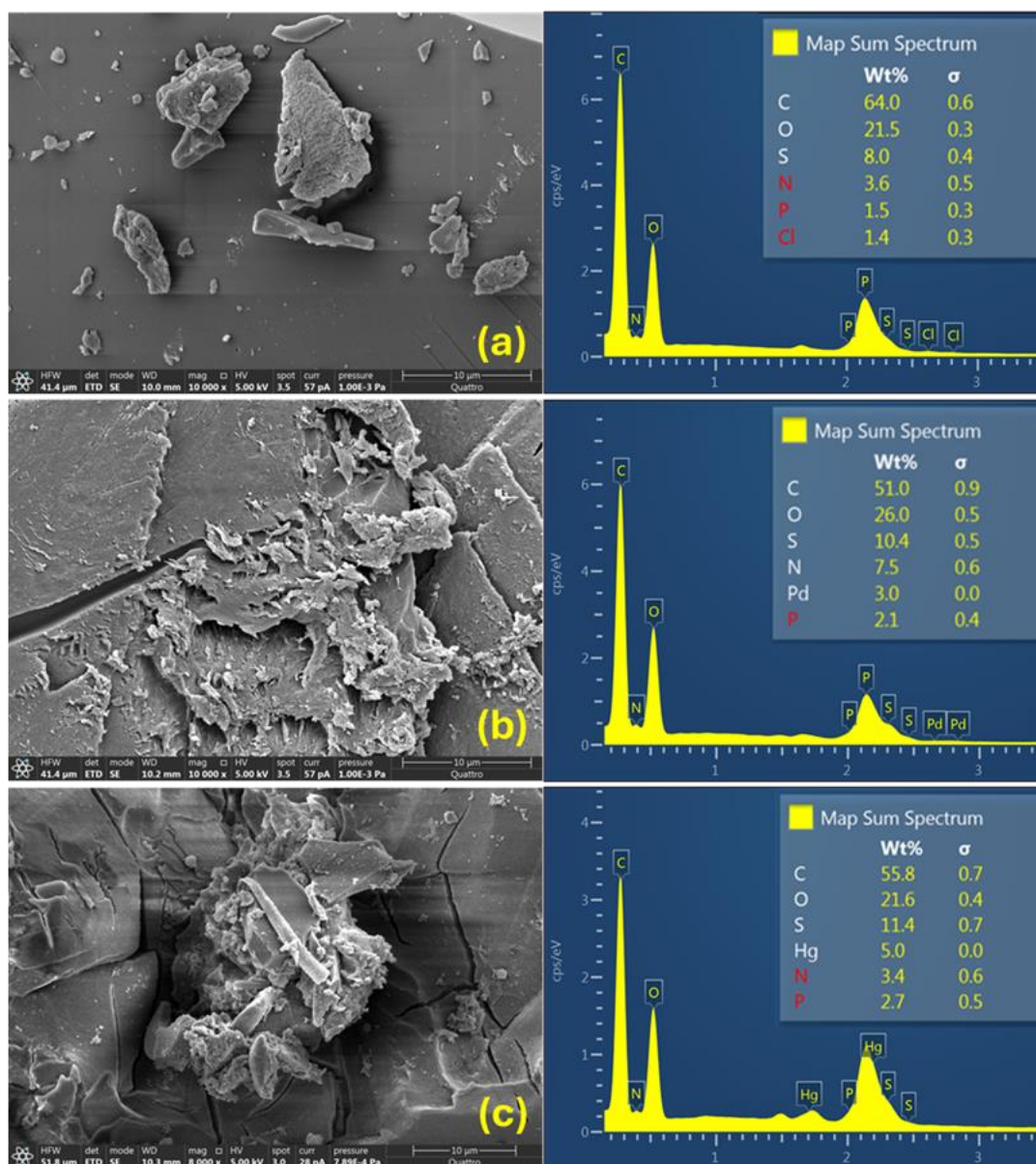


Figure 5.6. SEM and EDX analysis of unloaded CLTP (a), Pb²⁺ loaded CLTP (b) and Hg²⁺ loaded CLTP (c)

5.3.6. Adsorption

The C_e and q_e values were determined by Eq 5.1 (Table 5.2), using resin CLTP, with initial Pb(II) and Hg(II) concentrations (C_o) in the range 0.2 – 1 ppm (i.e., 200 ppb - 1 ppm) at pH 6.0 (for Pb(II)) and pH 5.2 (for Hg(II)) for 3 h at 298 K. The percent removal (R) of Pb(II) and Hg(II) adsorption by the CLTP was calculated by Eq 2. The linear

relation between the initial concentration (C_0) and equilibrium adsorption capacity (q_e) is found for both metals as shown in **Fig 5.7**. The adsorption mechanism can be explained by finding the relation between equilibrium concentration (C_e) and q_e . The construction of isotherm models helps to find this relation. Isotherm models are used to describe the layer formation on the adsorption sites, their nature, and type of interactions [277] . The Freundlich and Temkin isotherms were discussed for the current study.

Table 5.2. C_e , q_e and R values of Pb(II) and Hg(II) adsorption

Pb(II)			
C_0 (mg L ⁻¹)	C_e (mg L ⁻¹)	q_e (mg g ⁻¹)	Removal (%)
0.2	0.0375	0.0650	81.2
0.4	0.0875	0.125	78.2
0.6	0.138	0.185	77.1
0.8	0.175	0.250	78.2
1	0.200	0.320	80.0
Hg(II)			
0.2	0.071	0.0516	64.5
0.4	0.125	0.110	68.8
0.6	0.199	0.161	66.9
0.8	0.280	0.208	65.0
1	0.375	0.250	62.5

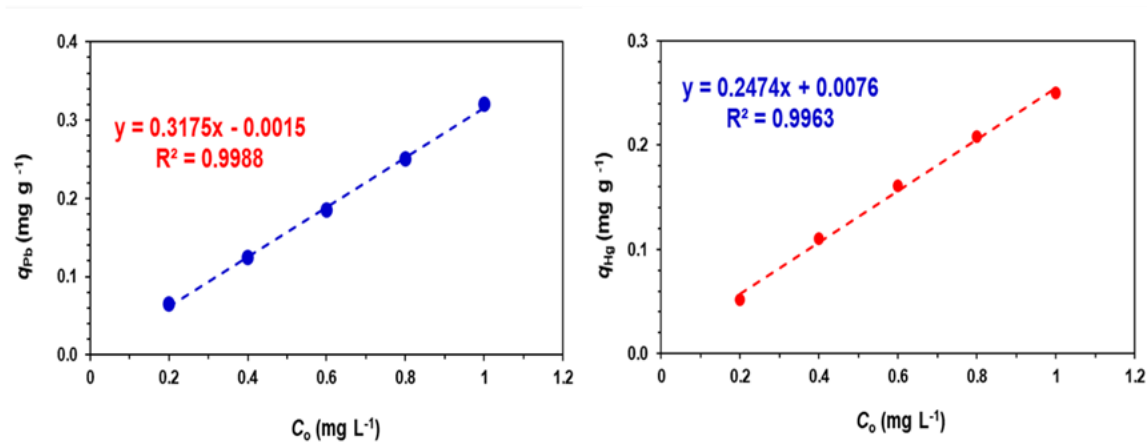


Figure 5.7. The adsorption capacity versus initial concentration of CLTP for Pb(II) (left) and Hg(II) (right)

5.3.7. Isotherm and kinetic studies of Pb(II)

For the explanation of heterogeneous adsorption with a system having uniform energy, Freundlich isotherm model (Eq 5.3) used. The constants n and k_f can be found from the graph (Fig.5.8) having linear relation (Table 5.3).

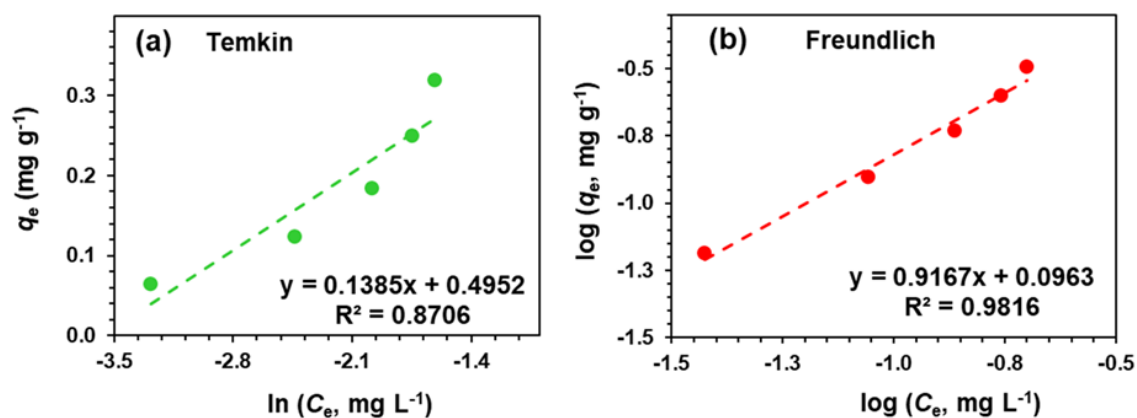


Figure 5.8. Temkin (a) and Freundlich (b) adsorption isotherms for Pb(II) with CLTP at 298 K

Table 5.3. Freundlich and Temkin isotherm constants for Pb(II) and Hg(II) adsorption at 298 K on CLTP

Freundlich Isotherm model			
Metal	n	$K_f (\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n})$	R^2
Pb(II)	1.091	1.25	0.9816
Hg(II)	1.069	0.68	0.9761
Temkin Isotherm			
Metal	A (L g^{-1})	B (J mol^{-1})	R^2
Pb(II)	36	0.139	0.8706
Hg(II)	21	0.118	0.994

The Freundlich isotherm with n value of 1.091 and 0.9816 R^2 value is well fitted in this case. The n value suggests that the selective adsorption is carried out through chemisorption route [278].

$$\text{Freundlich isotherm model: } \log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5.3)$$

The Temkin isotherm model (**Eq. 5.4**), based on the inverse relation among the surface coverage strength and heat of adsorption of the metal ions [278]. The heat of adsorption B and equilibrium binding constant A are found by plotting the graph and using **Eq. 5.4** (**Table 5.3**). The Temkin plot is not well fitted in the case of Pb(II).

$$\text{Temkin isotherm model: } q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e = B \ln A + B \ln C_e \quad (5.4)$$

For the kinetic behavior of the metal adsorption on the resin, pseudo first and second order linear equations (**Eqs. 5.5 & 5.6**) were applied [242].

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (5.5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5.6)$$

where k_1 (1/min) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the rate constants of first and second order respectively. The real time adsorption (q_t) can be calculated by the concentration (C_t) with time.

The metal uptake was 80 % by the resin within 10 minutes of experiment, then it was fixed until 100 minutes passed and the experiment was continued up to 150 minutes with constant 83 % removal (**Fig 5.9a**). The pseudo-second order model describes the kinetic behavior of the metal as the correlation R^2 value best fit in plot (**Fig 5.9c**) and the rate constant k_2 found to be $2.518 \text{ g mg}^{-1} \text{ min}^{-1}$.

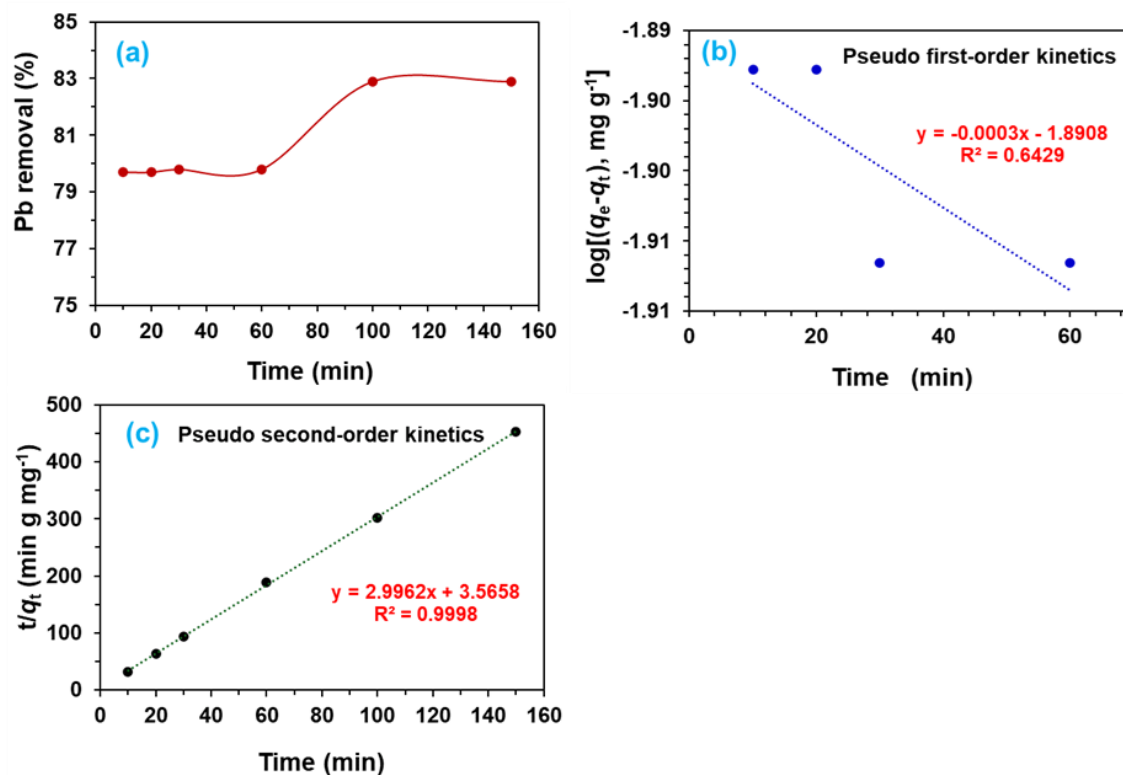


Figure 5.9. Kinetic behavior of metal adsorption by CLTP (a) percent removal versus time plot ($C_o = 1 \text{ ppm}$), (b) pseudo first-order kinetic plot, (c) Pseudo second-order kinetic plot

5.3.8. Isotherm analysis for Hg(II)

Freundlich isotherm showed n value of 1.069 and R^2 of 0.9761 for Hg(II) (**Fig 5.10**). The interaction between adsorbent and adsorbate (with uniform distribution) can be explained by the Temkin isotherm assuming that there is an inverse relation between heat of adsorption and surface coverage [279]. A linear plot between q_e and $\log C_e$ was constructed (**Fig 5.10**), the binding constant A represents the intercept, while slope is considered as b using **Eq 5.4** (**Table 5.3**). The Temkin isotherm is very well fitted in the case of Hg(II) because of the R^2 value that is equal to 0.994, so this isotherm model explain the equilibrium closely. It can be concluded from this data, that the adsorption process happens through the surface coverage due to the interaction between adsorbate and adsorbent.

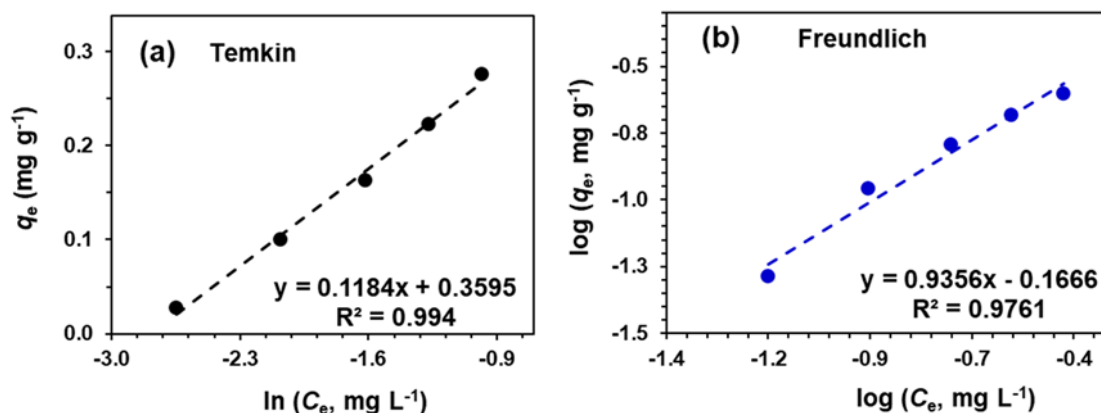


Figure 5.10. Temkin (a) and Freundlich (b) adsorption isotherms for Hg(II) with CLTP at 298 K

5.4. Optimization of CLTP packed SB- μ -SPE

5.4.1. Effect of resin loading on PAHs extraction

The understanding of interaction chemistry between sorbent-analytes is a key factor for the extraction of the target analyte. In this work, to extract the organic micropollutant analytes, the hydrophobic nature of the sorbent is the desired property including reasonable cavity surface area. The CLTP (30 mg) was sealed in PP bag and tested by GC-MS (5 ng mL⁻¹ sample concentration) after the running the extraction in SB- μ -SPE device for 2.5 minutes with PAHS containing sample (10 mL). Afterwards, methanol (200 μ L) was used for desorption of analytes. The extraction pattern was observed for the interested PAHS (**Fig. 5.11**) that show the relatively smaller in size (length) PAHs, like ACPH followed by PHEN, PYRE and ANTH have more interaction with sorbent.

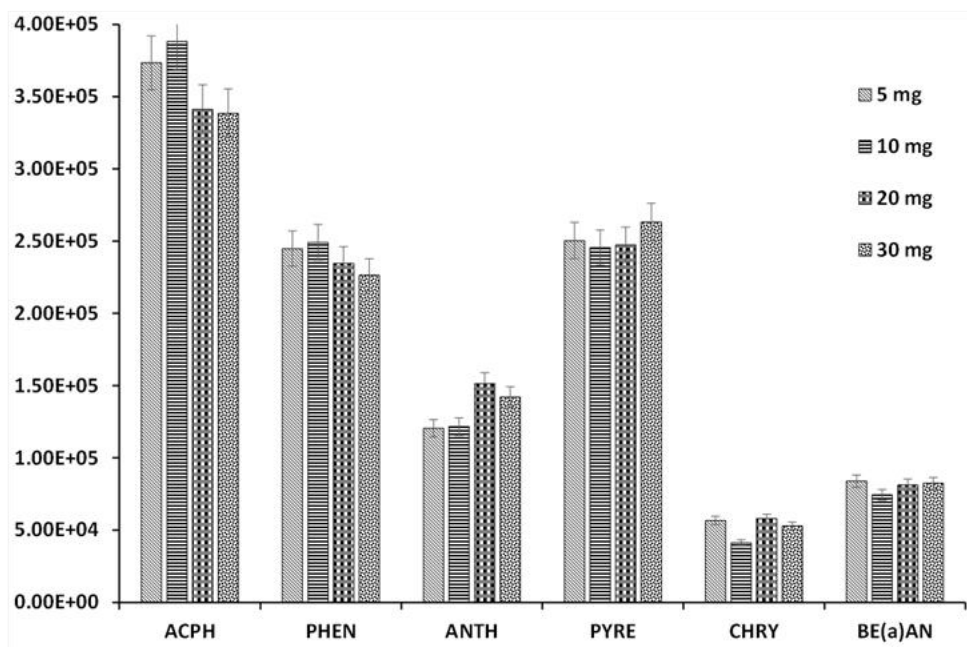


Figure 5.11. Conditions: PAH used concentration: 5 ng mL⁻¹; adsorbent material: CLTP; Extraction time: 2.5 min; desorption time: 10 min; desorption volume: 200 μ L; desorption solvent: methanol; salt mass: 2.0 g

5.4.2. Optimization of sorbent dosage in the extraction method

To check the effect on the extraction efficiency of the sorbent amount in the PAHs extraction, the varied amount of CLTP was taken in the range 5-30 mg and keeping other variables constant. Generally, the higher the amount of sorbent, more extraction is expected, as the more host sites available for PAHs. In this case, it was observed that increased sorbent amount did not affect significantly on the extraction of PAHs, from 5 mg to 10 mg, very small amount of extraction increased in some of PAHs, but that is almost similar with 5 mg sorbent amount. The CLTP achieved maximum extraction by using 5 mg of it. Therefore, the further extraction study was done in the same optimum sorbent amount (**Fig 5.11**).

5.4.3. The role of desorption solvent in extraction procedure

The selection of desorption solvent is critical for outstanding analyte desorption. Usually, the choice of solvent is dependent on the analyte's polarity, in this case, PAHs are fairly nonpolar so a non-polar solvent will be used. Therefore, five different solvents: methanol (METH), dichloromethane (DCM), hexane (HEX), acetone (ACE), and acetonitrile (ACNT) were used as the desorption solvent (**Fig. 5.12**). DCM demonstrated the best desorption ability for the desorption of PAHs from CLTP sorbent. The reason could be due to relatively less polar property and molecule size. DCM, which is a relatively nonpolar solvent, has shown excellent desorption for both highly nonpolar and relatively less nonpolar PAHs during desorption process. Hence, DCM is selected as desorption solvent.

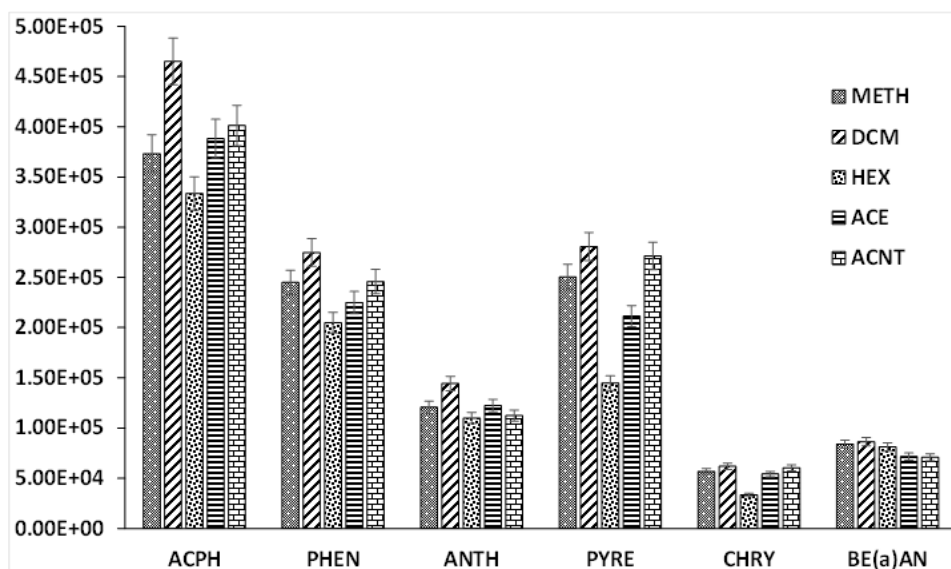


Figure 5.12. Effect of desorption solvent: Conditions: PAH used concentration: 5 ng mL⁻¹; sorbent material: CLTP; sorbent dosage = 5mg; Extraction time: 2.5 min; desorption time: 10 min; desorption volume: 200 μ L; salt mass: 2.0 g

5.4.4. The effect of the volume taken for desorption solvent

The desorption reproducibility and efficiency can be affected by the volume of solvent used for the desorption of analytes. A range of solvent volume (200 – 600 μ L) used to select the optimum volume that found to be 400 μ L in this case as this is volume when most of the analyte desorption was obtained (**Fig. 5.13**). The desorption efficiency reduced proportionately above 400 μ L solvent volume that can be because of the analyte dilution. so, lower response observed during analysis. In contrast, at lower desorption volumes (< 300 μ L) SB- μ -SPE device may immerse partially, thus, decreased desorption efficiency, and irreproducibility of the analysis was observed in some cases. Hence, 400 μ L volume was selected for succeeding extraction methods.

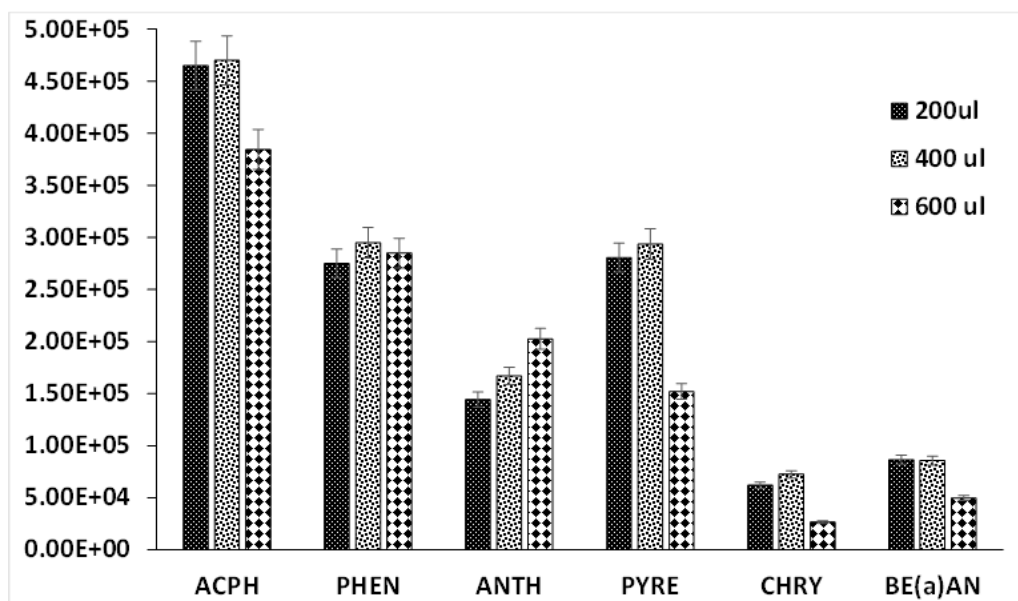


Figure 5.13. Effect of desorption solvent volume: Conditions: PAH used concentration: 5 ng mL⁻¹; sorbent material: CLTP; sorbent dosage = 5mg; Extraction time: 2.5 min; desorption solvent: DCM; desorption time: 10 min; salt mass: 2.0 g

5.4.5. The effect of salt analysis

The salting out effect is assessed according to the analyte properties. In general, analyte extraction can be enhanced by the addition of salt or vice versa. It is anticipated that by addition of salt to the sample solution, the solubility of the target PAHS such as non-polar analytes will decrease in aqueous solution. This will show a decrease in analyte extraction. The maximum analyte extraction ability was observed with the amount of 2g NaCl used after using different amounts of Salt (0.5 – 3.5 g) (Fig. 5.14). There was no effect observed after adding more salt on the PAH extraction. Hence, 2.0 g was is the optimum salt amount for further experiments.

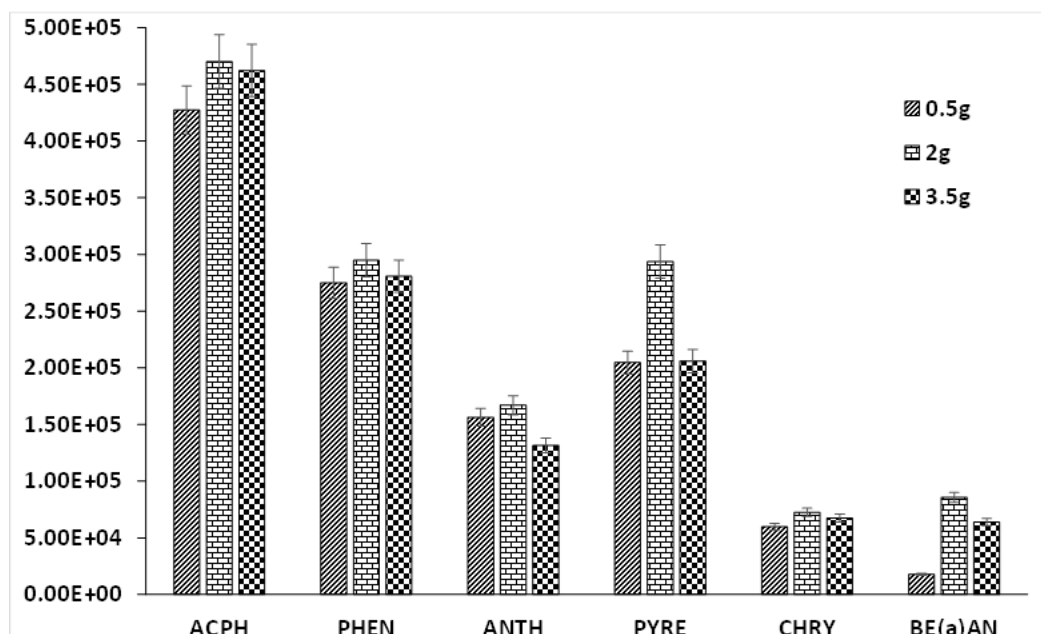


Figure 5.14. Effect of salt addition: Conditions: PAH used concentration: 5 ng mL⁻¹; sorbent material: CLTP ; sorbent dosage = 5mg; Extraction time: 2.5 min; desorption time: 10 min ; desorption solvent: DCM; desorption volume: 400 µL

5.4.6. The optimization of extraction method parameters (extraction and desorption time)

SB-µ-SPE is an equilibrium based, non-exhaustive technique; therefore, extraction time is a vital parameter to study. The extraction time usually has direct relation with the amount of analyte extracted before equilibrium state. The extraction time was optimized by running extraction experiment and varying the time (1 – 10 min). The maximum extraction was achieved at 2.5 min (**Fig. 5.15**). The desorption time is also an important parameter to achieve maximum extraction. The SB-µ-SPE (containing analytes) was submerged in DCM then sonicated by varying the sonication time (5 – 30 min). The desorption of the PAHS analytes increases with the desorption time up to 10 min and then decreased (**Fig. 5.16**). Consequently, 10 min was chosen as the optimized desorption time.

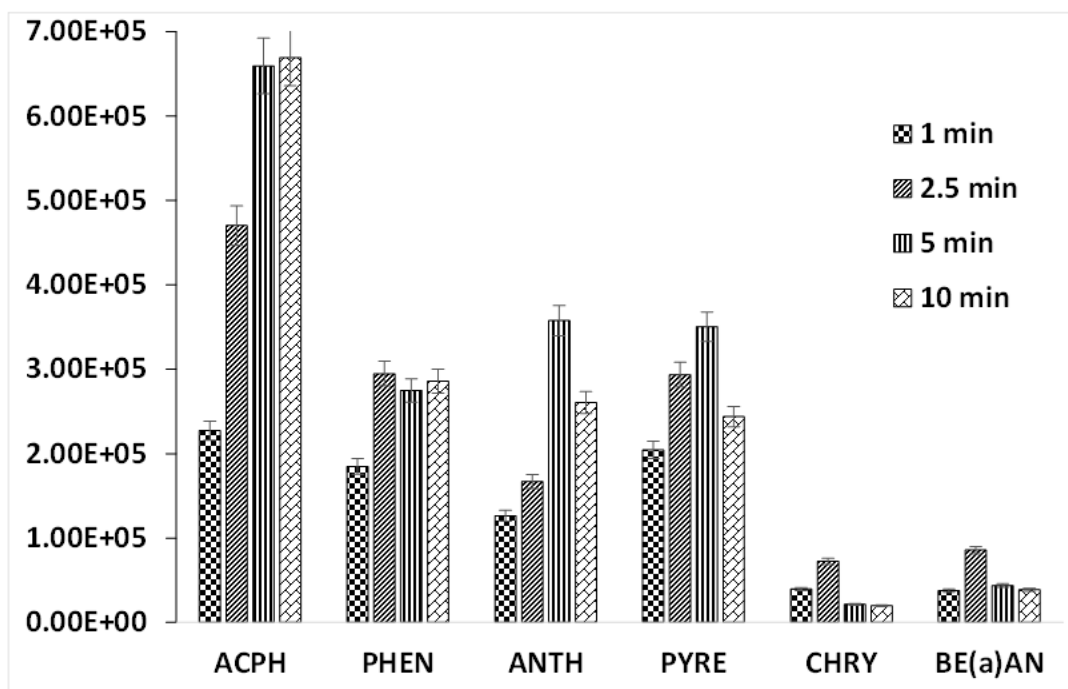


Figure 5.15. Effect of extraction time: Conditions: PAH used concentration: 5 ng mL⁻¹; sorbent material: CLTP; sorbent dosage = 5mg; desorption volume: 400 µL; desorption time: 10 min; desorption solvent: DCM; salt mass: 2.0 g

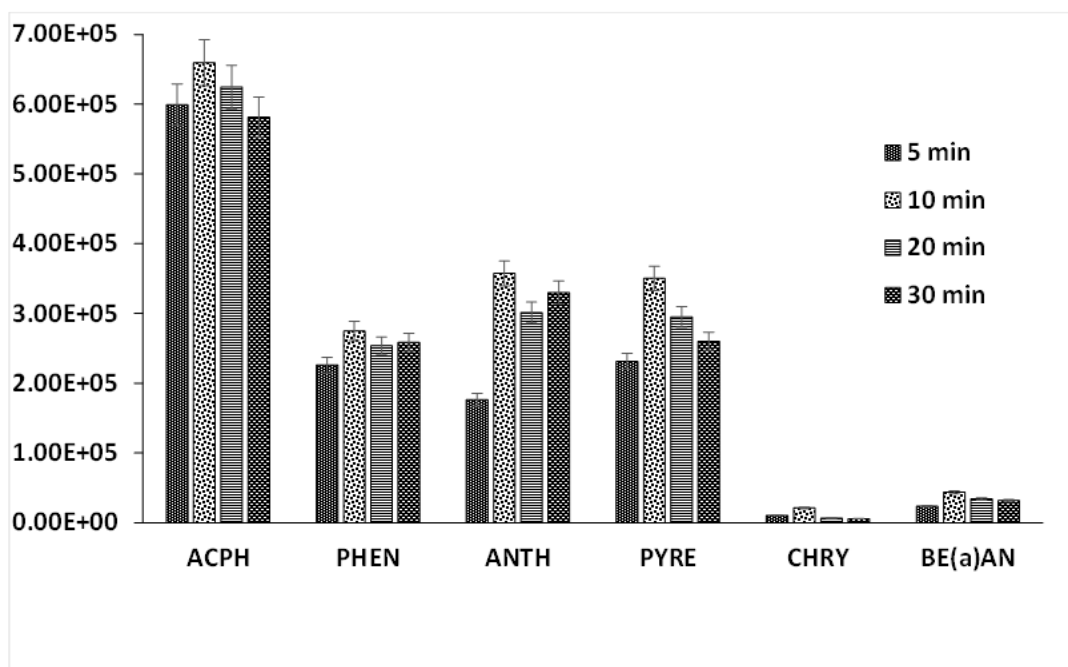


Figure 5.16. Effect of desorption time: Conditions: PAH used concentration: 5 ng mL⁻¹; sorbent material: CLTP ; sorbent dosage = 5mg; Extraction time: 5 min desorption volume: 400 µL; desorption solvent: DCM; salt mass: 2.0 g

5.5. Analytical parameters for GC-MS

The R^2 values are observed between 0.9621 and 0.9944 for analysis. There was less than 11 % difference in the reproducibility of the method. The analysis and extraction produced overall lower LODs between 0.013 and 0.35 ng mL⁻¹ (S/N = 3) as shown in

Table 5.4.

Table 5.4. Analytical features of the method

Analyte	R^2	Slope	LOD (ngmL ⁻¹)	Enrichment factor	Matrix effect and extraction efficiency (Mean relative recoveries n=3)			RSDs (%) (n=3)		
					1	5	20	1	5	20
ACPH	0.9939	99877	0.028	24.7	100.34	89.52	99.14	9.39	5.78	8.29
PHEN	0.9621	61159	0.035	25.2	96.81	99.44	97.89	7.26	8.52	9.08
ANTH	0.9773	18591	0.017	24.1	93.95	92.79	95.31	10.87	3.13	4.91
PYRE	0.9944	24657	0.013	23.6	98.49	93.42	99.44	10.33	4.91	10.9
CHRY	0.9319	980.41	0.019	23.8	91.01	98.29	96.69	6.30	5.63	9.69
BE(a)AN	0.9716	919.74	0.033	23.2	100.75	85.70	92.38	10.28	4.40	7.81

5.6. Conclusion

A cross linked adsorbent was successfully synthesized via cyclopolymerization of newly synthesized diallyl amine salt monomer bearing β -CD motif with metal chelating monomers using a cross linker. The extraction efficiency of the newly synthesized cross-linked resin for polyaromatic hydrocarbons and heavy metal ions from contaminated water sample was checked. A new analytical method is optimized to extract PAHs from aqueous sample using CLTP via GC-MS. The HMs adsorption experiments were performed to check the removal efficiency of the CLTP for metal ions. The resin can be used as dual-purpose adsorbent that will simultaneously remove the PAHs and HMs.

References

- [1] I.A. Ashcroft, J. Comyn, Effect of Water and Mechanical Stress on Durability, Handbook of Adhesion Technology (2011) 787–822. https://doi.org/10.1007/978-3-642-01169-6_31.
- [2] H. Zhao, C. Sun, R.J. Stewart, J.H. Waite, Cement proteins of the tube-building polychaete *Phragmatopoma californica*, Journal of Biological Chemistry 280 (2005) 42938–42944. <https://doi.org/10.1074/jbc.M508457200>.
- [3] H. Shao, R.J. Stewart, Biomimetic Underwater Adhesives with Environmentally Triggered Setting Mechanisms, Advanced Materials 22 (2010) 729–733. <https://doi.org/10.1002/ADMA.200902380>.
- [4] H. Lee, B.P. Lee, P.B. Messersmith, A reversible wet/dry adhesive inspired by mussels and geckos, Nature 2007 448:7151 448 (2007) 338–341. <https://doi.org/10.1038/nature05968>.
- [5] Y. Tian, Y. Cao, Y. Wang, W. Yang, J. Feng, Realizing Ultrahigh Modulus and High Strength of Macroscopic Graphene Oxide Papers Through Crosslinking of Mussel-Inspired Polymers, Advanced Materials 25 (2013) 2980–2983. <https://doi.org/10.1002/ADMA.201300118>.
- [6] F. Zhang, S. Liu, Y. Zhang, Y. Wei, J. Xu, Underwater bonding strength of marine mussel-inspired polymers containing DOPA-like units with amino groups, RSC Adv 2 (2012) 8919–8921. <https://doi.org/10.1039/C2RA21312E/>.
- [7] X.D. Pan, Z. Qin, Y.Y. Yan, P. Sadhukhan, Elastomers with chain-end mussel-mimetic modification for nanocomposites: Strong modifications to reinforcement and viscoelastic properties, Polymer (Guildf) 51 (2010) 3453–3461. <https://doi.org/10.1016/J.POLYMER.2010.05.031>.
- [8] B.P. Lee, K. Huang, F.N. Nunalee, K. Shull, P.B. Messersmith, Synthesis of 3,4-dihydroxyphenylalanine (DOPA) containing monomers and their co-polymerization with PEG-diacrylate to form hydrogels, J Biomater Sci Polym Ed 15 (2004) 449–464. <https://doi.org/10.1163/156856204323005307>.
- [9] H.C. Yang, J. Luo, Y. Lv, P. Shen, Z.K. Xu, Surface engineering of polymer membranes via mussel-inspired chemistry, J Memb Sci 483 (2015) 42–59. <https://doi.org/10.1016/J.MEMSCI.2015.02.027>.
- [10] Y. Tian, Y. Cao, Y. Wang, W. Yang, J. Feng, Realizing Ultrahigh Modulus and High Strength of Macroscopic Graphene Oxide Papers Through Crosslinking of

- Mussel-Inspired Polymers, *Advanced Materials* 25 (2013) 2980–2983.
<https://doi.org/10.1002/ADMA.201300118>.
- [11] K. Zhang, F. Zhang, Y. Song, J.B. Fan, S. Wang, Recent Progress of Mussel-Inspired Underwater Adhesives, *Chin J Chem* 35 (2017) 811–820.
<https://doi.org/10.1002/CJOC.201600778>.
- [12] N.K. Kaushik, N. Kaushik, S. Pardeshi, J.G. Sharma, S.H. Lee, E.H. Choi, Biomedical and Clinical Importance of Mussel-Inspired Polymers and Materials, *Marine Drugs* 2015, Vol. 13, Pages 6792–6817 13 (2015) 6792–6817.
<https://doi.org/10.3390/MD13116792>.
- [13] Z. Wang, Y. Duan, Y. Duan, Application of polydopamine in tumor targeted drug delivery system and its drug release behavior, *Journal of Controlled Release* 290 (2018) 56–74. <https://doi.org/10.1016/J.JCONREL.2018.10.009>.
- [14] B.P. Lee, P.B. Messersmith, J.N. Israelachvili, J.H. Waite, Mussel-Inspired Adhesives and Coatings, <https://doi.org/10.1146/Annurev-Matsci-062910-100429> 41 (2011) 99–132. <https://doi.org/10.1146/ANNUREV-MATSCI-062910-100429>.
- [15] X. Zhang, H. Liu, L. Yue, Y. Bai, J. He, Mussel-mimetic polymer underwater adhesives with l-Dopa functionality: influencing adhesion properties and simplified operation procedures, *J Mater Sci* 55 (2020) 7981–7997.
<https://doi.org/10.1007/S10853-020-04572-Z/FIGURES/7>.
- [16] J. Duan, W. Wu, Z. Wei, D. Zhu, H. Tu, A. Zhang, Synthesis of functional catechols as monomers of mussel-inspired biomimetic polymers, *Green Chemistry* 20 (2018) 912–920. <https://doi.org/10.1039/C7GC03323K>.
- [17] P. Kord Forooshani, B.P. Lee, Recent approaches in designing bioadhesive materials inspired by mussel adhesive protein, *J Polym Sci A Polym Chem* 55 (2017) 9–33. <https://doi.org/10.1002/POLA.28368>.
- [18] B. Wang, Y.S. Jeon, H.S. Park, Y.J. Kim, J.H. Kim, Mussel-mimetic self-healing polyaspartamide derivative gel via boron-catechol interactions, *Express Polym Lett* 9 (2015) 799–808. <https://doi.org/10.3144/EXPRESSPOLYMLET.2015.75>.
- [19] J. Li, H. Ejima, N. Yoshie, Seawater-Assisted Self-Healing of Catechol Polymers via Hydrogen Bonding and Coordination Interactions, *ACS Appl Mater Interfaces* 8 (2016) 19047–19053.
https://doi.org/10.1021/ACSAMI.6B04075/ASSET/IMAGES/LARGE/AM-2016-04075W_0008.JPEG.

- [20] J. Zhong, H. Ji, J. Duan, H. Tu, A. Zhang, Coating morphology and surface composition of acrylic terpolymers with pendant catechol, OEG and perfluoroalkyl groups in varying ratio and the effect on protein adsorption, *Colloids Surf B Biointerfaces* 140 (2016) 254–261.
<https://doi.org/10.1016/J.COLSURFB.2015.12.051>.
- [21] D.W.R. Balkenende, S.M. Winkler, P.B. Messersmith, Marine-inspired polymers in medical adhesion, *Eur Polym J* 116 (2019) 134–143.
<https://doi.org/10.1016/J.EURPOLYMJ.2019.03.059>.
- [22] Z. Basiri, A.H. Rezayan, B. Akbari, R.M. Aghdam, H.A. Tafti, Developing new synthetic biomimetic nanocomposite adhesives: Synthesis and evaluation of bond strength and solubilization, *React Funct Polym* 127 (2018) 85–93.
<https://doi.org/10.1016/J.REACTFUNCTPOLYM.2018.04.004>.
- [23] S.B. Lee, C. González-Cabezas, K.M. Kim, K.N. Kim, K. Kuroda, Catechol-Functionalized Synthetic Polymer as a Dental Adhesive to Contaminated Dentin Surface for a Composite Restoration, *Biomacromolecules* 16 (2015) 2265–2275.
https://doi.org/10.1021/ACS.BIOMAC.5B00451/SUPPL_FILE/BM5B00451_SI_001.PDF.
- [24] P. Wei, R. Song, C. Chen, Z. Li, Z. Zhu, S. Li, A pH-Responsive Molecularly Imprinted Hydrogel for Dexamethasone Release, *J Inorg Organomet Polym Mater* 29 (2019) 659–666. <https://doi.org/10.1007/S10904-018-1039-9/FIGURES/6>.
- [25] A. Roy, K. Manna, S. Dey, S. Pal, Chemical modification of β -cyclodextrin towards hydrogel formation, *Carbohydr Polym* 306 (2023) 120576.
<https://doi.org/10.1016/J.CARBPOL.2023.120576>.
- [26] K. Uekama, F. Hirayama, T. Irie, Cyclodextrin drug carrier systems, *Chem Rev* 98 (1998) 2045–2076.
<https://doi.org/10.1021/CR970025P/ASSET/IMAGES/LARGE/CR970025PF00011.JPEG>.
- [27] B. Gidwani, A. Vyas, A Comprehensive Review on Cyclodextrin-Based Carriers for Delivery of Chemotherapeutic Cytotoxic Anticancer Drugs, *Biomed Res Int* 2015 (2015). <https://doi.org/10.1155/2015/198268>.
- [28] J. Wankar, N.G. Kotla, S. Gera, S. Rasala, A. Pandit, Y.A. Rochev, J. Wankar, N.G. Kotla, S. Rasala, A. Pandit, Y.A. Rochev, S. Gera, Recent Advances in Host–Guest Self-Assembled Cyclodextrin Carriers: Implications for Responsive Drug Delivery and Biomedical Engineering, *Adv Funct Mater* 30 (2020) 1909049.
<https://doi.org/10.1002/ADFM.201909049>.

- [29] A. Motoyama, A. Suzuki, O. Shiota, R. Namba, Direct determination of pindolol enantiomers in human serum by column-switching LC-MS/MS using a phenylcarbamate- β -cyclodextrin chiral column, *J Pharm Biomed Anal* 28 (2002) 97–106. [https://doi.org/10.1016/S0731-7085\(01\)00631-8](https://doi.org/10.1016/S0731-7085(01)00631-8).
- [30] T. Wimmer, Cyclodextrins, *Ullmann's Encyclopedia of Industrial Chemistry* (2003). https://doi.org/10.1002/14356007.E08_E02.
- [31] G. Becket, L.J. Schep, M.Y. Tan, Improvement of the in vitro dissolution of praziquantel by complexation with α -, β - and γ -cyclodextrins, *Int J Pharm* 179 (1999) 65–71. [https://doi.org/10.1016/S0378-5173\(98\)00382-2](https://doi.org/10.1016/S0378-5173(98)00382-2).
- [32] B. Lade, A. Shanware, R. Sharma, Effect of β -Cyclodextrin Stabilized Silver Nanoparticles on Gills, Kidney, Liver of *Danio rerio*, *Letters in Applied NanoBioScience* 11 (2021) 2981–2995. <https://doi.org/10.33263/LIANBS111.29812995>.
- [33] K. Manna, P. Patra, A. Roy, R.K. Roy, K. Chaitanya 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 (2022) 4432–4444. https://doi.org/10.1021/ACSAPM.2C00393/ASSET/IMAGES/LARGE/AP2C00393_0009.JPEG.
- [34] B. Brady, N. Lynam, T. O'Sullivan, C. Ahern, R. Darcy, 6A-O-p-TOLUENESULFONYL-b-CYCLODEXTRIN, *Organic Syntheses* 77 (2000) 220. <https://doi.org/10.15227/orgsyn.077.0220>.
- [35] S.K. Rodal, G. Skretting, Ø. Garred, F. Vilhardt, B. Van Deurs, K. Sandvig, Extraction of cholesterol with methyl- β -cyclodextrin perturbs formation of clathrin-coated endocytic vesicles, *Mol Biol Cell* 10 (1999) 961–974. <https://doi.org/10.1091/MBC.10.4.961/ASSET/IMAGES/LARGE/MK0490821011.JPEG>.
- [36] C. Sebaaly, C. Charcosset, S. Fourmentin, H. Greige-Gerges, Potential Applications of Cyclodextrin Inclusion Complexes, Liposomes, and Drug-in-Cyclodextrin-in-Liposome in Food Industry and Packaging, *Role of Materials Science in Food Bioengineering* (2018) 187–234. <https://doi.org/10.1016/B978-0-12-811448-3.00006-1>.
- [37] S. Saha, A. Roy, K. Roy, M.N. Roy, Study to explore the mechanism to form inclusion complexes of β -cyclodextrin with vitamin molecules, *Scientific Reports* 2016 6:1 6 (2016) 1–12. <https://doi.org/10.1038/srep35764>.

- [38] M.A. Crumling, K.A. King, R.K. Duncan, Cyclodextrins and Iatrogenic Hearing Loss: New Drugs with Significant Risk, *Front Cell Neurosci* 11 (2017) 307236. <https://doi.org/10.3389/fncel.2017.00355>.
- [39] A. Roy, P.P. Maity, A. Bose, S. Dhara, S. Pal, β -Cyclodextrin based pH and thermo-responsive biopolymeric hydrogel as a dual drug carrier, *Mater Chem Front* 3 (2019) 385–393. <https://doi.org/10.1039/C8QM00452H>.
- [40] G. Giammona, G. Cavallaro, L. Maniscalco, E.F. Craparo, G. Pitarresi, Synthesis and characterisation of novel chemical conjugates based on α,β -polyaspartylhydrazide and β -cyclodextrins, *Eur Polym J* 42 (2006) 2715–2729. <https://doi.org/10.1016/J.EURPOLYMJ.2006.05.005>.
- [41] J. Ma, J. Ma, Q. Zhang, R. Peng, J. Wang, C. Liu, M. Wang, N. Li, M. Chen, X. Cheng, P. Gao, L. Gu, L.Q. Chen, P. Yu, J. Zhang, C.W. Nan, Controllable conductive readout in self-assembled, topologically confined ferroelectric domain walls, *Nature Nanotechnology* 2018 13:10 13 (2018) 947–952. <https://doi.org/10.1038/s41565-018-0204-1>.
- [42] S. Dey, A. Roy, K. Manna, S. Pal, The UCST phase transition of a dextran based copolymer in aqueous media with tunable thermoresponsive behavior, *Polym Chem* 13 (2022) 3865–3869. <https://doi.org/10.1039/D2PY00626J>.
- [43] S. Dey, A.S. Patra, P. Patra, B. Saha, A.K. Mukherjee, S. Pal, Macromolecular selective flocculant derived from functionalized starch towards beneficiation of low-quality iron ore: Atomistic simulations and experimental studies, *Mater Today Commun* 32 (2022) 103810. <https://doi.org/10.1016/J.MTCOMM.2022.103810>.
- [44] S.R. Popielarski, S. Mishra, M.E. Davis, Structural effects of carbohydrate-containing polycations on gene delivery. 3. Cyclodextrin type and functionalization, *Bioconj Chem* 14 (2003) 672–678. https://doi.org/10.1021/BC034010B/SUPPL_FILE/BC034010B_S.PDF.
- [45] Y. Rojas-Aguirre, M.A. Torres-Mena, L.J. López-Méndez, S.L. Alcaraz-Estrada, P. Guadarrama, J.M. Urucha-Ortíz, PEGylated β -cyclodextrins: Click synthesis and in vitro biological insights, *Carbohydr Polym* 223 (2019) 115113. <https://doi.org/10.1016/J.CARBPOL.2019.115113>.
- [46] S. Tan, K. Ladewig, Q. Fu, A. Blencowe, G.G. Qiao, S. Tan, K. Ladewig, Q. Fu, A. Blencowe, G.G. Qiao, Cyclodextrin-Based Supramolecular Assemblies and Hydrogels: Recent Advances and Future Perspectives, *Macromol Rapid Commun* 35 (2014) 1166–1184. <https://doi.org/10.1002/MARC.201400080>.

- [47] M. Petitjean, I.X. García-Zubiri, J.R. Isasi, History of cyclodextrin-based polymers in food and pharmacy: a review, *Environmental Chemistry Letters* 2021 19:4 19 (2021) 3465–3476. <https://doi.org/10.1007/S10311-021-01244-5>.
- [48] S. Amajjahe, S. Choi, M. Munteanu, H. Ritter, Pseudopolyanionen aus Poly(NIPAAm-co- β -Cyclodextrinmethacrylat) und ionischen Flüssigkeiten, *Angewandte Chemie* 120 (2008) 3484–3486. <https://doi.org/10.1002/ANGE.200704995>.
- [49] M. Arslan, R. Sanyal, A. Sanyal, Cyclodextrin embedded covalently crosslinked networks: synthesis and applications of hydrogels with nano-containers, *Polym Chem* 11 (2020) 615–629. <https://doi.org/10.1039/C9PY01679A>.
- [50] G.B. Butler, Cyclopolymerization and cyclocopolymerization, Published in **1992** in New York NY) by Dekker (1992) 210–218. <https://lib.ugent.be/catalog/rug01:000303603> (accessed March 12, 2024).
- [51] G.B. Butler, G. Bergen Butler, HIGHLIGHT Cyclopolymerization, *J Polym Sci A Polym Chem* 38 (1983) 3451–3461. <https://doi.org/10.1002/1099-0518>.
- [52] G.B. Butler, F.L. Ingley, Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. II. Halogenated Allyl Derivatives, *J Am Chem Soc* 73 (1951) 895–896. https://doi.org/10.1021/JA01147A003/ASSET/JA01147A003.FP.PNG_V03.
- [53] S. Harada, M. Katayama, The cyclo-copolymerization of diallyl compound and sulfur dioxide. I. Diallylamine hydrochloride and sulfur dioxide, *Die Makromolekulare Chemie* 90 (1966) 177–186. <https://doi.org/10.1002/MACP.1966.020900117>.
- [54] S. Harada, K. Arai, The cyclo-copolymerization of diallyl compounds and sulfur dioxide. II. Diallyldimethylammonium chloride and sulfur dioxide, *Die Makromolekulare Chemie* 107 (1967) 64–77. <https://doi.org/10.1002/MACP.1967.021070106>.
- [55] S.A. Ali, S.Z. Ahmed, M.I.M. Wazeer, E.Z. Hamad, Synthesis and aqueous phase behaviour of homo- and copolymers of 1,1-diallyl-4-formylpiperazinium chloride, *Polymer (Guildf)* 38 (1997) 3385–3393. [https://doi.org/10.1016/S0032-3861\(96\)00893-2](https://doi.org/10.1016/S0032-3861(96)00893-2).
- [56] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric betaines: Synthesis, characterization, and application, *Advances in Polymer Science* 201 (2006) 157–224. https://doi.org/10.1007/12_078/COVER.

- [57] A. Laschewsky, Structures and Synthesis of Zwitterionic Polymers, *Polymers* 2014, Vol. 6, Pages 1544-1601 6 (2014) 1544–1601.
<https://doi.org/10.3390/POLYM6051544>.
- [58] P.K. Singh, V.K. Singh, M. Singh, Zwitterionic polyelectrolytes: A review, *E-Polymers* 7 (2007) 1–34.
<https://doi.org/10.1515/EPOLY.2007.7.1.335/MACHINEREADABLECITATION/RIS>.
- [59] F.C. McGrew, Structure of synthetic high polymers, *J Chem Educ* 35 (1958) 178–186. <https://doi.org/10.1021/ED035P178>.
- [60] O. Charles, S. Al-Hamouz, S.A. Ali, S.A. Ali, pH-responsive polyphosphonates using butler’s cyclopolymerization, *J Polym Sci A Polym Chem* 50 (2012) 3580–3591. <https://doi.org/10.1002/POLA.26143>.
- [61] Z.A. Jamiu, S.A. Ali, Alternate cyclopolymer of diallylglutamic acid and sulfur dioxide, *RSC Adv* 6 (2016) 31019–31030. <https://doi.org/10.1039/C6RA03635J>.
- [62] A. V. Dobrynin, R.H. Colby, M. Rubinstein, Polyampholytes, *J Polym Sci B Polym Phys* 42 (2004) 3513–3538. <https://doi.org/10.1002/POLB.20207>.
- [63] A. Rabiee, A. Ershad-Langroudi, H. Jamshidi, Polyacrylamide-based polyampholytes and their applications, *Reviews in Chemical Engineering* 30 (2014) 501–519. https://doi.org/10.1515/REVCE-2014-0004/ASSET/GRAPHIC/REVCE-2014-0004_CV3.JPG.
- [64] R. Kumar, G.H. Fredrickson, Theory of polyzwitterion conformations, *Journal of Chemical Physics* 131 (2009) 104901. <https://doi.org/10.1063/1.3216107/905922>.
- [65] S.A. Haladu, S.A. Ali, A pH-responsive cyclopolymer having phospho- and sulfopropyl pendants in the same repeating unit: Synthesis, characterization, and its application as an antiscalant, *J Polym Sci A Polym Chem* 51 (2013) 5130–5142. <https://doi.org/10.1002/POLA.26945>.
- [66] 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>.
- [67] R.W. Revie, H.H. Uhlig, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering: Fourth Edition*, Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering: Fourth Edition (2008) 1–490. <https://doi.org/10.1002/9780470277270>.

- [68] V.S. (Vedula S.) Sastri, Corrosion inhibitors : principles and applications, (1998) 903.
- [69] N. Amirshaqai, M. Salami-Kalajahi, M. Mahdavian, Corrosion behavior of aluminum/silica/polystyrene nanostructured hybrid flakes, Iranian Polymer Journal (English Edition) 23 (2014) 699–706. <https://doi.org/10.1007/S13726-014-0264-5/FIGURES/6>.
- [70] F.C. Wang, L.H. Han, Analytical behavior of carbon steel-concrete-stainless steel double-skin tube (DST) used in submarine pipeline structure, Marine Structures 63 (2019) 99–116. <https://doi.org/10.1016/J.MARSTRUC.2018.09.001>.
- [71] R.S. Vidyarthi, P. Sivateja, Influence of activating flux tungsten inert gas welding on mechanical and metallurgical properties of the mild steel, Mater Today Proc 28 (2020) 977–981. <https://doi.org/10.1016/J.MATPR.2019.12.335>.
- [72] S. Nikkhah, H. Mirzadeh, M. Zamani, Improved mechanical properties of mild steel via combination of deformation, intercritical annealing, and quench aging, Materials Science and Engineering: A 756 (2019) 268–271. <https://doi.org/10.1016/J.MSEA.2019.04.071>.
- [73] R. Shukla, S.K. Ghosh, D. Chakrabarti, S. Chatterjee, Microstructure, texture, property relationship in thermo-mechanically processed ultra-low carbon microalloyed steel for pipeline application, Materials Science and Engineering: A 587 (2013) 201–208. <https://doi.org/10.1016/J.MSEA.2013.08.054>.
- [74] Q. Feng, B. Yan, P. Chen, S.A. Shirazi, Failure analysis and simulation model of pinhole corrosion of the refined oil pipeline, Eng Fail Anal 106 (2019) 104177. <https://doi.org/10.1016/J.ENGFAILANAL.2019.104177>.
- [75] M. Seghier, B. Keshtegar, J. Correia, A. De Jesus, G. Lesiuk, Structural Reliability Analysis of Corroded Pipeline made in X60 Steel Based on M5 Model Tree Algorithm and Monte Carlo Simulation, Procedia Structural Integrity 13 (2018) 1670–1675. <https://doi.org/10.1016/J.PROSTR.2018.12.349>.
- [76] W.W. Frenier, F.B. Growcock, V.R. Lopp, Mechanisms of Corrosion Inhibitors Used in Acidizing Wells, SPE Production Engineering 3 (1988) 584–590. <https://doi.org/10.2118/14092-PA>.
- [77] A. Singha, M.A. Quraishi, Acidizing corrosion inhibitors: A review, Journal of Materials and Environmental Science 6 (2015) 224–235.
- [78] R. Norsworthy, Understanding corrosion in underground pipelines: Basic principles, Elsevier Ltd., 2014. <https://doi.org/10.1533/9780857099266.1.3>.

- [79] M. Yadav, D. Behera, S. Kumar, R.R. Sinha, Experimental and quantum chemical studies on the corrosion inhibition performance of benzimidazole derivatives for mild steel in HCl, *Ind Eng Chem Res* 52 (2013) 6318–6328.
https://doi.org/10.1021/IE400099Q/SUPPL_FILE/IE400099Q_SI_001.PDF.
- [80] Y. Tang, F. Zhang, S. Hu, Z. Cao, Z. Wu, W. Jing, Novel benzimidazole derivatives as corrosion inhibitors of mild steel in the acidic media. Part I: Gravimetric, electrochemical, SEM and XPS studies, *Corros Sci* 74 (2013) 271–282. <https://doi.org/10.1016/J.CORSCI.2013.04.053>.
- [81] E. Ech-chihbi, A. Nahlé, R. Salim, F. Benhiba, A. Moussaif, F. El-Hajjaji, H. Oudda, A. Guenbour, M. Taleb, I. Warad, A. Zarrouk, Computational, MD simulation, SEM/EDX and experimental studies for understanding adsorption of benzimidazole derivatives as corrosion inhibitors in 1.0 M HCl solution, *J Alloys Compd* 844 (2020) 155842. <https://doi.org/10.1016/J.JALLCOM.2020.155842>.
- [82] U. Zulfiqar, A.G. Thomas, K. Yearsley, L.W. Bolton, A. Matthews, D.J. Lewis, Renewable Adsorbent for the Separation of Surfactant-Stabilized Oil in Water Emulsions Based on Nanostructured Sawdust, *ACS Sustain Chem Eng* 7 (2019) 18935–18942.
https://doi.org/10.1021/ACSSUSCHEMENG.9B04294/ASSET/IMAGES/LARGE/SC9B04294_0008.JPEG.
- [83] R.K. Gupta, G.J. Dunderdale, M.W. England, A. Hozumi, Oil/water separation techniques: a review of recent progresses and future directions, *J Mater Chem A Mater* 5 (2017) 16025–16058. <https://doi.org/10.1039/C7TA02070H>.
- [84] D.M. Alzate-Sánchez, Y. Ling, C. Li, B.P. Frank, R. Bleher, D.H. Fairbrother, D.E. Helbling, W.R. Dichtel, β -Cyclodextrin Polymers on Microcrystalline Cellulose as a Granular Media for Organic Micropollutant Removal from Water, *ACS Appl Mater Interfaces* 11 (2019) 8089–8096.
https://doi.org/10.1021/ACSAMI.8B22100/ASSET/IMAGES/LARGE/AM-2018-22100T_0009.JPEG.
- [85] A. Alsbaiee, B.J. Smith, L. Xiao, Y. Ling, D.E. Helbling, W.R. Dichtel, Rapid removal of organic micropollutants from water by a porous β -cyclodextrin polymer, *Nature* 2015 529:7585 529 (2015) 190–194.
<https://doi.org/10.1038/nature16185>.
- [86] 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 (2015) 120–129.
<https://doi.org/10.1016/J.REACTFUNCTPOLYM.2015.06.006>.

- [87] T.A. Saleh, A.M. Musa, B. Tawabini, S.A. Ali, Aminomethylphosphonate Chelating Ligand and Octadecyl Alkyl Chain in a Resin for Simultaneous Removal of Co(II) Ions and Organic Contaminants, *J Chem Eng Data* 61 (2016) 3377–3385.
https://doi.org/10.1021/ACS.JCED.6B00475/ASSET/IMAGES/LARGE/IE-2016-004755_0011.JPEG.
- [88] H.-S. Byun, N. Zhong, R. Bittman, 6A-O-p-TOLUENESULFONYL-b-CYCLODEXTRIN, *Organic Syntheses* 77 (2000) 225.
<https://doi.org/10.15227/orgsyn.077.0225>.
- [89] T.A. Saleh, S.A. Haladu, S.A. Ali, A novel cross-linked pH-responsive tetrapolymer: Synthesis, characterization and sorption evaluation towards Cr(III), *Chemical Engineering Journal* 269 (2015) 9–19.
<https://doi.org/10.1016/J.CEJ.2015.01.083>.
- [90] O.C.S. Al Hamouz, S.A. Ali, Removal of heavy metal ions using a novel cross-linked polyzwitterionic phosphonate, *Sep Purif Technol* 98 (2012) 94–101.
<https://doi.org/10.1016/J.SEPPUR.2012.07.019>.
- [91] A. Tanimu, S.M.S. Jillani, A.A. Alluhaidan, S.A. Ganiyu, K. Alhooshani, 4-phenyl-1,2,3-triazole functionalized mesoporous silica SBA-15 as sorbent in an efficient stir bar-supported micro-solid-phase extraction strategy for highly to moderately polar phenols, *Talanta* 194 (2019) 377–384.
<https://doi.org/10.1016/J.TALANTA.2018.10.012>.
- [92] J. Comyn, The relationship between joint durability and water diffusion, A.J. Kinloch (Ed.), *Developments in Adhesives*, Volume 2, Applied Science Publishers, Barking, UK (1981) 279–313.
<https://www.scopus.com/record/display.uri?eid=2-s2.0-84935041145&origin=inward#metrics> (accessed March 15, 2024).
- [93] G.B. Butler, *Cyclopolymerization and Cyclocopolymerization*, Cyclopolymerization and Cyclocopolymerization (2020).
<https://doi.org/10.1201/9781003066828>.
- [94] S.E. Kudaibergenov, N. Nuraje, Intra- and Interpolyelectrolyte Complexes of Polyampholytes, *Polymers* 2018, Vol. 10, Page 1146 10 (2018) 1146.
<https://doi.org/10.3390/POLYM10101146>.
- [95] L. Chen, Y. Honma, T. Mizutani, D.J. Liaw, J.P. Gong, Y. Osada, Effects of polyelectrolyte complexation on the UCST of zwitterionic polymer, *Polymer (Guildf)* 41 (2000) 141–147. [https://doi.org/10.1016/S0032-3861\(99\)00161-5](https://doi.org/10.1016/S0032-3861(99)00161-5).

- [96] V.A. Izumrudov, A.N. Zelikin, M. V. Zhiryakova, W. Jaeger, J. Bohrisch, Interpolyelectrolyte reactions in solutions of polycarboxybetaines, *Journal of Physical Chemistry B* 107 (2003) 7982–7986.
<https://doi.org/10.1021/JP027400O/ASSET/IMAGES/LARGE/JP027400OF00004.JPEG>.
- [97] S.A. Ali, S.A. Haladu, A.M.Z. El-Sharif, Diallylbis(3-ethoxycarbonylpropyl)ammonium chloride: A symmetrically substituted monomer for the synthesis of an alternate zwitterionic-anionic cyclopolymer, *Macromol Res* 24 (2016) 163–169. <https://doi.org/10.1007/S13233-016-4024-6/METRICS>.
- [98] S.A. Haladu, S.A. Ali, Cyclopolymerization protocol for the synthesis of a new poly(electrolyte-zwitterion) containing quaternary nitrogen, carboxylate, and sulfonate functionalities, *Eur Polym J* 49 (2013) 1591–1600.
<https://doi.org/10.1016/J.EURPOLYMJ.2013.02.007>.
- [99] 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 (2014) 187–198.
<https://doi.org/10.1016/J.CORSCI.2014.06.026>.
- [100] M.K. Aldahdooh, S.A. Ali, Synthesis and application of alternate cyclopolymers of β -diallylaminoethyliminodiacetic acid with maleic acid and sulfur dioxide, *React Funct Polym* 161 (2021) 104857.
<https://doi.org/10.1016/J.REACTFUNCTPOLYM.2021.104857>.
- [101] I.Y. Yaagoob, S.A. Ali, H.A. Al-Muallem, M.A.J. Mazumder, Scope of sulfur dioxide incorporation into alkylallylamine–maleic acid–SO₂ tercyclopolymer, *RSC Adv* 8 (2018) 38891–38902. <https://doi.org/10.1039/C8RA08723G>.
- [102] D.A. Topchiev, Y.A. Malkanduev, Y.G. Yanovsky, V.D. Oppengeim, V.A. Kabanov, Some features of dimethyl diallyl ammonium chloride high conversion polymerization in aqueous solutions, *Eur Polym J* 25 (1989) 1095–1098.
[https://doi.org/10.1016/0014-3057\(89\)90163-8](https://doi.org/10.1016/0014-3057(89)90163-8).
- [103] H.A. Al-Muallem, M.I.M. Wazeer, S.A. Ali, Synthesis and solution properties of a new ionic polymer and its behavior in aqueous two-phase polymer systems, *Polymer (Guildf)* 43 (2002) 1041–1050. [https://doi.org/10.1016/S0032-3861\(01\)00720-0](https://doi.org/10.1016/S0032-3861(01)00720-0).
- [104] G.B. Butler, R.J. Angelo, Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VIII. A Proposed Alternating Intramolecular-Intermolecular Chain Propagation, *J Am Chem Soc* 79 (1957)

3128–3131.

https://doi.org/10.1021/JA01569A037/ASSET/JA01569A037.FP.PNG_V03.

- [105] N.A. Odewunmi, M.A.J. Mazumder, M.K. Aldahdooh, S.A. Ali, N1,N1,N12,N12-Tetramethyl-N1, N12-dioctyldodecane-1,12-diaminium bromide: Its synthesis and application in inhibition of mild steel corrosion in 15% HCl, *J Mol Liq* 338 (2021) 116630. <https://doi.org/10.1016/J.MOLLIQ.2021.116630>.
- [106] A. Frumkin, Die Kapillarkurve der höheren Fettsäuren und die Zustandsgleichung der Oberflächenschicht, *Zeitschrift Für Physikalische Chemie* 116U (1925) 466–484. <https://doi.org/10.1515/ZPCH-1925-11629>.
- [107] W. Schmickler, J. O'M. Bockris, Shahed U.M. Khan: Surface electrochemistry, a molecular level approach. Plenum Press, New York, London, 1993. ISBN 0-306-44298-1, 1014 Seiten, Preis: \$79.50, *Berichte Der Bunsengesellschaft Für Physikalische Chemie* 98 (1994) 1207–1207. <https://doi.org/10.1002/BBPC.19940980933>.
- [108] S.M. Abd El Haleem, S. Abd El Wanees, A. Bahgat, Environmental factors affecting the corrosion behaviour of reinforcing steel. VI. Benzotriazole and its derivatives as corrosion inhibitors of steel, *Corros Sci* 87 (2014) 321–333. <https://doi.org/10.1016/J.CORSCI.2014.06.043>.
- [109] 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 (2008) 3070–3077. <https://doi.org/10.1016/J.CORSCI.2008.08.011>.
- [110] P. Singh, D.S. Chauhan, S.S. Chauhan, G. Singh, M.A. Quraishi, Bioinspired synergistic formulation from dihydropyrimidinones and iodide ions for corrosion inhibition of carbon steel in sulphuric acid, *J Mol Liq* 298 (2020) 112051. <https://doi.org/10.1016/J.MOLLIQ.2019.112051>.
- [111] S.A. Ali, A.J. Hamdan, A.A. Al-Taq, S.M.J. Zaidi, M.T. Saeed, In search of functionality for efficient inhibition of mild steel corrosion both in HCl and H₂SO₄, *Corrosion Engineering, Science and Technology* 46 (2011) 796–806. <https://doi.org/10.1179/1743278211Y.0000000011>.
- [112] S.K. Shukla, M.A. Quraishi, Cefotaxime sodium: A new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution, *Corros Sci* 51 (2009) 1007–1011. <https://doi.org/10.1016/J.CORSCI.2009.02.024>.
- [113] W. Lorenz, Zur Theorie partieller Ladungsübergangsreaktionen, *Zeitschrift Für Physikalische Chemie* 244O (1970) 65–84. <https://doi.org/10.1515/ZPCH-1970-24405>.

- [114] S.A. Umoren, M.M. Solomon, Polymeric Corrosion Inhibitors for Oil and Gas Industry, *Corrosion Inhibitors in the Oil and Gas Industry* (2020) 303–320.
<https://doi.org/10.1002/9783527822140.CH12>.
- [115] E. Udabe, A. Somers, M. Forsyth, D. Mecerreyes, Design of Polymeric Corrosion Inhibitors Based on Ionic Coumarate Groups, *ACS Appl Polym Mater* 3 (2021) 1739–1746.
https://doi.org/10.1021/ACSAPM.0C01266/ASSET/IMAGES/LARGE/AP0C01266_0007.JPEG.
- [116] T. Chen, M. Chen, Z. Chen, C. Fu, Comprehensive investigation of modified polyethyleneimine as an efficient polymeric corrosion inhibitor in neutral medium: Synthesis, experimental and theoretical assessments, *J Mol Liq* 339 (2021) 116803. <https://doi.org/10.1016/J.MOLLIQ.2021.116803>.
- [117] E. Kamali Ardakani, E. Kowsari, A. Ehsani, Imidazolium-derived polymeric ionic liquid as a green inhibitor for corrosion inhibition of mild steel in 1.0 M HCl: Experimental and computational study, *Colloids Surf A Physicochem Eng Asp* 586 (2020) 124195. <https://doi.org/10.1016/J.COLSURFA.2019.124195>.
- [118] J. Panchal, D. Shah, R. Patel, S. Shah, M. Prajapati, M. Shah, Comprehensive Review and Critical Data Analysis on Corrosion and Emphasizing on Green Eco-friendly Corrosion Inhibitors for Oil and Gas Industries, *J Bio Tribocorros* 7 (2021) 1–29. <https://doi.org/10.1007/S40735-021-00540-5/FIGURES/8>.
- [119] F.J. Solis, M. Olvera De La Cruz, Collapse of flexible polyelectrolytes in multivalent salt solutions, *J Chem Phys* 112 (2000) 2030–2035.
<https://doi.org/10.1063/1.480763>.
- [120] C. Schatz, J.M. Lucas, C. Viton, A. Domard, C. Pichot, T. Delair, Formation and properties of positively charged colloids based on polyelectrolyte complexes of biopolymers, *Langmuir* 20 (2004) 7766–7778.
<https://doi.org/10.1021/LA049460M/ASSET/IMAGES/LARGE/LA049460MF00011.JPEG>.
- [121] N.A.D. Burke, M.A.J. Mazumder, M. Hanna, H.D.H. Stöver, Polyelectrolyte complexation between poly(methacrylic acid, sodium salt) and poly(diallyldimethylammonium chloride) or poly[2-(methacryloyloxyethyl) trimethylammonium chloride], *J Polym Sci A Polym Chem* 45 (2007) 4129–4143.
<https://doi.org/10.1002/POLA.22247>.
- [122] G.G. Cameron, Polyelectrolytes: formation, characterization and application. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, Ch. Seidel and D. Stscherbina. Carl

Hanser Verlag, Munich, 1994. pp. xiv + 343, price DM168.00. ISBN 1-56990-127-9. ISBN 3-446-17127-4, Polym Int 38 (1995) 106–106.
<https://doi.org/10.1002/PI.1995.210380118>.

- [123] U. Zulficar, A. G. Thomas, K. Yearsley, L. W. Bolton, A. Matthews, D. J. Lewis, Renewable Adsorbent for the Separation of Surfactant-Stabilized Oil in Water Emulsions Based on Nanostructured Sawdust, ACS Sustainable Chemistry & Engineering 7 (2019) 18935–18942.
<https://doi.org/10.1021/acssuschemeng.9b04294>.
- [124] G. Shi, M. Wu, Q. Zhong, P. Mu, J. Li, Superhydrophobic Waste Cardboard Aerogels as Effective and Reusable Oil Absorbents, Langmuir 37 (2021) 7843–7850. <https://doi.org/10.1021/acs.langmuir.1c01216>.
- [125] R.K. Gupta, G.J. Dunderdale, M.W. England, A. Hozumi, Oil/water separation techniques: a review of recent progresses and future directions, J. Mater. Chem. A 5 (2017) 16025–16058. <https://doi.org/10.1039/C7TA02070H>.
- [126] Y. Sun, Y. Zong, N. Yang, N. Zhang, B. Jiang, L. Zhang, X. Xiao, Surface hydrophilic modification of PVDF membranes based on tannin and zwitterionic substance towards effective oil-in-water emulsion separation, Sep Purif Technol 234 (2020) 116015. <https://doi.org/10.1016/J.SEPPUR.2019.116015>.
- [127] Y. Hu, M. Yue, F. Yuan, L. Yang, C. Chen, D. Sun, Bio-inspired fabrication of highly permeable and anti-fouling ultrafiltration membranes based on bacterial cellulose for efficient removal of soluble dyes and insoluble oils, J Memb Sci 621 (2021) 118982. <https://doi.org/10.1016/J.MEMSCI.2020.118982>.
- [128] X. Yue, Z. Li, T. Zhang, D. Yang, F. Qiu, Design and fabrication of superwetting fiber-based membranes for oil/water separation applications, Chemical Engineering Journal 364 (2019) 292–309.
<https://doi.org/10.1016/J.CEJ.2019.01.149>.
- [129] B. Xiang, Q. Sun, Q. Zhong, P. Mu, J. Li, Current research situation and future prospect of superwetting smart oil/water separation materials, J Mater Chem A Mater 10 (2022) 20190–20217. <https://doi.org/10.1039/D2TA04469B>.
- [130] H.J. Tanudjaja, C.A. Hejase, V. V. Tarabara, A.G. Fane, J.W. Chew, Membrane-based separation for oily wastewater: A practical perspective, Water Res 156 (2019) 347–365. <https://doi.org/10.1016/J.WATRES.2019.03.021>.
- [131] Y. Hu, M. Yue, F. Yuan, L. Yang, C. Chen, D. Sun, Bio-inspired fabrication of highly permeable and anti-fouling ultrafiltration membranes based on bacterial

- cellulose for efficient removal of soluble dyes and insoluble oils, *J Memb Sci* 621 (2021) 118982. <https://doi.org/10.1016/J.MEMSCI.2020.118982>.
- [132] H. Li, Q. Zhong, Q. Sun, B. Xiang, J. Li, Upcycling Waste Pine nut Shell Membrane for Highly Efficient Separation of Crude Oil-in-Water Emulsion, *Langmuir* 38 (2022) 3493–3500. <https://doi.org/10.1021/acs.langmuir.1c03386>.
- [133] N. Baig, Z. Arshad, S.A. Ali, Synthesis of a biomimetic zwitterionic pentapolymer to fabricate high-performance PVDF membranes for efficient separation of oil-in-water nano-emulsions, *Sci Rep* 12 (2022). <https://doi.org/10.1038/s41598-022-09046-7>.
- [134] A. Karimi, A. Khataee, V. Vatanpour, M. Safarpour, High-flux PVDF mixed matrix membranes embedded with size-controlled ZIF-8 nanoparticles, *Sep Purif Technol* 229 (2019) 115838. <https://doi.org/10.1016/j.seppur.2019.115838>.
- [135] V. Vatanpour, M.E. Yekavalangi, M. Safarpour, Preparation and characterization of nanocomposite PVDF ultrafiltration membrane embedded with nanoporous SAPO-34 to improve permeability and antifouling performance, *Sep Purif Technol* 163 (2016) 300–309. <https://doi.org/10.1016/j.seppur.2016.03.011>.
- [136] C. Zhao, X. Xu, J. Chen, F. Yang, Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes, *J Environ Chem Eng* 1 (2013) 349–354. <https://doi.org/10.1016/J.JECE.2013.05.014>.
- [137] V. Vatanpour, A. Ghadimi, A. Karimi, A. Khataee, M.E. Yekavalangi, Antifouling polyvinylidene fluoride ultrafiltration membrane fabricated from embedding polypyrrole coated multiwalled carbon nanotubes, *Materials Science and Engineering: C* 89 (2018) 41–51. <https://doi.org/10.1016/j.msec.2018.03.026>.
- [138] H. Younas, Y. Zhou, X. Li, X. Li, Q. Sun, Z. Cui, Z. Wang, Fabrication of high flux and fouling resistant membrane: A unique hydrophilic blend of polyvinylidene fluoride/polyethylene glycol/polymethyl methacrylate, *Polymer (Guildf)* 179 (2019) 121593. <https://doi.org/10.1016/J.POLYMER.2019.121593>.
- [139] M. Li, J. Li, M. Zhou, Y. Xian, Y. Shui, M. Wu, Y. Yao, Super-hydrophilic electrospun PVDF/PVA-blended nanofiber membrane for microfiltration with ultrahigh water flux, *J Appl Polym Sci* 137 (2020) 48416. <https://doi.org/10.1002/APP.48416>.
- [140] S. Almaie, V. Vatanpour, M.H. Rasoulifard, M.S. Seyed Dorraji, Novel negatively-charged amphiphilic copolymers of PVDF-g-PAMPS and PVDF-g-PAA to improve permeability and fouling resistance of PVDF UF membrane,

React Funct Polym 179 (2022) 105386.
<https://doi.org/10.1016/J.REACTFUNCTPOLYM.2022.105386>.

- [141] A. Venault, Y.H. Liu, J.R. Wu, H.S. Yang, Y. Chang, J.Y. Lai, P. Aimar, Low-biofouling membranes prepared by liquid-induced phase separation of the PVDF/polystyrene-*b*-poly (ethylene glycol) methacrylate blend, *J Memb Sci* 450 (2014) 340–350. <https://doi.org/10.1016/J.MEMSCI.2013.09.004>.
- [142] D.E. Apostolides, C.S. Patrickios, T. Sakai, M. Guerre, G. Lopez, B. Améduri, V. Ladmiral, M. Simon, M. Gradzielski, D. Clemens, C. Krumm, J.C. Tiller, B. Ernould, J.F. Gohy, Near-Model Amphiphilic Polymer Conetworks Based on Four-Arm Stars of Poly(vinylidene fluoride) and Poly(ethylene glycol): Synthesis and Characterization, *Macromolecules* 51 (2018) 2476–2488.
https://doi.org/10.1021/ACS.MACROMOL.7B02475/ASSET/IMAGES/LARGE/MA-2017-02475E_0008.JPEG.
- [143] F. Chen, X. Shi, X. Chen, W. Chen, Preparation and characterization of amphiphilic copolymer PVDF-*g*-PMABS and its application in improving hydrophilicity and protein fouling resistance of PVDF membrane, *Appl Surf Sci* 427 (2018) 787–797. <https://doi.org/10.1016/J.APSUSC.2017.08.096>.
- [144] S. Wang, T. Li, C. Chen, S. Chen, B. Liu, J. Crittenden, Non-woven PET fabric reinforced and enhanced the performance of ultrafiltration membranes composed of PVDF blended with PVDF-*g*-PEGMA for industrial applications, *Appl Surf Sci* 435 (2018) 1072–1079. <https://doi.org/10.1016/J.APSUSC.2017.11.193>.
- [145] M. Li, L. Wu, C. Zhang, W. Chen, C. Liu, Hydrophilic and antifouling modification of PVDF membranes by one-step assembly of tannic acid and polyvinylpyrrolidone, *Appl Surf Sci* 483 (2019) 967–978.
<https://doi.org/10.1016/J.APSUSC.2019.04.057>.
- [146] N. Baig, A. Martin, M. Faizan, D. Anand, I. Ahmad, S.A. Khan, Antifouling low-pressure highly permeable single step produced loose nanofiltration polysulfone membrane for efficient Erichrome Black T/divalent salts fractionation, *J Environ Chem Eng* 10 (2022) 108166. <https://doi.org/10.1016/J.JECE.2022.108166>.
- [147] Y.Q. Zhang, X. Bin Yang, Z.X. Wang, J. Long, L. Shao, Designing multifunctional 3D magnetic foam for effective insoluble oil separation and rapid selective dye removal for use in wastewater remediation, *J Mater Chem A Mater* 5 (2017) 7316–7325. <https://doi.org/10.1039/C6TA11252H>.
- [148] S. Huang, Mussel-Inspired One-Step Copolymerization to Engineer Hierarchically Structured Surface with Superhydrophobic Properties for Removing Oil from

- Water, *ACS Applied Materials & Interfaces* 6 (2014) 17144–17150.
<https://doi.org/10.1021/am5048174>.
- [149] Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, Mussel-Inspired Chemistry and Michael Addition Reaction for Efficient Oil/Water Separation, *ACS Applied Materials & Interfaces* 5 (2013) 4438–4442.
<https://doi.org/10.1021/am4008598>.
- [150] D. Li, R. Wu, J. Li, W. Li, Y. Zhang, H. She, Facile fabrication of an underwater superoleophobic mesh for effective separation of oil/simulated seawater mixtures, *RSC Adv* 6 (2016) 77908–77912. <https://doi.org/10.1039/C6RA16900G>.
- [151] Y. Cao, N. Liu, W. Zhang, L. Feng, Y. Wei, One-Step Coating toward Multifunctional Applications: Oil/Water Mixtures and Emulsions Separation and Contaminants Adsorption, *ACS Applied Materials & Interfaces* 8 (2016) 3333–3339. <https://doi.org/10.1021/acsami.5b11226>.
- [152] N. Cao, Q. Lyu, J. Li, Y. Wang, B. Yang, S. Szunerits, R. Boukherroub, Facile synthesis of fluorinated polydopamine/chitosan/reduced graphene oxide composite aerogel for efficient oil/water separation, *Chemical Engineering Journal* 326 (2017) 17–28. <https://doi.org/10.1016/J.CEJ.2017.05.117>.
- [153] J. Gu, P. Xiao, P. Chen, L. Zhang, H. Wang, L. Dai, L. Song, Y. Huang, J. Zhang, T. Chen, Functionalization of Biodegradable PLA Nonwoven Fabric as Superoleophilic and Superhydrophobic Material for Efficient Oil Absorption and Oil/Water Separation, *ACS Applied Materials & Interfaces* 9 (2017) 5968–5973. <https://doi.org/10.1021/acsami.6b13547>.
- [154] S. Xue, C. Li, J. Li, H. Zhu, Y. Guo, A catechol-based biomimetic strategy combined with surface mineralization to enhance hydrophilicity and anti-fouling property of PTFE flat membrane, *J Memb Sci* 524 (2017) 409–418.
<https://doi.org/10.1016/J.MEMSCI.2016.11.075>.
- [155] Z.X. Wang, C.H. Lau, N.Q. Zhang, Y.P. Bai, L. Shao, Mussel-inspired tailoring of membrane wettability for harsh water treatment, *J Mater Chem A Mater* 3 (2015) 2650–2657. <https://doi.org/10.1039/C4TA05970K>.
- [156] Q. Xue, H. Cao, F. Meng, M. Quan, Y.K. Gong, Cell membrane mimetic coating immobilized by mussel-inspired adhesion on commercial ultrafiltration membrane to enhance antifouling performance, *J Memb Sci* 528 (2017) 1–11.
<https://doi.org/10.1016/J.MEMSCI.2017.01.009>.

- [157] M.J. Sever, J.J. Wilker, Visible absorption spectra of metal–catecholate and metal–tironate complexes, *Dalton Transactions* 4 (2004) 1061–1072.
<https://doi.org/10.1039/B315811J>.
- [158] J. Bijlsma, W.J.C. De Bruijn, J.A. Hageman, P. Goos, K.P. Velikov, J.-P. Vincken, Revealing the main factors and two-way interactions contributing to food discolouration caused by iron-catechol complexation, (n.d.).
<https://doi.org/10.1038/s41598-020-65171-1>.
- [159] N.R.P. Ae, J.L. Brumaghim, A Review of the Antioxidant Mechanisms of Polyphenol Compounds Related to Iron Binding, (n.d.).
<https://doi.org/10.1007/s12013-009-9043-x>.
- [160] M. Elhabiri, C. Carrër, F. Marmolle, H. Traboulsi, Complexation of iron(III) by catecholate-type polyphenols, *Inorganica Chim Acta* 360 (2007) 353–359.
<https://doi.org/10.1016/J.ICA.2006.07.110>.
- [161] B.D. McCloskey, H.B. Park, H. Ju, B.W. Rowe, D.J. Miller, B.J. Chun, K. Kin, B.D. Freeman, Influence of polydopamine deposition conditions on pure water flux and foulant adhesion resistance of reverse osmosis, ultrafiltration, and microfiltration membranes, *Polymer (Guildf)* 51 (2010) 3472–3485.
<https://doi.org/10.1016/J.POLYMER.2010.05.008>.
- [162] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric Betaines: Synthesis, Characterization, and Application, in: 2006: pp. 157–224.
https://doi.org/10.1007/12_078.
- [163] G.B. Butler, Cyclopolymerization, *J Polym Sci A Polym Chem* 38 (2000) 3451–3461. [https://doi.org/https://doi.org/10.1002/1099-0518\(20001001\)38:19<3451::AID-POLA10>3.0.CO;2-N](https://doi.org/https://doi.org/10.1002/1099-0518(20001001)38:19<3451::AID-POLA10>3.0.CO;2-N).
- [164] G.B. Butler, *Cyclopolymerization and Cyclocopolymerization*, CRC Press, 2020.
<https://doi.org/10.1201/9781003066828>.
- [165] F. C. McGrew, Structure of synthetic high polymers, *J Chem Educ* 35 (1958).
<https://doi.org/10.1021/ed035p178>.
- [166] Y. Umar, H.A. Al-Muallem, B.F. Abu-Sharkh, S.A. Ali, Synthesis and solution properties of hydrophobically associating ionic polymers made from diallylammonium salts/sulfur dioxide cyclocopolymerization, *Polymer (Guildf)* 45 (2004) 3651–3661. <https://doi.org/10.1016/J.POLYMER.2004.03.057>.

- [167] Z. Arshad, S.A. Ali, Synthesis and anticorrosive application of biomimetic dopamine-based cationic polyelectrolytes derived from diallylammonium salts, *Polymer (Guildf)* 264 (2023). <https://doi.org/10.1016/j.polymer.2022.125537>.
- [168] A. Thakur, S. Ranote, D. Kumar, K. Kumar Bhardwaj, R. Gupta, G. S. Chauhan, Synthesis of a PEGylated Dopamine Ester with Enhanced Antibacterial and Antifungal Activity, *ACS Omega* 3 (2018) 7925–7933. <https://doi.org/10.1021/acsomega.8b01099>.
- [169] G.B. Butler, R.J. Angelo, Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VIII. A Proposed Alternating Intramolecular-Intermolecular Chain Propagation 1, *J Am Chem Soc* 79 (1957) 3128–3131. <https://doi.org/10.1021/ja01569a037>.
- [170] Fatma Yalcinkaya, Anna Siekierka, Marek Bryjak, Surface modification of electrospun nanofibrous membranes for oily wastewater separation, *RSC Adv* 7 (2017) 56704–56712. <https://doi.org/10.1039/C7RA11904F>.
- [171] G. Kolev, M. Aleksandrova, Y. Vucheva, K. Denishev, Thin Film Microsensing Elements, Technology and Application in Microsystems for Environment Control, *J Phys Conf Ser* 559 (2014) 012015. <https://doi.org/10.1088/1742-6596/559/1/012015>.
- [172] Y. Ren, Y. Wang, W. Zhang, X. Yan, B. Huang, Improved battery performance contributed by the optimized phase ratio of β and α of PVDF, *RSC Adv* 9 (2019) 29760–29764. <https://doi.org/10.1039/C9RA04724G>.
- [173] F. Yang, G. Ding, J. Wang, Z. Liang, B. Gao, M. Dou, C. Xu, S. Li, Self-cleaning, antimicrobial, and antifouling membrane via integrating mesoporous graphitic carbon nitride into polyvinylidene fluoride, *J Memb Sci* 606 (2020) 118146. <https://doi.org/10.1016/J.MEMSCI.2020.118146>.
- [174] H. Younas, Y. Zhou, X. Li, X. Li, Q. Sun, Z. Cui, Z. Wang, Fabrication of high flux and fouling resistant membrane: A unique hydrophilic blend of polyvinylidene fluoride/polyethylene glycol/polymethyl methacrylate, *Polymer (Guildf)* 179 (2019) 121593. <https://doi.org/10.1016/J.POLYMER.2019.121593>.
- [175] X. hao Liu, J. Duan, J. hui Yang, T. Huang, N. Zhang, Y. Wang, Z. wan Zhou, Hydrophilicity, morphology and excellent adsorption ability of poly(vinylidene fluoride) membranes induced by graphene oxide and polyvinylpyrrolidone, *Colloids Surf A Physicochem Eng Asp* 486 (2015) 172–184. <https://doi.org/10.1016/J.COLSURFA.2015.09.036>.

- [176] N. Baig, I. Kammakakam, Special wetttable *Azadirachta indica* leaves like microarchitecture mesh filtration membrane produced by galvanic replacement reaction for layered oil/water separation, *Chemosphere* 313 (2023) 137544. <https://doi.org/10.1016/J.CHEMOSPHERE.2022.137544>.
- [177] F. Tang, D. Wang, C. Zhou, X. Zeng, J. Du, L. Chen, W. Zhou, Z. Lu, L. Tan, L. Dong, Natural polyphenol chemistry inspired organic-inorganic composite coating decorated PVDF membrane for oil-in-water emulsions separation, *Mater Res Bull* 132 (2020) 110995. <https://doi.org/10.1016/j.materresbull.2020.110995>.
- [178] Y. Wang, Z. Liu, X. Wei, K. Liu, J. Wang, J. Hu, J. Lin, An integrated strategy for achieving oil-in-water separation, removal, and anti-oil/dye/bacteria-fouling, *Chemical Engineering Journal* 413 (2021) 127493. <https://doi.org/10.1016/j.cej.2020.127493>.
- [179] H. Mahdavi, R. Ghanbari, Preparation of loose nanofiltration PVDF membrane coated with dopamine and EPPTMS layers based on mussel inspired technique and ring-opening reaction via a facile VIPS-NIGPS method for dye separation applications, *Journal of Industrial and Engineering Chemistry* 113 (2022) 132–141. <https://doi.org/10.1016/J.JIEC.2022.04.029>.
- [180] J. Wu, W. Wei, S. Li, Q. Zhong, F. Liu, J. Zheng, J. Wang, The effect of membrane surface charges on demulsification and fouling resistance during emulsion separation, *J Memb Sci* 563 (2018) 126–133. <https://doi.org/10.1016/J.MEMSCI.2018.05.065>.
- [181] J. Bijlsma, W.J.C. de Bruijn, J.A. Hageman, P. Goos, K.P. Velikov, J.P. Vincken, Revealing the main factors and two-way interactions contributing to food discolouration caused by iron-catechol complexation, *Scientific Reports* 2020 10:1 10 (2020) 1–11. <https://doi.org/10.1038/s41598-020-65171-1>.
- [182] M.J. Sever, J.J. Wilker, Visible absorption spectra of metal–catecholate and metal–tironate complexes, *Dalton Transactions* 4 (2004) 1061–1072. <https://doi.org/10.1039/B315811J>.
- [183] A.C. Bovell-Benjamin, J.X. Guinard, Novel Approaches and Application of Contemporary Sensory Evaluation Practices in Iron Fortification Programs, [Http://Dx.Doi.Org/10.1080/10408690390826563](http://Dx.Doi.Org/10.1080/10408690390826563) 43 (2010) 379–400. <https://doi.org/10.1080/10408690390826563>.
- [184] M. Elhabiri, C. Carrër, F. Marmolle, H. Traboulsi, Complexation of iron(III) by catecholate-type polyphenols, *Inorganica Chim Acta* 360 (2007) 353–359. <https://doi.org/10.1016/J.ICA.2006.07.110>.

- [185] N. Baig, A.M. Alowaid, I. Abdulazeez, B. Salhi, M. Sajid, I. Kammakakam, Designing of nanotextured inorganic-organic hybrid PVDF membrane for efficient separation of the oil-in-water emulsions, *Chemosphere* 308 (2022) 136531. <https://doi.org/10.1016/J.CHEMOSPHERE.2022.136531>.
- [186] A. Roy, K. Manna, S. Dey, S. Pal, Chemical modification of β -cyclodextrin towards hydrogel formation, *Carbohydr Polym* 306 (2023) 120576. <https://doi.org/10.1016/J.CARBPOL.2023.120576>.
- [187] K. Uekama, F. Hirayama, T. Irie, Cyclodextrin drug carrier systems, *Chem Rev* 98 (1998) 2045–2076. <https://doi.org/10.1021/CR970025P/ASSET/IMAGES/LARGE/CR970025PF00011.JPEG>.
- [188] B. Gidwani, A. Vyas, A Comprehensive Review on Cyclodextrin-Based Carriers for Delivery of Chemotherapeutic Cytotoxic Anticancer Drugs, *Biomed Res Int* 2015 (2015). <https://doi.org/10.1155/2015/198268>.
- [189] J. Wankar, N.G. Kotla, S. Gera, S. Rasala, A. Pandit, Y.A. Rochev, J. Wankar, N.G. Kotla, S. Rasala, A. Pandit, Y.A. Rochev, S. Gera, Recent Advances in Host–Guest Self-Assembled Cyclodextrin Carriers: Implications for Responsive Drug Delivery and Biomedical Engineering, *Adv Funct Mater* 30 (2020) 1909049. <https://doi.org/10.1002/ADFM.201909049>.
- [190] A. Motoyama, A. Suzuki, O. Shiota, R. Namba, Direct determination of pindolol enantiomers in human serum by column-switching LC-MS/MS using a phenylcarbamate- β -cyclodextrin chiral column, *J Pharm Biomed Anal* 28 (2002) 97–106. [https://doi.org/10.1016/S0731-7085\(01\)00631-8](https://doi.org/10.1016/S0731-7085(01)00631-8).
- [191] T. Wimmer, Cyclodextrins, *Ullmann’s Encyclopedia of Industrial Chemistry* (2003). https://doi.org/10.1002/14356007.E08_E02.
- [192] G. Becket, L.J. Schep, M.Y. Tan, Improvement of the in vitro dissolution of praziquantel by complexation with α -, β - and γ -cyclodextrins, *Int J Pharm* 179 (1999) 65–71. [https://doi.org/10.1016/S0378-5173\(98\)00382-2](https://doi.org/10.1016/S0378-5173(98)00382-2).
- [193] K. Manna, P. Patra, A. Roy, R.K. Roy, K. Chaitanya 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 (2022) 4432–4444. <https://doi.org/10.1021/acsapm.2c00393>.
- [194] S.K. Rodal, G. Skretting, Ø. Garred, F. Vilhardt, B. van Deurs, K. Sandvig, Extraction of Cholesterol with Methyl- β -Cyclodextrin Perturbs Formation of

Clathrin-coated Endocytic Vesicles, *Mol Biol Cell* 10 (1999) 961–974.
<https://doi.org/10.1091/mbc.10.4.961>.

- [195] C. Sebaaly, C. Charcosset, S. Fourmentin, H. Greige-Gerges, Potential Applications of Cyclodextrin Inclusion Complexes, Liposomes, and Drug-in-Cyclodextrin-in-Liposome in Food Industry and Packaging, *Role of Materials Science in Food Bioengineering* (2018) 187–234. <https://doi.org/10.1016/B978-0-12-811448-3.00006-1>.
- [196] S. Saha, A. Roy, K. Roy, M.N. Roy, Study to explore the mechanism to form inclusion complexes of β -cyclodextrin with vitamin molecules, *Scientific Reports* 2016 6:1 6 (2016) 1–12. <https://doi.org/10.1038/srep35764>.
- [197] M.A. Crumling, K.A. King, R.K. Duncan, Cyclodextrins and Iatrogenic Hearing Loss: New Drugs with Significant Risk, *Front Cell Neurosci* 11 (2017) 307236. <https://doi.org/10.3389/fncel.2017.00355>.
- [198] D.M. Alzate-Sánchez, Y. Ling, C. Li, B.P. Frank, R. Bleher, D.H. Fairbrother, D.E. Helbling, W.R. Dichtel, β -Cyclodextrin Polymers on Microcrystalline Cellulose as a Granular Media for Organic Micropollutant Removal from Water, *ACS Appl Mater Interfaces* 11 (2019) 8089–8096. <https://doi.org/10.1021/acsami.8b22100>.
- [199] A. Alsbaiee, B.J. Smith, L. Xiao, Y. Ling, D.E. Helbling, W.R. Dichtel, Rapid removal of organic micropollutants from water by a porous β -cyclodextrin polymer, *Nature* 2015 529:7585 529 (2015) 190–194. <https://doi.org/10.1038/nature16185>.
- [200] A. Roy, P.P. Maity, A. Bose, S. Dhara, S. Pal, β -Cyclodextrin based pH and thermo-responsive biopolymeric hydrogel as a dual drug carrier, *Mater Chem Front* 3 (2019) 385–393. <https://doi.org/10.1039/C8QM00452H>.
- [201] G. Giammona, G. Cavallaro, L. Maniscalco, E.F. Craparo, G. Pitarresi, Synthesis and characterisation of novel chemical conjugates based on α,β -polyaspartylhydrazide and β -cyclodextrins, *Eur Polym J* 42 (2006) 2715–2729. <https://doi.org/10.1016/J.EURPOLYMJ.2006.05.005>.
- [202] J. Ma, J. Ma, Q. Zhang, R. Peng, J. Wang, C. Liu, M. Wang, N. Li, M. Chen, X. Cheng, P. Gao, L. Gu, L.Q. Chen, P. Yu, J. Zhang, C.W. Nan, Controllable conductive readout in self-assembled, topologically confined ferroelectric domain walls, *Nature Nanotechnology* 2018 13:10 13 (2018) 947–952. <https://doi.org/10.1038/s41565-018-0204-1>.

- [203] S. Dey, A. Roy, K. Manna, S. Pal, The UCST phase transition of a dextran based copolymer in aqueous media with tunable thermoresponsive behavior, *Polym Chem* 13 (2022) 3865–3869. <https://doi.org/10.1039/D2PY00626J>.
- [204] S. Dey, A.S. Patra, P. Patra, B. Saha, A.K. Mukherjee, S. Pal, Macromolecular selective flocculant derived from functionalized starch towards beneficiation of low-quality iron ore: Atomistic simulations and experimental studies, *Mater Today Commun* 32 (2022) 103810. <https://doi.org/10.1016/J.MTCOMM.2022.103810>.
- [205] S.R. Popielarski, S. Mishra, M.E. Davis, Structural Effects of Carbohydrate-Containing Polycations on Gene Delivery. 3. Cyclodextrin Type and Functionalization, *Bioconjug Chem* 14 (2003) 672–678. <https://doi.org/10.1021/bc034010b>.
- [206] Y. Rojas-Aguirre, M.A. Torres-Mena, L.J. López-Méndez, S.L. Alcaraz-Estrada, P. Guadarrama, J.M. Urucha-Ortiz, PEGylated β -cyclodextrins: Click synthesis and in vitro biological insights, *Carbohydr Polym* 223 (2019) 115113. <https://doi.org/10.1016/J.CARBPOL.2019.115113>.
- [207] S. Tan, K. Ladewig, Q. Fu, A. Blencowe, G.G. Qiao, S. Tan, K. Ladewig, Q. Fu, A. Blencowe, G.G. Qiao, Cyclodextrin-Based Supramolecular Assemblies and Hydrogels: Recent Advances and Future Perspectives, *Macromol Rapid Commun* 35 (2014) 1166–1184. <https://doi.org/10.1002/MARC.201400080>.
- [208] M. Petitjean, I.X. García-Zubiri, J.R. Isasi, History of cyclodextrin-based polymers in food and pharmacy: a review, *Environmental Chemistry Letters* 2021 19:4 19 (2021) 3465–3476. <https://doi.org/10.1007/S10311-021-01244-5>.
- [209] S. Amajjahe, S. Choi, M. Munteanu, H. Ritter, Pseudopolyanionen aus Poly(NIPAAm-co- β -Cyclodextrinmethacrylat) und ionischen Flüssigkeiten, *Angewandte Chemie* 120 (2008) 3484–3486. <https://doi.org/10.1002/ANGE.200704995>.
- [210] M. Arslan, R. Sanyal, A. Sanyal, Cyclodextrin embedded covalently crosslinked networks: synthesis and applications of hydrogels with nano-containers, *Polym Chem* 11 (2020) 615–629. <https://doi.org/10.1039/C9PY01679A>.
- [211] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric Betaines: Synthesis, Characterization, and Application, in: *Advances in Polymer Science*, Springer, Berlin, Heidelberg, 2006: pp. 157–224. https://doi.org/10.1007/12_078.
- [212] A. Laschewsky, Structures and Synthesis of Zwitterionic Polymers, *Polymers* 2014, Vol. 6, Pages 1544-1601 6 (2014) 1544–1601. <https://doi.org/10.3390/POLYM6051544>.

- [213] P.K. Singh, V.K. Singh, M. Singh, Zwitterionic Polyelectrolytes: A Review, *E-Polymers* 7 (2007) 1–34. <https://doi.org/10.1515/epoly.2007.7.1.335>.
- [214] S. Kudaibergenov, W. Jaeger, A. Laschewsky, Polymeric betaines: Synthesis, characterization, and application, *Advances in Polymer Science* 201 (2006) 157–224. https://doi.org/10.1007/12_078.
- [215] S.A. Ali, H.A. Al-Muallem, M.A.J. Mazumder, Stimuli-Responsive Macromolecular Architecture by Butler Cyclopolymerizations: Synthesis and Applications, *The Chemical Record* 23 (2023) e202200235. <https://doi.org/10.1002/TCR.202200235>.
- [216] G.B. Butler, Cyclopolymerization and Cyclocopolymerization, *Cyclopolymerization and Cyclocopolymerization* (2020). <https://doi.org/10.1201/9781003066828>.
- [217] S.A. Ali, Z. Arshad, L.K.M.O. Goni, I.Y. Yaagoob, H.A. Al-Muallem, M.A.J. Mazumder, Cross-linked cyclopolymers from pH-responsive diallyl amine salts for environmental remediation, *J Environ Chem Eng* 11 (2023) 110995. <https://doi.org/10.1016/J.JECE.2023.110995>.
- [218] J. Elaridi, A. Ezzeddine, L. Abramian, A. Koubeissi, N. Vladimirov, K.H. Bouhadir, Synthesis and polymerization of 1-(2-diallylaminoethyl)pyrimidines, *Des Monomers Polym* 21 (2018) 64–74. <https://doi.org/10.1080/15685551.2018.1448232>.
- [219] G.B. Butler, Cyclopolymerization, *J Polym Sci A Polym Chem* 38 (1983) 3451–3461. <https://doi.org/10.1002/1099-0518>.
- [220] F.C. McGrew, Structure of synthetic high polymers, *J Chem Educ* 35 (1958) 178–186. <https://doi.org/10.1021/ED035P178>.
- [221] T.A. Saleh, A.M. Musa, B. Tawabini, S.A. Ali, Aminomethylphosphonate Chelating Ligand and Octadecyl Alkyl Chain in a Resin for Simultaneous Removal of Co(II) Ions and Organic Contaminants, *J Chem Eng Data* 61 (2016) 3377–3385. <https://doi.org/10.1021/acs.jced.6b00475>.
- [222] 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 (2015) 120–129. <https://doi.org/10.1016/J.REACTFUNCTPOLYM.2015.06.006>.
- [223] 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 Cu²⁺ from aqueous solution

- at low concentrations, *J Hazard Mater* 248–249 (2013) 47–58.
<https://doi.org/10.1016/J.JHAZMAT.2012.12.052>.
- [224] Z. Arshad, S.A. Ali, Synthesis and anticorrosive application of biomimetic dopamine-based cationic polyelectrolytes derived from diallylammonium salts, *Polymer (Guildf)* 264 (2023) 125537.
<https://doi.org/10.1016/J.POLYMER.2022.125537>.
- [225] S.A. Ali, Z.A. Jamiu, Poly(N,N-diallylaspartic acid-alt-sulfur dioxide): its synthesis and application, *Polymer Bulletin* 73 (2016) 2179–2198.
<https://doi.org/10.1007/s00289-016-1602-x>.
- [226] H.A. Al-Muallem, M.I.M. Wazeer, S.A. Ali, Synthesis and solution properties of a new ionic polymer and its behavior in aqueous two-phase polymer systems, *Polymer (Guildf)* 43 (2002) 1041–1050. [https://doi.org/10.1016/S0032-3861\(01\)00720-0](https://doi.org/10.1016/S0032-3861(01)00720-0).
- [227] 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>.
- [228] J.F. Pearson, M.A. Slifkin, The infrared spectra of amino acids and dipeptides, *Spectrochim Acta A* 28 (1972) 2403–2417. [https://doi.org/10.1016/0584-8539\(72\)80220-4](https://doi.org/10.1016/0584-8539(72)80220-4).
- [229] S.A. Ali, O.C.S. Al-Hamouz, Comparative solution properties of cyclocopolymers having cationic, anionic, zwitterionic and zwitterionic/anionic backbones of similar degree of polymerization, *Polymer (Guildf)* 53 (2012) 3368–3377.
<https://doi.org/10.1016/J.POLYMER.2012.05.034>.
- [230] T.A. Wielema, J.B.F.N. Engberts, Zwitterionic polymers—I. Synthesis of a novel series of poly(vinylsulphobetaines). Effect of structure of polymer on solubility in water, *Eur Polym J* 23 (1987) 947–950. [https://doi.org/10.1016/0014-3057\(87\)90038-3](https://doi.org/10.1016/0014-3057(87)90038-3).
- [231] J.C. Salamone, W. Volksen, A.P. Olson, S.C. Israel, Aqueous solution properties of a poly(vinyl imidazolium sulphobetaine), *Polymer (Guildf)* 19 (1978) 1157–1162. [https://doi.org/10.1016/0032-3861\(78\)90064-2](https://doi.org/10.1016/0032-3861(78)90064-2).
- [232] M. Yoshizawa, H. Ohno, Molecular Brush Having Molten Salt Domain for Fast Ion Conduction, *Chem Lett* 28 (1999) 889–890.
<https://doi.org/10.1246/CL.1999.889>.

- [233] S.A. Ali, M.A.J. Mazumber, H.A. Al-Muallem, Synthesis and solution properties of a new pH-responsive polymer containing amino propanesulfonic acid residues, *J Polym Sci A Polym Chem* 41 (2003) 172–184. <https://doi.org/10.1002/POLA.10565>.
- [234] S.A. Ali, H.A. Al-Muallem, M.A.J. Mazumber, Stimuli-Responsive Macromolecular Architecture by Butler Cyclopolymerizations: Synthesis and Applications, *The Chemical Record* 23 (2023) e202200235. <https://doi.org/10.1002/TCR.202200235>.
- [235] F. Rullens, M. Devillers, A. Laschewsky, New Regular, Amphiphilic Poly(ampholyte)s: Synthesis and Characterization, *Macromol Chem Phys* 205 (2004) 1155–1166. <https://doi.org/10.1002/MACP.200400081>.
- [236] G.B. Butler, R.J. Angelo, Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VIII. A Proposed Alternating Intramolecular-Intermolecular Chain Propagation ¹, *J Am Chem Soc* 79 (1957) 3128–3131. <https://doi.org/10.1021/ja01569a037>.
- [237] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C.A. Johnson, U. Von Gunten, B. Wehrli, The Challenge of Micropollutants in Aquatic Systems, *Science* (1979) 313 (2006) 1072–1077. <https://doi.org/10.1126/SCIENCE.1127291>.
- [238] S.D. Richardson, T.A. Ternes, Water Analysis: Emerging Contaminants and Current Issues, *Anal Chem* 86 (2014) 2813–2848. <https://doi.org/10.1021/ac500508t>.
- [239] N. Morin-Crini, G. Crini, Environmental applications of water-insoluble β -cyclodextrin–epichlorohydrin polymers, *Prog Polym Sci* 38 (2013) 344–368. <https://doi.org/10.1016/J.PROGPOLYMSCI.2012.06.005>.
- [240] B. Gidwani, A. Vyas, Synthesis, characterization and application of Epichlorohydrin- β -cyclodextrin polymer, *Colloids Surf B Biointerfaces* 114 (2014) 130–137. <https://doi.org/10.1016/J.COLSURFB.2013.09.035>.
- [241] A. Bright, F. Li, M. Movahed, H. Shi, B. Xue, Chronic Exposure to Low-Molecular-Weight Polycyclic Aromatic Hydrocarbons Promotes Lipid Accumulation and Metabolic Inflammation, *Biomolecules* 2023, Vol. 13, Page 196 13 (2023) 196. <https://doi.org/10.3390/BIOM13020196>.
- [242] H. Liu, X. Cai, Y. Wang, J. Chen, Adsorption mechanism-based screening of cyclodextrin polymers for adsorption and separation of pesticides from water, *Water Res* 45 (2011) 3499–3511. <https://doi.org/10.1016/J.WATRES.2011.04.004>.

- [243] A. Kortenkamp, M. Faust, Regulate to reduce chemical mixture risk, *Science* (1979) 361 (2018) 224–226. <https://doi.org/10.1126/science.aat9219>.
- [244] E.S. Bernhardt, E.J. Rosi, M.O. Gessner, Synthetic chemicals as agents of global change, *Front Ecol Environ* 15 (2017) 84–90. <https://doi.org/10.1002/FEE.1450>.
- [245] P.T. Gauthier, W.P. Norwood, E.E. Prepas, G.G. Pyle, Metal–PAH mixtures in the aquatic environment: A review of co-toxic mechanisms leading to more-than-additive outcomes, *Aquatic Toxicology* 154 (2014) 253–269. <https://doi.org/10.1016/J.AQUATOX.2014.05.026>.
- [246] B. Armstrong, E. Hutchinson, J. Unwin, T. Fletcher, Lung Cancer Risk after Exposure to Polycyclic Aromatic Hydrocarbons: A Review and Meta-Analysis, *Environ Health Perspect* 112 (2004) 970–978. <https://doi.org/10.1289/ehp.6895>.
- [247] M. devi M, Heavy Metals Removal from Industrial Wastewater by Nano Adsorbent Prepared from Cucumis Melo peel Activated Carbon, *J Nanomed Res* Volume 5 (2017). <https://doi.org/10.15406/JNMR.2017.05.00102>.
- [248] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J Environ Manage* 92 (2011) 407–418. <https://doi.org/10.1016/J.JENVMAN.2010.11.011>.
- [249] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, Q. Zhang, Heavy metal removal from water/wastewater by nanosized metal oxides: A review, *J Hazard Mater* 211–212 (2012) 317–331. <https://doi.org/10.1016/J.JHAZMAT.2011.10.016>.
- [250] A.K. Haritash, C.P. Kaushik, Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): A review, *J Hazard Mater* 169 (2009) 1–15. <https://doi.org/10.1016/J.JHAZMAT.2009.03.137>.
- [251] M. Ahmaruzzaman, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, *Adv Colloid Interface Sci* 166 (2011) 36–59. <https://doi.org/10.1016/J.CIS.2011.04.005>.
- [252] S.M. Yakout, A.A.M. Daifullah, S.A. El-Reefy, Adsorption of Naphthalene, Phenanthrene and Pyrene from Aqueous Solution Using Low-Cost Activated Carbon Derived from Agricultural Wastes, *Adsorption Science & Technology* 31 (2013) 293–302. <https://doi.org/10.1260/0263-6174.31.4.293>.
- [253] S. Lamichhane, K.C. Bal Krishna, R. Sarukkalige, Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review, *Chemosphere* 148 (2016) 336–353. <https://doi.org/10.1016/J.CHEMOSPHERE.2016.01.036>.

- [254] A. Balati, A. Shahbazi, M.M. Amini, S.H. Hashemi, Adsorption of polycyclic aromatic hydrocarbons from wastewater by using silica-based organic–inorganic nanohybrid material, *Journal of Water Reuse and Desalination* 5 (2015) 50–63. <https://doi.org/10.2166/WRD.2014.013>.
- [255] G. Karaca, H.S. Baskaya, Y. Tasdemir, Removal of polycyclic aromatic hydrocarbons (PAHs) from inorganic clay mineral: Bentonite, *Environmental Science and Pollution Research* 23 (2016) 242–252. <https://doi.org/10.1007/s11356-015-5676-z>.
- [256] R. Crisafulli, M.A.L. Milhome, R.M. Cavalcante, E.R. Silveira, D. De Keukeleire, R.F. Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin, *Bioresour Technol* 99 (2008) 4515–4519. <https://doi.org/10.1016/J.BIORTECH.2007.08.041>.
- [257] S.M. Yakout, A.A.M. Daifullah, Removal of selected polycyclic aromatic hydrocarbons from aqueous solution onto various adsorbent materials, *Desalination Water Treat* 51 (2013) 6711–6718. <https://doi.org/10.1080/19443994.2013.769916>.
- [258] M. Paszkiewicz, C. Sikorska, D. Leszczyńska, P. Stepnowski, Helical Multi-walled Carbon Nanotubes as an Efficient Material for the Dispersive Solid-Phase Extraction of Low and High Molecular Weight Polycyclic Aromatic Hydrocarbons from Water Samples: Theoretical Study, *Water Air Soil Pollut* 229 (2018) 1–15. <https://doi.org/10.1007/S11270-018-3884-0/TABLES/5>.
- [259] A.M. Dowaidar, M.S. El-Shahawi, I. Ashour, Adsorption of Polycyclic Aromatic Hydrocarbons onto Activated Carbon from Non-Aqueous Media: 1. The Influence of the Organic Solvent Polarity, *Sep Sci Technol* 42 (2007) 3609–3622. <https://doi.org/10.1080/01496390701626537>.
- [260] C.B. Vidal, A.L. Barros, C.P. Moura, A.C.A. de Lima, F.S. Dias, L.C.G. Vasconcellos, P.B.A. Fachine, R.F. Nascimento, Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica, *J Colloid Interface Sci* 357 (2011) 466–473. <https://doi.org/10.1016/J.JCIS.2011.02.013>.
- [261] W. Guo, S. Wang, Y. Wang, S. Lu, Y. Gao, Sorptive removal of phenanthrene from aqueous solutions using magnetic and non-magnetic rice husk-derived biochars, *R Soc Open Sci* 5 (2018). <https://doi.org/10.1098/RSOS.172382>.

- [262] B. Li, P. Ou, Y. Wei, X. Zhang, J. Song, Polycyclic Aromatic Hydrocarbons Adsorption onto Graphene: A DFT and AIMD Study, *Materials* 2018, Vol. 11, Page 726 11 (2018) 726. <https://doi.org/10.3390/MA11050726>.
- [263] N. Morin-Crini, P. Winterton, S. Fourmentin, L.D. Wilson, É. Fenyvesi, G. Crini, Water-insoluble β -cyclodextrin–epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using batch studies: A review of inclusion mechanisms, *Prog Polym Sci* 78 (2018) 1–23. <https://doi.org/10.1016/J.PROGPOLYMSCI.2017.07.004>.
- [264] M.L. Brusseau, X. Wang, W.-Z. Wang, Simultaneous Elution of Heavy Metals and Organic Compounds from Soil by Cyclodextrin, *Environ Sci Technol* 31 (1997) 1087–1092. <https://doi.org/10.1021/es960612c>.
- [265] Xiaojiang. Wang, M.L. Brusseau, Simultaneous Complexation of Organic Compounds and Heavy Metals by a Modified Cyclodextrin, *Environ Sci Technol* 29 (1995) 2632–2635. <https://doi.org/10.1021/es00010a026>.
- [266] X. Wang, I. Yolcubal, W. Wang, J. Artiola, R. Maier, M. Brusseau, Use of cyclodextrin and calcium chloride for enhanced removal of mercury from soil, *Environ Toxicol Chem* 23 (2004) 1888–1892. <https://doi.org/10.1897/03-379>.
- [267] 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 (2015) 120–129. <https://doi.org/10.1016/J.REACTFUNCTPOLYM.2015.06.006>.
- [268] T.A. Saleh, A.M. Musa, B. Tawabini, S.A. Ali, Aminomethylphosphonate Chelating Ligand and Octadecyl Alkyl Chain in a Resin for Simultaneous Removal of Co(II) Ions and Organic Contaminants, *J Chem Eng Data* 61 (2016) 3377–3385. <https://doi.org/10.1021/acs.jced.6b00475>.
- [269] 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 Adv* 12 (2022) 5938–5952. <https://doi.org/10.1039/D1RA09234K>.
- [270] D.L. Poster, M.M. Schantz, L.C. Sander, S.A. Wise, Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods, *Anal Bioanal Chem* 386 (2006) 859–881. <https://doi.org/10.1007/s00216-006-0771-0>.
- [271] A. Tanimu, S.M.S. Jillani, A.A. Alluhaidan, S.A. Ganiyu, K. Alhooshani, 4-phenyl-1,2,3-triazole functionalized mesoporous silica SBA-15 as sorbent in an

efficient stir bar-supported micro-solid-phase extraction strategy for highly to moderately polar phenols, *Talanta* 194 (2019) 377–384.
<https://doi.org/10.1016/J.TALANTA.2018.10.012>.

- [272] S.A. Ali, M.T. Saeed, Synthesis and corrosion inhibition study of some 1,6-hexanediamine-based N,N-diallyl quaternary ammonium salts and their polymers, *Polymer (Guildf)* 42 (2001) 2785–2794. [https://doi.org/10.1016/S0032-3861\(00\)00665-0](https://doi.org/10.1016/S0032-3861(00)00665-0).
- [273] S. Amani, A. Bagheri Garmarudi, N. Rahmani, M. Khanmohammadi, The β -cyclodextrin-modified nanosized ZSM-5 zeolite as a carrier for curcumin, *RSC Adv* 9 (2019) 32348–32356. <https://doi.org/10.1039/C9RA04739E>.
- [274] J.F. Pearson, M.A. Slifkin, The infrared spectra of amino acids and dipeptides, *Spectrochim Acta A* 28 (1972) 2403–2417. [https://doi.org/10.1016/0584-8539\(72\)80220-4](https://doi.org/10.1016/0584-8539(72)80220-4).
- [275] O.C.S. Al Hamouz, S.A. Ali, Novel Cross-Linked Polyphosphonate for the Removal of Pb^{2+} and Cu^{2+} from Aqueous Solution, *Ind Eng Chem Res* 51 (2012) 14178–14187. <https://doi.org/10.1021/ie301231k>.
- [276] S.A. Mubarak, S.A. Ali, I.Y. Yaagoob, M.A.J. Mazumder, Design and Synthesis of a Dual-Purpose Superadsorbent Containing a High Density of Chelating Motifs for the Fast Mitigation of Methylene Blue and Pb(II) , *ACS Omega* 5 (2020) 27833–27845. <https://doi.org/10.1021/acsomega.0c02860>.
- [277] 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, *J Hazard Mater* 350 (2018) 169–179. <https://doi.org/10.1016/j.jhazmat.2018.02.033>.
- [278] F. Haghseresht, G.Q. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, *Energy and Fuels* 12 (1998) 1100–1107. <https://doi.org/10.1021/ef9801165>.
- [279] J.M. 'Tempkin, V. 'Pyzhev, Kinetics of Ammonia Synthesis on Promoted Iron Catalysts, *Acta Physicochim URSS* 12 (1940) 217–222.

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Publications

1. **Arshad, Z.,** & Ali, S. A. Synthesis and anticorrosive application of biomimetic dopamine-based cationic polyelectrolytes derived from diallylammonium salts. **Polymer**, 2023, 264, 125537.
<https://doi.org/10.1016/J.POLYMER.2022.125537>
2. **Arshad, Z.,** Salhi, B., Baig, N., Aljundi, I.H., Ali, S.A. Fabrication of a new rationally designed mussel-inspired cationic amphiphilic terpolymer to enhance the separation and anti-fouling performance of membranes. **Langmuir** 2023, 39, 9186–9199.
<https://doi.org/10.1021/ACS.LANGMUIR.3C009883>
3. **Arshad, Z.,** Baig, N, Ali, S. A. Synthesis of a novel next-generation positively charged polymer and its in-situ grafting into thin film composite membranes to enhance the performance for desalination. **Process Saf. Environ. Prot.**, 2023, 178, 34-45.
<https://doi.org/10.1016/j.psep.2023.07.0894>.
4. Ali, S. A. **Arshad, Z.,** LKMO Goni, IY Yaagoob, HA Al-Muallem MAJ Mazumder, Cross-linked cyclopolymers from pH-Responsive diallyl amine salts for environmental remediation. **J. Environ. Chem. Eng**, 2023, 11, 110995.
<https://doi.org/10.1016/j.jece.2023.110995>

5. Baig N, **Arshad, Z.**, Ali, S. A. Synthesis of a biomimetic zwitterionic pentapolymer to fabricate high-performance PVDF membranes for efficient separation of oil-in-water nano-emulsions. **Sci. Rep.**, 2022, 12, 5028. <https://doi.org/10.1038/s41598-022-09046-7>

6. Ali, S. A. SA Mubarak, IY Yaagoob, **Arshad, Z.**, MAJ Mazumder. A sorbent containing pH-responsive chelating residues of aspartic and maleic acids for mitigation of toxic metal ions, cationic, and anionic dyes. **RSC Adv.**, 2022, 12, 5938-5952. <https://doi.org/10.1039/D1RA09234K>

Conference Paper

1. **Arshad, Z.**, Baig, N, Ali, S. A. Insertion of the rationally designed new cationic polymer in the polyamide membrane for efficient separation applications in water desalination.

In person Poster presentation at 16th International conference on materials chemistry (**MC16**) organized by **Royal Society of Chemistry**, UCD Dublin, Ireland. 3-6 July 2023. <https://online.flippingbook.com/view/381939913/108/#zoom=true>

2. **Arshad, Z.**, & Ali, S. A. Synthesis of catechol-based cyclopolymers: application in inhibition of mild steel corrosion.

In person Oral Presentation at **ACS Spring Conference** “Crossroads of Chemistry”, Indianapolis, USA. 26-30 March 2023. <https://doi.org/10.1021/scimeetings.3c00082>

3. **Arshad, Z.**, Baig, N, Ali, S. A. Synthesis of a zwitterionic polymer for fabrication of PVDF membranes to enhance their performance for efficient separation of oil-in-water nano-emulsions.

In person Poster Presentation at **ACS Spring Conference** “Crossroads of Chemistry”, Indianapolis, USA. 26-30 March 2023. <https://doi.org/10.1021/scimeetings.3c00083>