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Traditio et Innovatio

**Synthesis and Incorporation of Poly(Imidazolium)-based
Ionic Liquids in Non-isocyanate Polyurethane Networks
and Sustainable Hydrogel Systems**

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Dedication

Dedicated to those who wish their homeland was a place to stay.

“

“When a man has learned how to remain alone with his suffering, how to overcome his longing to flee, then he has little left to learn.”

— Albert Camus (1913 - 1960)

Table of Contents

Table of Contents.....	I
Abstract.....	III
Zusammenfassung	IV
1. Introduction.....	1
1.1 Non-isocyanate polyurethane (NIPU)	2
1.2 Polyionic liquids.....	10
1.3 Hydrogel.....	16
1.3.1 Poly(succinimide) hydrogels	17
1.3.2 Chitosan-based hydrogels	21
2. Research objectives.....	26
3. Materials and methods	29
3.1 Chemicals	29
3.2 Experimental methods	30
3.2.1 Synthesis of cyclic carbonated compounds	30
3.2.2 Synthesis of poly imidazolium-based ionic liquids (PIMs).....	32
3.2.3 Synthesis of non-isocyanate polyurethanes (NIPUs)	40
3.2.4 Synthesis of polysuccinimide (PSI).....	42
3.2.5 Synthesis of PSI-based hydrogel	43
3.2.6 Synthesis of Chitosan-based hydrogel.....	44
3.3 Characterization techniques	45
3.3.1 Fourier transform infrared spectroscopy (FT-IR)	45
3.3.2 Nuclear magnetic resonance spectroscopy (NMR)	46
3.3.3 Gel permeation chromatography (GPC)	46
3.3.4 Epoxy content determination	47
3.3.5 High-resolution mass spectroscopy (HRMS)	47
3.3.6 Rheological analysis.....	48
4. Results and discussion	49

4.1	Cyclic carbonated compounds	49
4.2	Poly imidazolium-based ionic liquids (PIMs)	62
4.3	Non-isocyanate polyurethanes (NIPUs).....	74
4.4	Hydrogels	80
4.4.1	PSI Hydrogel	80
4.4.2	Chitosan-based hydrogel	84
5.	Summary	88
6.	Outlook	91
7.	References	92
	Appendix.....	104
	Curriculum Vitae.....	127
	Eidesstattliche Erklärung.....	128

Abstract

Polymer and polyurethane technologies are critical in sustainable chemistry, necessitating the exploration of non-isocyanate alternatives to traditional polyurethanes (PUs). Green chemistry principles advocate for the design of processes that minimize waste and reduce environmental impact, making it imperative to identify sustainable approaches in polymer synthesis.

This work explores non-isocyanate polyurethane (NIPU) synthesis using renewable resources. Cyclic carbonated oils and epoxysiloxane compounds were synthesized *via* batch processing and autoclave reactions. A diverse array of amino-terminated poly(imidazolium)-based ionic liquids (PIMs) was developed *via* the Debus-Radziszewski reaction, employing various diamines, dicarbonyls, aldehydes, and acids. These PIMs functioned dual roles as curing agents for non-isocyanate polyurethanes (NIPUs) as well as crosslinkers in hydrogel formulations. The NIPUs were characterized for their molecular weight distribution and viscoelastic properties, essential for applications in coatings, adhesives, and biomedical devices. Furthermore, the research investigated two distinct types of PIM-crosslinked hydrogels: polysuccinimide (PSI) and chitosan-based hydrogels. Comprehensive analyses, including swelling behavior, antibacterial assessments, dye adsorption capacity, and rheological properties such as amplitude sweep and creep recovery, were conducted to evaluate the performance of these novel materials.

Zusammenfassung

Polymer- und Polyurethan-Technologien sind entscheidend für die nachhaltige Chemie, was die Erforschung von nicht-isocyanatbasierten Alternativen zu traditionellen Polyurethanen (PUs) erforderlich macht. Die Prinzipien der grünen Chemie plädieren für die Gestaltung von Prozessen, die Abfall minimieren und die Umweltauswirkungen reduzieren, wodurch es unerlässlich wird, nachhaltige Ansätze in der Polymer-Synthese zu identifizieren.

Dieser Arbeit untersucht die Synthese von nicht-isocyanatbasierten Polyurethanen (NIPUs) unter Verwendung erneuerbarer Ressourcen. Zyklisch karbonisierte Öle und Epoxysiloxan-Verbindungen wurden durch Batch-Verfahren und Autoklav-Reaktionen synthetisiert. Eine vielfältige Reihe von aminoterminierten poly(imidazolium)-basierten ionischen Flüssigkeiten (PIMs) wurde über die Debus-Radziszewski-Reaktion entwickelt, wobei verschiedene Diamine, Dicarbonyle, Aldehyde und Säuren verwendet wurden. Diese PIMs erfüllten eine doppelte Rolle als Härter für nicht-isocyanatbasierte Polyurethane (NIPUs) sowie als Vernetzer in Hydrogel-Formulierungen. Die NIPUs wurden hinsichtlich ihrer Molekulargewichtsverteilung und viskoelastischen Eigenschaften charakterisiert, die für Anwendungen in Beschichtungen, Klebstoffen und biomedizinischen Geräten von wesentlicher Bedeutung sind. Darüber hinaus untersuchte die Forschung zwei verschiedene Typen von PIM-vernetzten Hydrogelen: Polysuccinimid (PSI) und chitosanbasierte Hydrogelen. Umfassende Analysen, einschließlich Schwellverhalten, antibakterieller Bewertungen, Farbstoffadsorptionskapazität und rheologischen Eigenschaften wie Amplitudensweep und Kriechregeneration, wurden durchgeführt, um die Leistung dieser neuartigen Materialien zu bewerten.

1. Introduction

Polymers are universal materials that play a fundamental role in the daily life of the modern human. They consist of macromolecules formed from the covalent bonding of many repeating units called monomers. These materials include a variety of naturally occurring products (e.g., proteins, cellulose) and synthetic forms (e.g., nylons, polyesters). Their diversity is due to the fact that they can be engineered with a wide range of properties, which enables them to be used in a varied myriad of application. Some key characteristics of polymers include:

- **Strength and durability:** Polymers can be incredibly strong and resistant to wear and tear.
- **Flexibility and elasticity:** Some polymers can stretch and deform without breaking. This makes them ideal for applications such as rubber bands.
- **Electrical properties:** depending on their structure, polymers can be insulating, conductive, or semi-conductive.
- **Chemical resistance:** Certain polymers are corrosion-resistant and resistant to harsh chemicals.
- **Thermal properties:** Polymers can have different melting points and thermal stability, suiting diverse temperature applications.

Due to the remarkable diversity of polymers available, their classification encompasses a wide range of parameters that take into account different properties. These parameters include the structure of the polymer (linear, branched, crosslinked, and networked), functionality (e.g., biocompatible, conductive), origin (natural, synthetic), and more.¹

To gain a deeper understanding, three specific and widely used types of polymers are explored in this section: **polyurethanes**, **poly(ionic liquid)s**, and **hydrogels**. Briefly, during this research, a series of amino-terminated poly(imidazolium)-based ionic liquids were synthesized by the Debus-Radziszewski multicomponent reaction and applied for two major purposes:

- Curing agents in non-isocyanate polyurethanes (NIPUs)**
- Crosslinkers in the preparation of hydrogels**

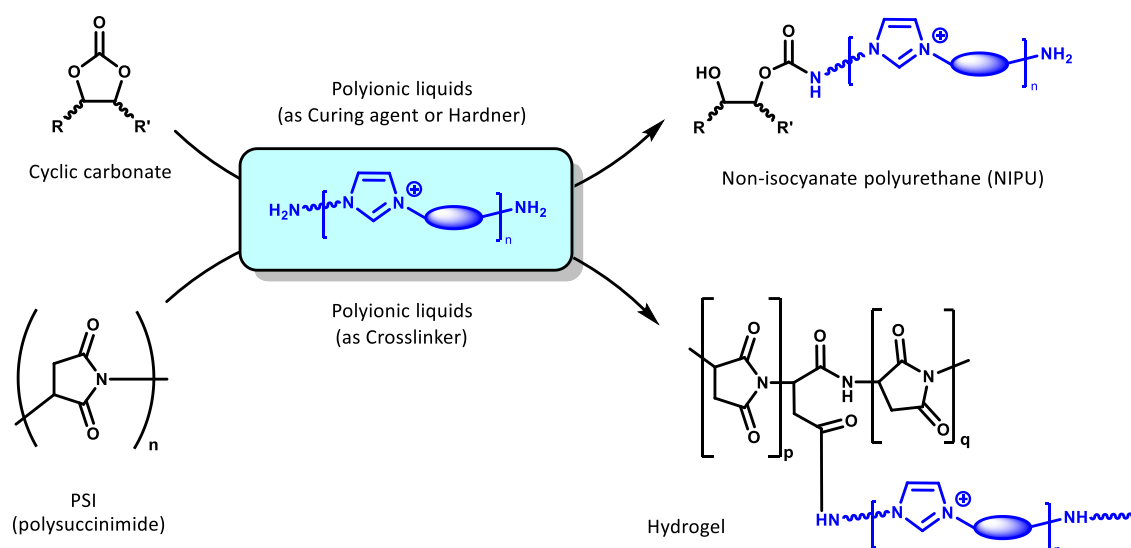


Figure 1.1 Schematic representation of non-isocyanate polyurethane synthesis (top) and the preparation of PSI-hydrogel (bottom) *via* utilization of amino-terminated poly(imidazolium)-based ionic liquids (counteranions are not shown in the schematic drawing for reasons of image clarity).

1.1 Non-isocyanate polyurethane (NIPU)

Among the various types of polymers, polyurethanes (PU) have found significant use for several compelling reasons. This widespread use of PUs is due to their diverse range of applications, which include soft and rigid foams, thermoplastics, elastomers, adhesives, coatings, sealants, and fibers. These versatile forms of polyurethane find immense use in industries such as construction, automotive, coatings, marine, biomedical, apparel, wood composites, household appliances, flooring, and packaging.²⁻³

Conventional PUs are synthesized by the step-growth polymerization of di- or polyols (soft segments) with di- or polyisocyanates (hard segments), which was first developed by OTTO BAYER (**Figure 1.2**).⁴ Considering that the primary starting materials for classic PUs are mainly derived from petroleum, and due to their finite nature, as well as the global urgency to reduce reliance on fossil resources, the search for alternative materials is critically important. Moreover, to comply with green chemistry principles and develop more sustainable synthesis methods, it is

also crucial to pursue alternative approaches, as conventional PUs present many risks to the environment and human health.⁵

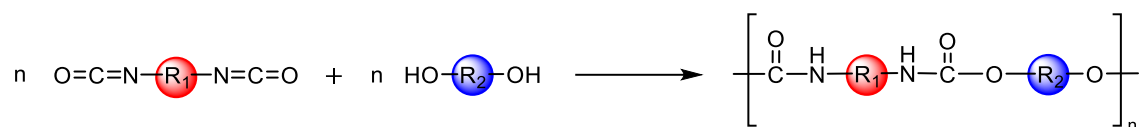


Figure 1.2 Conventional polyurethane preparation *via* the polyaddition of diols and diisocyanates.

A significant concern associated with conventional PU production lies in the inherent toxicity of isocyanates which have been classified as CMR; carcinogenic, mutagenic, and reprotoxic. Exposure to isocyanates can cause significant health problems, including skin irritation, respiratory tract (lung) issues, and eye. These acute effects can lead to more serious consequences such as occupational asthma and hypersensitivity pneumonitis with repeated or high-level Inhalation.⁶⁻⁷ In addition, the environmental impact of isocyanate emissions from PU production cannot be overlooked, as they can damage ecosystems and contribute to air pollution.⁸⁻⁹ Furthermore, the utilization of phosgene gas in the large-scale synthesis of many commercial isocyanates poses another major challenge to conventional PU production. Phosgene is classified as a highly toxic and lethal compound and poses a severe threat to human health and environmental safety in the event of accidental releases or leaks. Strict regulations and rigorous safety protocols are necessary throughout the production process to minimize the risk of phosgene exposure to workers and the surrounding environment. This intrinsic danger associated with phosgene necessitates the development of alternative, greener routes for sustainable PU synthesis.¹⁰ Beyond the inherent toxicity of the primary precursors in conventional PU production, concerns extend to certain additives employed to enhance reaction efficiency. Historically, organocatalysts, exemplified by dibutyltin dilaurate (DBTDL), were widely used to accelerate the crucial gelation reaction between polyols and isocyanates.¹¹ However, extensive research has shown that exposure to organotins has adverse health effects, such as endocrine disruption, immunotoxicity, and neurotoxicity. Given these risks, regulatory authorities have imposed restrictions on the use of these substances. Accordingly, the PU industry has actively sought to develop and implement safer, more environmentally friendly

alternatives as a result of the REACH¹ regulation. This continuous shift towards the principles of green chemistry is essential for the sustainability and long-term profitability of PU production.¹²⁻¹³

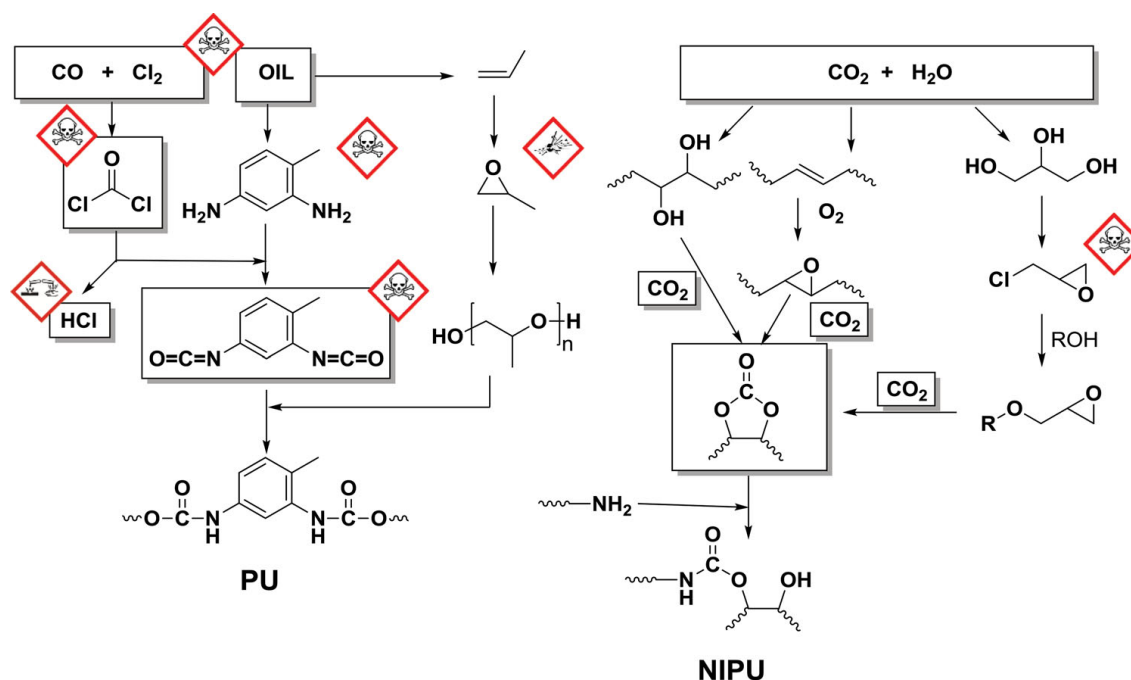


Figure 1.3 Synthesis routes for conventional polyurethane (left) versus non-isocyanate polyurethane (right), (taken from: BLATTMANN *et al.*, 2014).¹⁴

Non-isocyanate polyurethane (NIPU)—as one promising alternative strategy—has gained widespread attention due to its green aspects. This growing enthusiasm is reflected in the recent reviews dedicated to NIPU synthesis and its diverse applications.¹⁴⁻¹⁹ As depicted in **Figure 1.3**, the left side shows the classical synthesis of conventional PU through the reaction of toluene diisocyanate (TDI) with polyol. These starting materials are derived from petroleum-oil sources, and the production of diisocyanates involves the use of highly poisonous compounds such as phosgene. In contrast, the right side illustrates the synthesis of NIPU, which offers a safer and more environmentally friendly alternative. The NIPU synthesis route does not involve the use of isocyanates or phosgene, instead relying on the

¹ Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) is an EU regulation to protect human health and the environment from the risks that can be posed by chemicals.

reaction of cyclic carbonates with amines to form hydroxyurethane linkages. Cyclic carbonates can be derived from CO₂ reduction reactions, offering the advantage of using carbon dioxide as a readily available and renewable building block. Amines, on the other hand, can be obtained from various natural and synthetic sources. Additionally, the NIPU synthesis pathway avoids the generation of hazardous byproducts associated with conventional PU production, such as hydrogen chloride (HCl).

The history of NIPU synthesis dates back to 1957 when the pioneering work of DYER and SCOTT involved reacting amines with ethylene carbonates to generate the urethane linkage.²⁰ This initial discovery paved the way for significant advancements in NIPU synthesis techniques, which have become considerably more versatile. Over the decades, numerous research groups have explored alternative methods for producing NIPUs, greatly expanding the field's scope and versatility. As summarized in **Figure 1.4**, there are four main approaches to the synthesis of NIPUs including: **polycondensation**, **rearrangement**, **ring-opening polymerizations**, and **step-growth polyaddition**.²¹

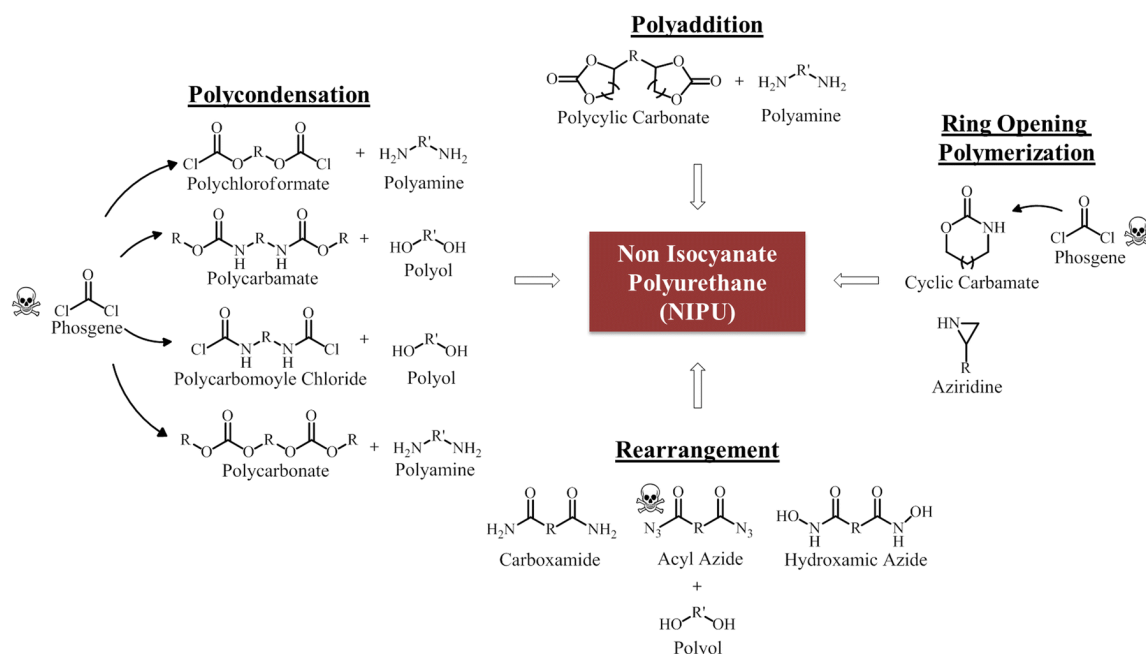


Figure 1.4 Main synthesis routes of NIPU synthesis (Source: RAYUNG *et al.*, 2024).²²

NIPU synthesis via **polycondensation** offers several reaction routes, involving the condensation of precursors such as polychloroformates, polycarbamates, polycarbamoyl chlorides, and polycarbonates with polyamines or polyols. However, these precursors are often derived from toxic phosgene or its derivatives, limiting the environmental advantages over conventional isocyanate-based polyurethanes. Furthermore, this route generates undesirable side products like alcohols or HCl, posing challenges for industrial applications.^{17, 23-24}

Rearrangement reactions can also be employed, generating isocyanates in situ for polyurethane synthesis. However, these routes still involve the use of hazardous reactants like azides, carboxamides, or hydroxamic azides, requiring careful handling and limiting their overall sustainability.²⁵

Another method for NIPU synthesis is **ring-opening polymerization**, utilizing cyclic monomers like aziridines or cyclic carbamates. Although this process avoids side-product formation, the precursors are frequently derived from phosgene or involve toxic compounds, limiting its sustainability.²⁶

The **step-growth polyaddition** route is the most promising and preferred approach for NIPU synthesis, involving the reaction between cyclic carbonates and amines. This method offers several advantages, including the flexibility to choose from a wide range of reactive compounds, even natural and renewable resources, enabling tailored properties for specific applications. Additionally, the polyaddition of cyclic carbonates and diamines or polyamines is extensively studied for its potential to produce NIPUs with desirable properties. From an industrial perspective, this route is economically favorable as it eliminates the need for solvents and catalysts, as well as avoids the generation of by-products.

Cyclic carbonates have received considerable attention as primary agents in polyaddition reactions with amine components to produce non-isocyanate polyurethane (NIPU) compounds. Their attractive properties, including relative non-toxicity, low volatility, and thermal and mechanical stability, make them highly desirable. Likewise, the diversity of cyclic carbonates has caused their application in various fields. They act as green, polar aprotic solvents in numerous chemical reactions, offering a more environmentally friendly alternative to ordinary organic solvents.²⁷ In polymer science, cyclic carbonates serve as precursors for novel

materials with tailored properties.²⁸ Their electrochemical stability and high dielectric constant make them suitable components in battery electrolytes, helping to design more efficient energy storage devices.²⁹ Moreover, their lubricating performance is found in the industry to help reduce friction and wear in mechanical systems.³⁰

Several techniques exist for synthesizing cyclic carbonate compounds. Among them, the cycloaddition of CO₂ and epoxides to produce cyclic carbonates is considered one of the most promising CO₂ conversion routes due to its 100% atom economy. This approach aligns with the principles of green chemistry and supports carbon capture and utilization (CCU) technologies.³¹

The catalytic process of converting CO₂ into cyclic carbonates has been extensively studied, and various catalytic systems are being explored to optimize yield and selectivity.³² These include organocatalysts,³³ ionic liquids,³⁴⁻³⁵ polyoxometalates,³⁶ etc. Notably, quaternary ammonium halides such as tetrabutylammonium bromide (TBAB), have shown particular effectiveness in facilitating oxirane ring opening and subsequent CO₂ fixation.³⁷

As illustrated in **Figure 1.5**, the proposed mechanism for CO₂ cycloaddition to epoxides catalyzed by an ammonium halide typically proceeds through the following steps:

- i. **Epoxide activation:** The reaction is initiated by the nucleophilic attack of the halide ion on the less substituted carbon of the epoxide ring. This results in ring-opening of the epoxide.
- ii. **CO₂ insertion:** The opened epoxide intermediate then reacts with CO₂, inserting it into the structure to form a linear carbonate species.
- iii. **Ring closure:** Finally, an intramolecular nucleophilic displacement occurs, where the oxygen from the original epoxide attacks the carbonyl carbon, displacing the halide. This step results in the formation of the cyclic carbonate product and regeneration of the halide catalyst.

This mechanism highlights the dual role of the ammonium halide: the halide anion acts as a nucleophile to activate the epoxide and initiate the reaction, while the

ammonium cation likely serves as a phase-transfer agent, facilitating the solubility and transport of reactants in the reaction medium.

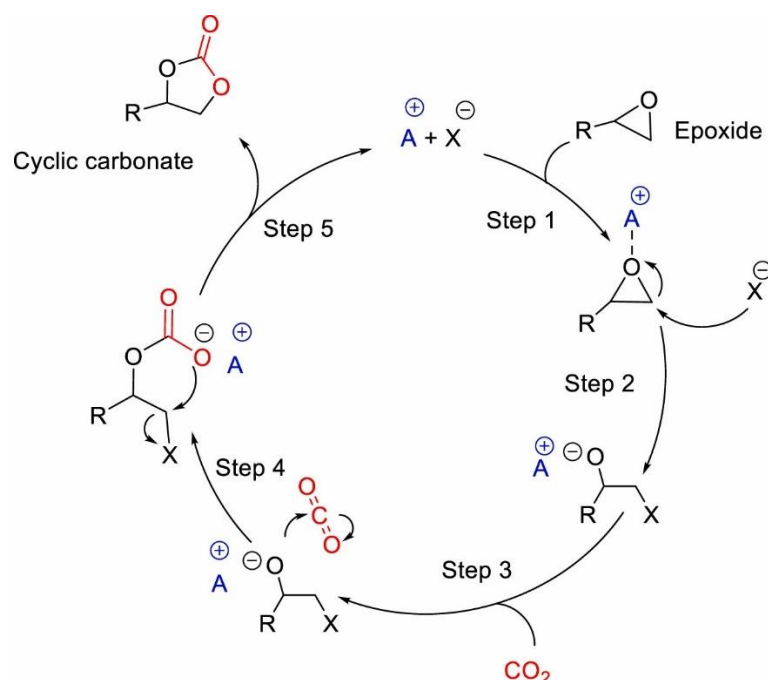


Figure 1.5 General mechanism of CO₂ cycloaddition to an epoxide (taken from: REHMAN *et al.*, 2021).³⁸

In recent years, there has been a growing emphasis on utilizing renewable resources and cost-effective starting materials for cyclic carbonate synthesis. Terpenes and plant-based oils, such as soybean, linseed, castor, and sunflower oils, have been investigated as potential precursors for cyclic carbonates.³⁹⁻⁴⁸ These bio-based feedstocks offer several advantages, including sustainability, biodegradability, and a reduced carbon footprint compared to petroleum-derived alternatives.

The polymerization of cyclic carbonates with amines to produce NIPUs has also been extensively studied, revealing unique reaction kinetics and mechanisms. The ring-opening of cyclic carbonates by amines proceeds through a nucleophilic addition mechanism, resulting in the formation of hydroxyurethane linkages. This reaction can be tailored by adjusting factors such as the structure of the cyclic carbonate, amine type, and the reaction conditions.⁴⁹

Recent advancements in this field include the development of renewable resource-based NIPUs that have revealed promising properties, such as improved thermal

and chemical stability, controlled biodegradability, and enhanced mechanical strength. Some of these materials also exhibit self-healing capabilities and reprocessability. Consequently, a wide spectrum of applications has been reported for NIPUs, including foams,⁵⁰ adhesives and coatings,⁵¹⁻⁵² flexible sensors,⁵³ recyclable,⁴⁴ reprocessable,⁴⁸ and self-healable networks.⁵⁴

Furthermore, many researchers have employed NIPU networks in biological applications. For instance, HAMID YEGANEH's research group has investigated the use of NIPU networks as antibacterial coatings and wound dressing scaffolds.⁵⁵⁻⁵⁹

In conclusion, NIPU compounds, especially those derived from bio-based sources, represent a promising class of materials with significant potential in sustainable chemistry and materials science. Ongoing research in this field continues to uncover new applications and improve existing processes, paving the way for innovative solutions to global challenges in materials, biomedical applications, and environmental sustainability.

1.2 Polyionic liquids

Polyionic liquids (PILs) are another promising class of polymeric materials derived via the polymerization of ionic liquid monomers. They integrate the remarkable property profiles of ionic liquids (ILs) with the flexibility of macromolecular polymers, offering novel characteristics and functions that are appropriate for a wide range of applications.⁶⁰

ILs themselves, as low-melting-point salts, possess unique properties and have been identified as “green” or “designable” solvents.⁶¹ They have occupied a specific place in sustainable chemistry and material science. However, the origin of ILs can be traced back to the early 20th century when PAUL WALDEN reported the first observation of molten salts that possess unexpectedly low melting points of 13-14 °C through the neutralization of ethylamine with concentrated nitric acid to obtain ethylammonium nitrate, $[\text{EtNH}_3][\text{NO}_3]$.⁶² Nevertheless, the initial report of these novel compounds did not gain much attention at that time, but it is now acknowledged and recognized as the foundation upon which ionic liquids research was built.⁶³

Despite its discovery, the potential of ILs remained largely unexplored for several decades. It was not until the turn of the 21st century that the field of ILs gained significant attention. This increasing interest was driven by the unique properties exhibited by ILs, such as high thermal and (electro)chemical stability, negligible vapor pressure, ionic conductivity, non-flammability, and solvation capabilities.⁶⁴ These noteworthy characteristics have enabled the widespread application of ILs across various fields, including catalysis, separations, electrochemistry, materials science, and biomedical applications.⁶⁵⁻⁶⁶

On the other hand, the initial discovery of PILs can be attributed to the 1970s, when the free radical polymerization of vinylimidazolium ionic liquids gained attention.⁶⁷ However, the term “poly(ionic liquid)” to explicitly describe polymers derived from ionic liquids was first coined by HIROYUKI OHNO *et al.*⁶⁸

In addition to inheriting the advantages of ILs, PILs can combine and bring the beneficial properties of polymers such as structural versatility and mechanical robustness.⁶⁹ This synergistic combination allows for the development of materials

with tailored properties and functionalities. Furthermore, compared to ILs, poly(ionic liquid)s offer significant benefits, including superior mechanical strength, enhanced processability, increased durability, and greater spatial control over the distribution of ionic species, making them desirable for a wide range of applications.⁷⁰⁻⁷²

There are several methods to categorize PILs, but one of the most common approaches is based on the nature of the ionic species present in their structures. Accordingly, PILs can be classified into three major groups: cationic, anionic, and zwitterionic.⁷³

- i. **Cationic PILs:** These PILs contain cationic groups, such as imidazolium, pyridinium, ammonium, or phosphonium, tethered to the polymeric backbone. The counterions associated with these cationic groups can be various anions, including halides, hexafluoro phosphate, tetrafluoro borate, or bis(trifluoromethanesulfonyl) imide.
- ii. **Anionic PILs:** In these PILs, anionic groups are incorporated into the polymer chain. These anionic groups can be sulfonate, carboxylate, phosphonate, or other negatively charged moieties.
- iii. **Zwitterionic PILs:** Zwitterionic PILs possess both cationic and anionic groups within the same repeating monomers, resulting in an overall neutral charge.

Besides, PILs can be synthesized through various polymerization techniques, such as step-growth polymerization, free radical polymerization, ring-opening polymerization, post-polymerization modification, etc.⁷⁴

Among these approaches, the Debus-Radziszewski reaction is a crucial step-growth polymerization method that has been extensively employed for the synthesis of poly(imidazolium)-based PILs. This reaction involves the condensation of an amine with carbonyl and dicarbonyl components in the presence of an acid catalyst, yielding imidazolium-based polymers with ionic liquid characteristics.⁷⁵⁻⁷⁶

The Debus-Radziszewski reaction has a rich history spanning over a century. It was first reported by HEINRICH DEBUS in 1858, who synthesized imidazole derivatives by

reacting glyoxal with ammonia and formaldehyde.⁷⁷ Later, in 1882, BRONISŁAW RADZISZEWSKI developed this reaction with different precursors.⁷⁸ These pioneering works laid the foundation for the efficient Debus-Radziszewski reaction.

Moreover, the experiment conducted by DEBUS was the first reported reaction to obtain imidazole, which was initially named glyoxaline.⁷⁷ However, nowadays several synthetic routes have been identified to obtain imidazole and its derivatives.⁷⁹⁻⁸⁰ Due to their unique properties, imidazoles have been utilized in a diverse range of applications, particularly in pharmaceutical and biological fields. Imidazole derivatives exhibit a wide spectrum of medicinal activities, including anticancer, antifungal, antibacterial, antimicrobial, antiviral, antioxidant, and anti-inflammatory agents.⁸¹⁻⁸²

As illustrated in **Figure 1.6**, during the condensation reaction for imidazole synthesis via the classic Debus-Radziszewski reaction, the dicarbonyl component first reacts with ammonia to form a diimine intermediate. Followingly, the diimine undergoes a cyclocondensation with the aldehyde, leading to the formation of the imidazole ring.⁸³

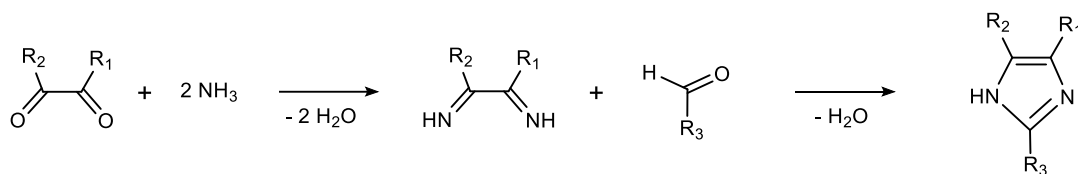


Figure 1.6 General reaction scheme for the synthesis of imidazoles via the classic Debus-Radziszewski reaction (adapted from ⁸³).

Despite its significance, the traditional Debus-Radziszewski reaction suffers from several drawbacks that limit its practical utility. These limitations include the requirement for harsh reaction conditions, the use of hazardous chemicals, the need for costly acid catalysts, and complex work-up and purification procedures. Additionally, the occurrence of side reactions during the synthesis can lead to decreased yields of desired products, limiting the overall efficiency of the classic Debus-Radziszewski reaction.⁸⁴

To address these challenges, researchers have modified and expanded the scope of this reaction in various aspects. One modification involves the use of aqueous media under ambient conditions, eliminating the need for elevated temperatures and hazardous solvents. Likewise, these modifications often produce only water as a by-product, improving the reaction's effectiveness, and obtaining the desired product in higher yields, in line with green and sustainable chemistry by reducing the need for intermediate purification steps. Furthermore, one-pot procedures have been developed to improve the scalability of imidazolium derivative synthesis.⁸⁵

Another modification involves replacing ammonia with a primary amine, enabling the synthesis of N-substituted imidazoles. By employing a wide variety of precursors including diamines, aldehydes, dicarbonyl compounds (e.g., glyoxal), and even various acid catalysts during this multicomponent reaction, researchers can access a diverse range of imidazole-based products. Consequently, the Debus-Radziszewski reaction has evolved into a powerful tool for the synthesis of imidazole derivatives, with researchers exploring diverse combinations of starting materials to access a broad range of imidazole-based compounds. The ability to tune the reaction conditions and precursors has significantly expanded the applications of this reaction in various fields, such as organic synthesis, materials science, and related areas.⁸⁶⁻⁸⁷

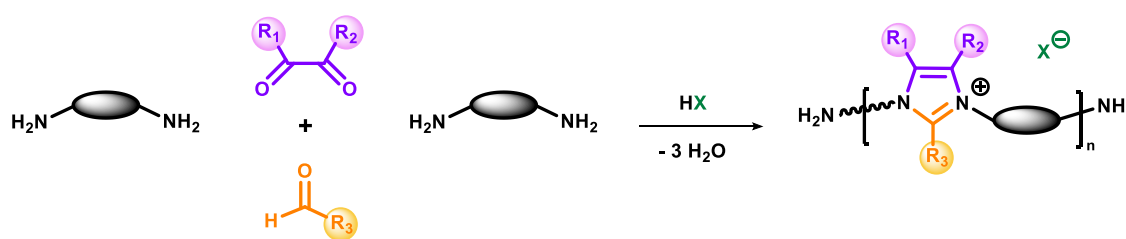


Figure 1.7 General reaction scheme of modified Debus-Radziszewski reaction (adapted from ⁸⁸).

In recent years, numerous researchers have utilized this modified Debus-Radziszewski reaction, as evidenced by its appearance in many research articles, books, and patents.⁸⁴ As noted in research articles, the classic version of this reaction was practically “forgotten” for many years, but due to modifications to the Debus-Radziszewski reaction, its usage has gained significant attention.⁸⁹ For instance,

MARKUS ANTONIETTI and his research group have employed this reaction to form imidazolium-based building blocks from biomass molecules, enabling the synthesis of renewable ionic liquids and materials.⁹⁰⁻⁹¹ Furthermore, they have developed highly efficient methods for transferring amino groups to imidazolium entities, facilitating polymer coupling and cross-linking.^{83, 89} They have also explored the creation of main-chain poly(imidazolium) polymers through one-pot synthesis, which can be used as precursors for nitrogen-doped carbon materials.⁹²

By replacing acetic acid with hydrochloric acid in the Debus-Radziszewski reaction, researchers have created broad-spectrum poly(imidazolium) antibiotics, which have demonstrated potent antibacterial activities against a range of pathogens. These poly(imidazolium) compounds have shown efficiency in both *in-vitro* and *in-vivo* models, effectively reducing bacterial loads and improving survival rates in infected mice.⁹³ Additionally, biodegradable poly(imidazolium) and oligoimidazoliums synthesized through this modified reaction offer the dual benefits of antimicrobial activity and environmental sustainability, making them promising candidates for various applications in healthcare and beyond.⁹⁴⁻⁹⁵

Besides, JEAN-PIERRE LINDNER and his colleagues at BASF SE have extensively studied the synthesis of poly(imidazolium)-based ionic liquids using the modified Debus-Radziszewski reaction.⁹⁶⁻⁹⁷ Their research has focused on understanding how various parameters, such as reaction time, temperature, and the molar ratios of starting materials, influence the molecular weight of the resulting poly(imidazolium) salts. By experimenting with different diamines and varying the molar ratios of the reactants, they have produced versatile PIMs with a wide range of molecular weights and properties. Their findings indicate that nonstoichiometric ratios of starting materials can yield high molecular weight PIMs, highlighting the versatility and efficiency of the poly-Radziszewski reaction in producing imidazolium-containing polymers with tunable properties for various applications.⁸⁸

Other research groups have employed the modified Debus-Radziszewski reaction for various purposes, such as the preparation of ionogels,⁹⁸ porous membranes,⁹⁹⁻¹⁰⁰ including specific membranes for CO₂ capture,¹⁰¹⁻¹⁰² and siloxane-based porous membranes.¹⁰³ Additionally, the reaction has been used in the preparation of

sustainable imidazolium-crosslinked chitosan aerogels,¹⁰⁴ and hydrogels.¹⁰⁵ The utilization of Debus-Radziszewski reaction to prepare chitosan-based hydrogel is discussed further in section **1.3.2**.

1.3 Hydrogel

Hydrogels are another fascinating class of polymeric materials that have attracted considerable attention in various fields, particularly in chemistry, materials science, and biotechnology.¹⁰⁶⁻¹⁰⁷ These unique three-dimensional (3D) networks, can be formed by crosslinking hydrophilic monomers, that are capable of absorbing and retaining massive amounts of water or biological fluids within their structure.¹⁰⁸⁻¹⁰⁹ In addition to their excellent swelling behavior, hydrogels have several remarkable properties as well as versatile methods of production that make them an appealing material for a variety of applications. Their ability to mimic the extracellular matrix, combined with their biocompatibility and tunable mechanical properties, has made them invaluable in the field of regenerative medicine, where they facilitate the growth and integration of new tissues.¹¹⁰⁻¹¹² Therefore, hydrogels have found widespread use in biomedical engineering, serving as scaffolds for tissue engineering,¹¹³ contact lenses,¹¹⁴ wound healing,¹¹⁵ biosensors,¹¹⁶ artificial organs and implants,¹¹⁷ cartilage fillers,¹¹⁸ 3D printing,¹¹⁹ and even as biocatalyst via enzyme immobilization in polymerized ionic liquids-based hydrogels.¹²⁰ Additionally, hydrogels have been extensively explored for their potential in controlled drug release, where their swelling and degradation characteristics can be adjusted to achieve targeted and sustained drug delivery.¹²¹

For over two decades, the research group led by Professor Dr. UDO KRAGL at the University of Rostock has working on hydrogel compounds, with a particular focus on their applications and the development of polymerized ionic liquid (PIL) based hydrogels.¹²² Their work has significantly contributed to the field of materials science and biotechnology.¹²³⁻¹²⁵

There are various approaches employed in the classification of hydrogels, and one of these methods involves categorizing them based on their composition and structure. Consequently, hydrogels can be classified into three major categories: **natural**, **synthetic**, and **hybrid** hydrogels. **Natural** hydrogels, such as those based on polysaccharides (e.g., chitosan) or proteins (e.g., collagen, gelatin), offer inherent biocompatibility and often mimic the native extracellular matrix. **Synthetic** hydrogels, on the other hand, are typically composed of polymers like polyethylene glycol (PEG) or polyacrylic acid, can be tailored to possess specific physicochemical

properties and functionalities, allowing for greater control over their behavior and properties. **Hybrid** hydrogels combine the advantages of both natural and synthetic components, often resulting in enhanced performance, versatility, and biological functionality.¹²⁶

The versatility of hydrogels is further amplified by their tunable properties, which can be tailored through various fabrication methods and crosslinking strategies.¹²⁷ The degree of crosslinking, the nature of the polymer chains, and the incorporation of functional groups can all contribute to the hydrogel's swelling behavior, mechanical strength, and responsiveness to environmental stimuli such as pH, temperature, and ionic strength.¹²⁸

This dissertation will focus on two distinct types of hydrogels: **polysuccinimide / polyaspartic acid (PSI/PASP)** hydrogels and **chitosan-based** hydrogels. PSI/PASP hydrogels are synthetic hydrogels that can be readily functionalized and have shown fascinating in biomedical applications.¹²⁹ Chitosan-based hydrogels, derived from the natural biopolymer chitin, exhibit excellent biocompatibility, biodegradability, and antimicrobial properties, making them attractive for wound healing, tissue engineering, and pharmaceutical applications.¹³⁰

1.3.1 Poly(succinimide) hydrogels

Polyaspartic acid (PASP), a synthetic anionic poly(amino acid) that mimics the peptide bonds found in proteins, has attracted significant interest due to its biocompatibility, biodegradability, and diverse applications across various fields. Its unique advantage lies in its amine-reactive anhydride precursor, polysuccinimide (PSI) which facilitates the straightforward modification of PASP derivatives. This adaptability provides extensive opportunities for the design and development of innovative biomaterials with specific functional properties.

There are two primary methods for synthesizing PSI, as illustrated in **Figure 1.8**. The first method (a) involves the thermal polycondensation of aspartic acid, utilizing phosphoric acid as a catalyst at high temperatures ($>160\text{ }^{\circ}\text{C}$).¹³¹ The second method employs the polymerization of a maleamic acid intermediate, which is formed from the reaction of maleic anhydride—or maleic acid—with a nitrogen source such as urea or ammonia (NH_3).¹³²⁻¹³³

Following its synthesis, PSI can undergo a ring-opening reaction to form poly(aspartamide) or poly(aspartic acid) through either amidation with primary amines or hydrolysis. These reactions lead to the formation of products that exhibit a mix of α and β configurations in their final structure. This configurational diversity in PASP structures enhances the potential for tailoring material properties to meet specific application needs, further underscoring the versatility and utility of PASP in the development of advanced biomaterials.¹³⁴⁻¹³⁵

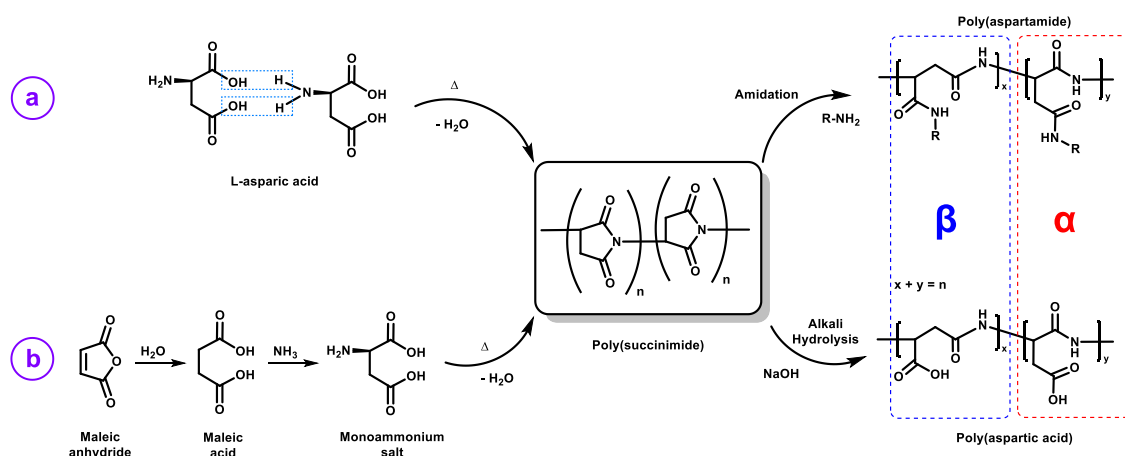


Figure 1.8 Schematic representations of polysuccinimide (PSI) synthesis and its derivatives, (a) through thermal polycondensation of aspartic acid (b) *via* polymerization of maleamic acid intermediate. Subsequently, PSI can be ring-opened to yield poly(aspartamide) or poly(aspartic acid) through an amidation reaction with primary amines or a hydrolysis reaction (adapted from ¹³⁶).

In addition, hydrogels based on PSI/PASP also garnered considerable attention due to their unique properties and potential applications.¹³⁷ These hydrogels are particularly noted for their simple succinimide ring-opening reactions facilitated by primary amines, which allow for the incorporation of various diamines. The high water content, biocompatibility, stimuli-responsive, and environmentally friendly degradation products of PSI/PASP hydrogels make them ideal for a range of biomedical applications, including drug and DNA delivery carriers, tissue engineering scaffolds, bioimaging, and wound dressings (**Figure 1.9**).¹³⁸

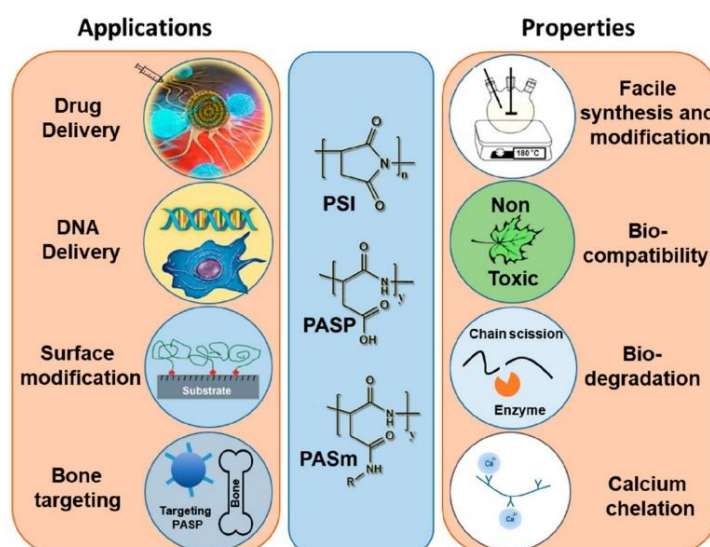


Figure 1.9 Overview of the properties and biomedical applications of Poly(aspartic acid) and its Derivatives (taken from: ADELNIA *et al.*, 2021).¹³⁶

Traditional methods for synthesizing PASP hydrogels often involve the use of organic solvents such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). However, recent advancements have led to a more environmentally friendly approach that avoids these solvents. This "green" synthesis method involves a combination of hydrolysis, modification, and in situ cross-linking, which not only results in hydrogels with improved properties but also reduces preparation costs. This innovative approach underscores the ongoing efforts to develop more sustainable and effective materials for a variety of applications.¹³⁹

The physical and chemical properties of PASP hydrogels can be finely tuned by altering the polymerization and cross-linking conditions, enhancing their utility in medical and environmental applications. These hydrogels can be engineered to respond to various stimuli, such as pH, temperature, and redox conditions, which broadens their applicability. Different cross-linking agents, particularly diamines, are used to achieve the desired properties and functionalities in these hydrogels. The development of PSI and PASP hydrogels represents a promising area of research, with potential breakthroughs in medical technologies and sustainable materials science. Their synthesis from naturally occurring amino acids and the ease of functionalization make these hydrogels an attractive option for future innovations.

Figure 1.10 depicts the preparation of PSI/PASP hydrogels in the presence of various diamines as cross-linking agents. The versatility of these hydrogels is highlighted by the use of a range of amines, including diamines, amino acids, and natural polyamines, which have been extensively studied and reported in the literature. For instance, GYENES *et al.* have explored the use of natural polyamines such as putrescine, spermidine, and spermine, as well as amino acid derivatives like lysine methyl ester and cystamine, as effective cross-linking agents in the formation of these hydrogels.¹⁴⁰ Additionally, dibutylamine (DBA) has been employed as an initiator of gelation, serving to activate the amine groups within the hydrogel network.¹²⁹ Moreover, GYARMATI *et al.* reported the synthesis of super-macroporous PASP hydrogels through the utilization 1,4-diaminobutane for crosslinking under cryogenic condition of DMSO.¹⁴¹

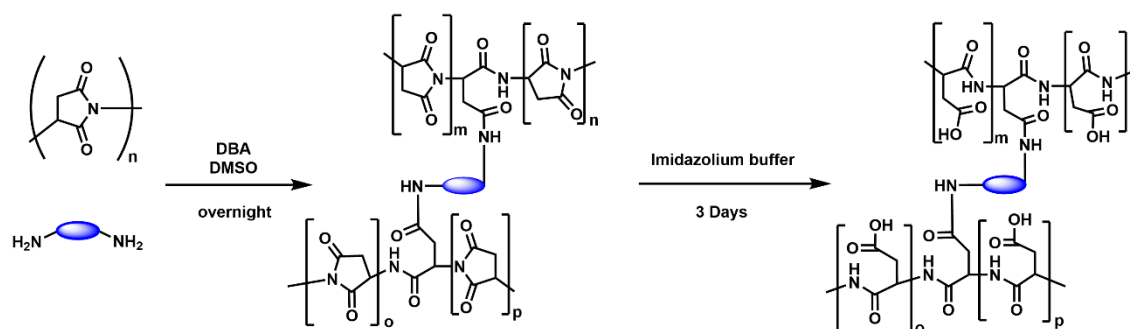


Figure 1.10 Synthesis of PSI/PASP hydrogel with diamines.

The choice of cross-linking agent significantly influences the mechanical properties, biocompatibility, and degradation rate of the hydrogels, making this aspect of hydrogel design crucial for specific applications. In the case of PSI/PASP hydrogels, the cross-linking process introduces functional groups that can undergo further reactions, providing additional sites for bioconjugation and drug loading. These characteristics make PSI/PASP hydrogels especially suitable for a range of biomedical applications.¹⁴²

The mechanism by which DBA initiates gelation involves the activation of amine groups on the polymer chain, facilitating the cross-linking process. This initiation step is critical for controlling the network structure of the hydrogel, which in turn affects its physical properties and functionality. The ability to fine-tune these

properties through the choice of cross-linking agents and initiators opens up new avenues for the development of advanced materials tailored for specific therapeutic and environmental applications.

On the other hand, as detailed in the previous section, a diverse range of amino-terminated poly-imidazolium based ionic liquids (PIMs) can be synthesized through the Debus-Radziszewski reaction. Accordingly, novel structures of PASP hydrogels have been developed by employing this synthetic pathway with amino-terminated PIMs. To the best of our knowledge, this marks the first instance of employing a combination of the Debus-Radziszewski reaction and PSI/PASP hydrogel formation to synthesize such compounds. Moreover, this study represents the pioneering effort of integrating charged moieties into PASP hydrogels, accomplished by the inherent ionic character of poly ionic liquids (PILs).

1.3.2 Chitosan-based hydrogels

Chitosan is a naturally occurring cationic polysaccharide derived from chitin, the second most abundant polysaccharide in nature after cellulose.¹⁴³ It is obtained through the deacetylation process of chitin, which is primarily found in the exoskeletons of crustaceans (such as crabs and shrimps), insects, and microorganisms.¹⁴⁴ The chitosan molecule is a copolymer composed of *N*-acetyl-D-glucosamine and D-glucosamine units. The degree of deacetylation (DD) in chitosan determines the molar percentage of glucosamine units within the polymer structure. It reflects the extent to which acetyl groups have been removed from chitin. This parameter significantly influences chitosan's physicochemical and biological properties, making it a crucial factor in determining the polymer's behavior and potential applications.

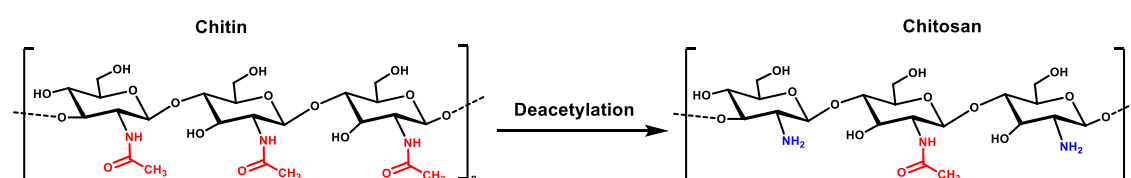


Figure 1.11 Schematic representation of the deacetylation reaction of chitin to obtain chitosan.

The unique properties of chitosan stem primarily from the presence of free amino groups ($-\text{NH}_2$) along its glucosidic backbone. These amino groups become protonated in dilute acidic solutions, transforming chitosan into a cationic polyelectrolyte with enhanced solubility. This cationic nature allows chitosan to interact with various biomolecules, including proteins and nucleic acids, making it a valuable tool in drug delivery and gene therapy applications.

Beyond its solubility, the amino and hydroxyl groups on chitosan offer versatile functionalities. The $-\text{OH}$ groups participate in non-covalent interactions like hydrogen bonding, while the $-\text{NH}_2$ groups can undergo covalent modifications through reductive amination or other reactions. This tunability allows for the introduction of specific functionalities onto the chitosan backbone, tailoring its properties for targeted applications.

In addition, biocompatibility, biodegradability, and low toxicity are crucial advantages of chitosan. In the human body, enzymes like lysozyme and chitosanases can degrade chitosan, minimizing long-term accumulation and potential toxicity. This biodegradability makes chitosan particularly attractive for biomedical applications such as drug delivery and tissue engineering.¹⁴⁵

The ability of chitosan to form hydrogels via crosslinking is an exciting area for its utilization. Functionalizing chitosan and creating hydrogels with self-healing properties, high elasticity, and responsive behavior has become a challenging yet captivating pursuit. Crosslinking techniques, either physical or chemical, create a three-dimensional network of chitosan chains, resulting in hydrogels with tunable properties like mechanical strength, swelling behavior, and degradation rate. These hydrogels can encapsulate various biomolecules, including drugs, cells, and growth factors, for controlled release and targeted delivery.¹⁴⁶⁻¹⁴⁹

In recent years, the application of the Debus-Radziszewski reaction to chitosan hydrogel preparation has garnered significant attention due to its innovative and sustainable approach for creating advanced functional materials with tailored properties. This method represents a carefully controlled process where reaction conditions, including pH, temperature, and reactant ratios, play crucial roles in determining the final properties of the hydrogel.¹⁰⁴

This reaction mechanism allows for the incorporation of imidazolium groups into the chitosan structure, leading to several advantageous features:

1. **Enhanced pH-responsiveness:** The basic nature of imidazole rings introduces dynamic pH-responsivity to the hydrogel network, allowing for controlled swelling and deswelling behaviors across a wider pH range.
2. **Improved ion exchange and chelation capabilities:** The imidazolium groups provide additional coordination sites for ions and metal complexes, enhancing the hydrogel's potential for environmental remediation and catalysis applications.
3. **Increased thermal stability:** The formation of imidazolium moieties contributes to a more robust hydrogel network, potentially improving its resistance to thermal degradation.
4. **Novel bioactive properties:** The incorporation of imidazole functionality may confer new bioactive properties, such as antimicrobial activity or improved cell adhesion, expanding the hydrogel's potential in biomedical applications.

The versatility of the Debus-Radziszewski reaction in chitosan hydrogel synthesis has led to its application in various fields. For example, in water treatment and dye removal, JUHO ANTTI SIRVIÖ *et al.* have developed imidazolium-crosslinked chitosan (ICC) aerogels with remarkable adsorption capacities for anionic dyes.¹⁰⁴ These materials exhibited a maximum adsorption of 3.5 mmol g⁻¹ for Direct Yellow 27 at pH 4. Notably, the permanent cationic charge of the imidazolium groups enabled effective adsorption even under alkaline conditions, expanding the operational pH range of these materials.¹⁰⁴

Moreover, in the realm of oil/water separation, zwitterionic poly(imidazolium)-based hydrogel coatings prepared via the Debus-Radziszewski reaction have shown promise. These coatings exhibit superhydrophilic and underwater superoleophobic properties, facilitating efficient oil/water separation with high efficiency (>99.5%). The antibacterial nature of the imidazolium ring contributes to the coating's anti-biofouling performance, which is further enhanced by the zwitterion's improved water-binding ability and the formation of a compressed hydration layer.¹⁵⁰

Furthermore, the Debus-Radziszewski reaction has been employed to synthesize a diverse range of sustainable polyelectrolyte networks. As depicted in **Figure 1.12**, TRÖGER-MÜLLER *et al.* reported that these networks exhibit a high density of cationic charges within the polymer backbone, enabling customization to produce either flexible elastic or brittle 3D structures. Notably, these materials can absorb up to 1500% of their mass in water, underscoring their potential as superabsorbent materials.¹⁰⁵

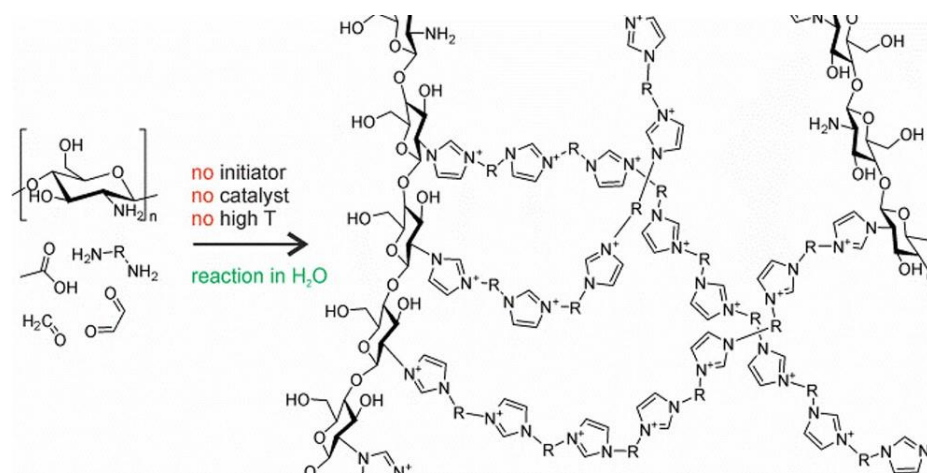


Figure 1.12 Synthetic pathway for main-chain polyelectrolyte networks *via* modified Debus-Radziszewski polymerization. Counterions are omitted for image clarity (taken from: TRÖGER-MÜLLER *et al.*, 2019).¹⁰⁵

The unique combination of chitosan's inherent biocompatibility with the versatile chemistry of the Debus-Radziszewski reaction opens new avenues for designing advanced functional materials with precisely controlled and tunable properties at the molecular level for specific applications in environmental remediation, biomedical engineering, and materials science. Future research in this area may focus on optimizing reaction conditions, exploring new combinations of reactants, and investigating the long-term stability and performance of these novel hydrogel systems in real-world applications.

Building upon the synthetic procedure reported in the literature, our study introduces some modifications to the standard process. Our methodology incorporates a key alteration by introducing various amine components, specifically

commercially available diamines and synthesized polymeric amines, as reactants in the Debus-Radziszewski reaction for chitosan-based hydrogel preparation.

This modification aims to expand the versatility and tailor the properties of the resulting hydrogels. By diversifying the amine reactants, we seek to enhance the structural variability and functional characteristics of the hydrogels. The inclusion of diamines offers the potential for additional crosslinking points, potentially improving the mechanical strength and stability of the hydrogel network. Simultaneously, the incorporation of polymeric amines presents opportunities to introduce new functionalities and alter the hydrogel's physicochemical properties, such as swelling behavior, charge density, and responsiveness to external stimuli.

This modified synthesis strategy not only broadens the scope of chitosan-based hydrogels derived from the Debus-Radziszewski reaction but also paves the way for customizing these materials to meet specific requirements in various applications. The potential applications range from environmental remediation to biomedical engineering, offering a versatile platform for the development of advanced functional materials.

2. Research objectives

The pursuit of sustainable chemistry and the development of environmentally benign approaches have garnered significant attention across various disciplines. This is driven by the necessity to follow the principles of green chemistry, which serve as guidelines for researchers and industries working towards sustainability.^{5, 151} Consequently, concerted efforts are being directed towards the exploration of alternative pathways that align with these principles.

The primary objective of this doctoral research is to contribute to the advancement of sustainable chemistry by investigating and developing novel materials and methodologies from multiple interconnected points.



Figure 2.1 Graphical summary of this doctoral research.

As depicted in **Figure 2.1**, a central focus lies in developing non-isocyanate polyurethane (NIPU) routes that are entirely free of hazardous isocyanates and

phosgene gas. This approach addresses the environmental and health concerns associated with conventional polyurethane synthesis. Furthermore, the conversion of carbon dioxide (CO₂), an abundant and nontoxic C1 building block resource and a major greenhouse gas, into valuable chemicals complies with the principles of waste prevention and atom economy while addressing a critical climate challenge. Likewise, the incorporation of renewable resource-based oils, such as epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO), as sustainable alternatives to petroleum-derived feedstocks, aligns with the principle of reducing reliance on non-renewable petroleum resources and promoting the utilization of bio-based feedstocks.

Moreover, the green synthesis of a series of poly(imidazolium)-based ionic liquids (PILs) via the multicomponent Debus-Radziszewski reaction, a favorable reaction in sustainable chemistry, is explored. The influence of different precursors (diamines, dicarbonyls, aldehydes, and acids) and amine/carbonyl molar ratios on the properties and molecular weight of synthesized PILs is investigated, allowing for the tailoring of molecular structures and properties.

To pursue the NIPU preparation, this work examines the combination of cyclic carbonates with PILs as curing agents, thereby avoiding the use of isocyanates.

Additionally, this dissertation delves into the development of hydrogels derived from renewable and sustainable compounds. It explores a novel crosslinking strategy via the reaction of polysuccinimide (PSI) and amino-terminated poly(imidazolium) ionic liquids (PIMs) for the development of polysuccinimide/polyaspartic acid hydrogels. Likewise, it investigates the synthesis of hydrogels through the Debus-Radziszewski reaction using chitosan in combination with various diamines and polymeric amines.

Specific research tasks include:

- a) Conducting CO₂ utilization reactions with various epoxide components, including renewable resource-based oils (ESBO and ELO) and epoxysiloxane substances, under different experimental conditions (batch-condition and autoclave).

- b) Synthesizing a versatile series of poly(imidazolium)-based ionic liquids *via* the Debus-Radziszewski reaction, optimizing precursor ratios and exploring a diverse range of diamines, dicarbonyls, aldehydes, and acids.
- c) Developing non-isocyanate polyurethanes (NIPUs) using cyclic carbonates and poly(imidazolium)s (PIMs) as curing agents.
- d) Preparing novel polysuccinimide/polyaspartic acid hydrogels through the reaction of polysuccinimide (PSI) and amino-terminated PIMs as crosslinkers.
- e) Producing a wide range of hydrogels using chitosan through the Debus-Radziszewski reaction, incorporating various diamines and polymeric amines.

By pursuing these objectives, this doctoral study aims to contribute to the advancement of sustainable chemistry through the development of environmentally friendly materials and processes with potential applications in various fields.

3. Materials and methods

3.1 Chemicals

Epoxidized soybean oil (ESBO) (CAS number: 8013-07-8 EG number: 232-391-0) and epoxidized linseed oil (ELO) (CAS number: 8016-11-3 EG number: 232-401-3) were kindly supplied from HOBUM Oleochemicals GmbH, Hamburg, Germany.

The following chemicals were used in this research: polydimethylsiloxane epoxy propoxypropyl terminated (viscosity 8-11 cSt; abcr), tetrabutylammonium bromide (TBAB) ($\geq 99\%$; Acros Organics), calcium chloride (96% anhydrous; Acros Organics), sodium sulfate ($\geq 99.0\%$; Sigma-Aldrich), ethyl acetate ($> 99.7\%$; Honeywell), 1,4-butanediamine (99%; Acros Organics), 1,6-hexanediamine (98%; Sigma-Aldrich), L-lysine (98%; Carbolution Chemicals GmbH), L-glutamine (99.5%; Sigma-Aldrich), diethylene glycol bis(3-aminopropyl) ether ($> 98.0\%$; TCI), 1,3-bis(3-aminopropyl)tetramethyldisiloxane (TMDS^{NH₂}) (97%; abcr), glacial acetic acid ($\geq 99.7\%$; Sigma-Aldrich), hydrochloric acid (37%; Honeywell), glyoxal (40 wt.% solution in H₂O; Sigma-Aldrich), methylglyoxal [synonym: Pyruvic aldehyde] (35-45 wt.% solution in H₂O; Fisher Scientific), dimethyl glyoxal [synonym: 2,3-Butanedione] (99%; abcr), formaldehyde (37 wt.% in H₂O; Fisher Scientific), acetaldehyde ($\geq 99.5\%$; Sigma-Aldrich), *N,N*-dimethylformamide (DMF) ($\geq 99.8\%$ extra dry; Acros Organics), triethylamine (TEA) (99%; Acros Organics), L-aspartic acid ($> 98\%$; Thermo Fisher Scientific), mesitylene (99%; Merck), sulfolane (99%; Carbolution Chemicals GmbH), phosphoric acid (85%, Merck), dibutylamine (99%, Sigma-Aldrich), dimethyl sulfoxide (DMSO) ($\geq 99.9\%$ anhydrous; Sigma-Aldrich), sodium chloride ($\geq 99.5\%$; Fisher Scientific), potassium chloride ($> 99\%$; Merck), sodium phosphate dibasic dihydrate (99.0%; Merck), imidazole (99%; Acros Organics), carbon dioxide gas (Linde-gas & more), and chitosan compounds of low molecular weight (30-100 cps) as well as medium molecular weight (300-1000 cps) from Glentham Life Sciences.

Ultrapure water obtained using a PURELAB purification device was used throughout the study.

Buffer solutions were prepared as follows:

Phosphate-buffered saline (PBS, pH 7.4) was prepared by dissolving 4.0 g of sodium chloride (NaCl), 0.2 g of potassium chloride (KCl), and 1.84 g of sodium phosphate dibasic (Na_2HPO_4) in ultrapure water. The pH was adjusted to 7.4 using a pH meter (WTW pH 3210), and the final volume was brought to 1 L with ultrapure water.

Similarly, an imidazole buffer (pH 8.0, 0.15 M) was prepared by dissolving 6.81 g of imidazole and 10.39 g of potassium chloride (KCl) in approximately 800 mL of ultrapure water. The pH was adjusted to 8.0 using hydrochloric acid (HCl) or potassium hydroxide (KOH) as needed, and the final volume was brought to 1 L with additional ultrapure water.

3.2 Experimental methods

3.2.1 Synthesis of cyclic carbonated compounds

The cycloaddition reaction of CO_2 to epoxide compounds has been broadly studied, and a wide spectrum of catalytic systems have been investigated for this process. Among these catalysts, tetrabutylammonium bromide (TBAB) has emerged as one of the most frequently used. TBAB can effectively facilitate the ring-opening of epoxides and incorporate CO_2 into the resulting intermediate, even at ambient CO_2 pressure. Moreover, researchers have examined various additive compounds as co-catalysts to enhance the yield and efficiency of the CO_2 fixation reaction. Among these co-catalysts, calcium salts such as calcium chloride (CaCl_2) and calcium iodide (CaI_2) have been widely employed. These calcium salts can act as Lewis acids, further activating the epoxide and promoting the overall reaction.

Cyclic carbonates were synthesized from bio-based epoxidized oils following procedures described in the literature. Epoxidized bio-based oils, specifically epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO), were used as starting materials. The reaction was catalyzed by a system comprising tetrabutylammonium bromide (TBAB) as the primary catalyst and calcium chloride (CaCl_2) as a co-catalyst.

In a typical reaction, 200 g of epoxidized bio-based oil was combined with 10.70 g TBAB (5 mol% relative to epoxy groups) and 1.83 g anhydrous CaCl_2 (0.0165 mol) in a 500 mL three-necked flask equipped with a reflux condenser. The reaction

mixture was heated to 110 °C under magnetic stirring. CO₂ was then continuously fed into the mixture through a gas-dispersion tube fitted with a sintered glass frit.

The progress of the carbonation reaction was monitored by FT-IR and NMR spectroscopy, as well as by the determination of epoxy content via titration. Upon completion of the reaction, the viscous crude product was diluted with ethyl acetate, and the resulting mixture was centrifuged. To remove excess catalysts, the mixture was washed three times with saturated brine followed by deionized water. Finally, to obtain the pure product, the organic phase was dried over anhydrous Na₂SO₄ and concentrated under vacuum. **Figure 3.1** depicts the synthetic route for the CO₂ fixation reaction with epoxidized bio-based oils.

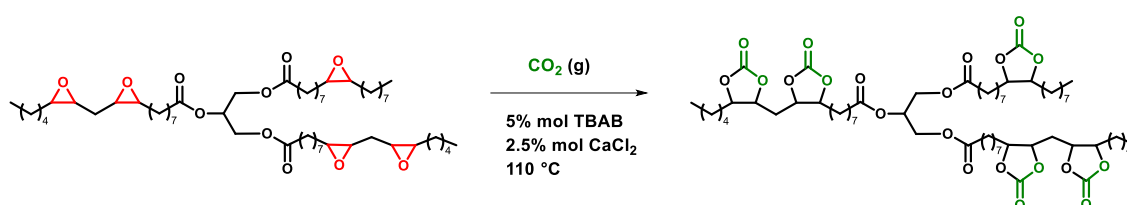


Figure 3.1 Schematic representation of the CO₂ cycloaddition reaction to epoxidized bio-based oils.

Moreover, to investigate the effect of CO₂ pressure on reaction kinetics and to potentially enhance the reaction rate, a parallel experiment was conducted using an autoclave. This high-pressure reaction employed the same precursors and catalytic system but was carried out under elevated CO₂ pressure (20 bar).

Similarly, the CO₂ cycloaddition reaction was extended to epoxy-functionalized silicone compounds using the same catalytic system. For this purpose, polydimethylsiloxane with epoxy propoxypropyl terminal groups was selected as the substrate. As exhibited in **Figure 3.2**, this compound features two terminal epoxy functional groups with a siloxane backbone, making it an ideal candidate to investigate the applicability of the developed catalytic system to silicon-containing epoxy materials.

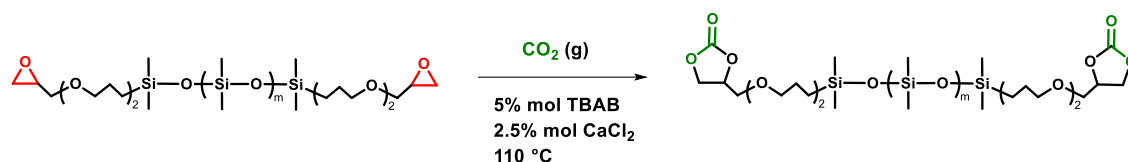


Figure 3.2 Synthetic route for the incorporation of CO₂ into the epoxy-functional silicone.

3.2.2 Synthesis of poly(imidazolium)-based ionic liquids (PIMs)

A diverse range of amino-terminated poly(imidazolium)-based ionic liquids (PIMs) were synthesized using a modified Debus-Radziszewski reaction. **Figure 3.3** presents a general schematic of this multicomponent reaction. Various precursors, including diamines, dicarbonyls, aldehydes, and acids, were employed in this research. Additionally, different amine/carbonyl molar ratios were utilized to effectively tune the molecular weight of the resulting PIMs.

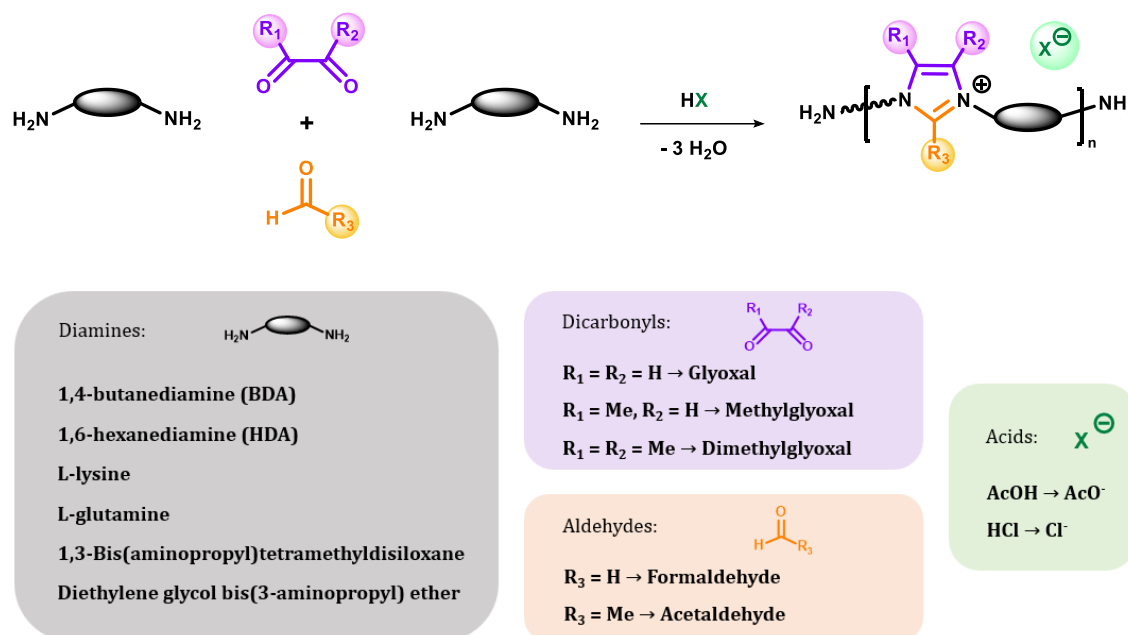


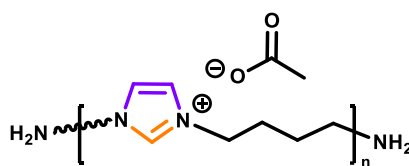
Figure 3.3 Synthesis of amino-terminated poly(imidazolium)-based ionic liquids (PIMs). (Top) General reaction scheme for the modified Debus-Radziszewski polymerization. (Below) Various precursors were used in this research, including diamines, dicarbonyls, aldehydes, and acids.

General procedure for preparation PIMs:

In a typical experiment, 2.0 equivalents of acid were added under vigorous stirring to an aqueous solution of 1.0 equivalent diamine (40 wt.% concentration) at 0 °C for 30 minutes. Afterward, a mixture of carbonyl components, including formaldehyde (37 wt.% in water) and glyoxal (40 wt.% in water), was added dropwise to the amine solution. The temperature was maintained at 0 °C during the addition of the carbonyl solution using an ice bath. Upon completion of the addition, the reaction mixture was heated to 100 °C and maintained at this temperature for one hour.

The resulting brownish solution was then subjected to solvent and residual monomer removal under vacuum at 80 °C for 12 hours. The crude poly(imidazolium)-based ionic liquids were used without further purification in most cases. When additional purification was required, dialysis was employed using appropriate molecular weight cut-off dialysis membranes.

PIM C4 AcO: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing 1,4-butanedi-amine (BDA) (1.0



eq., 20 mmol, 1.763 g) and ultrapure water. Subsequently, a premixed solution of carbonyl components, comprising glyoxal 40 wt.% and formaldehyde 37 wt.%, was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution.

To investigate the influence of precursor molar ratios on the molecular weight distribution of the synthesized PIMs, various PIM C4 formulations were prepared using different initial starting materials, including 1,4-butanedi-amine and carbonyl compounds (glyoxal and formaldehyde). **Table 3.1** presents the specific amounts of the required precursors for preparing PIM C4 AcO at nine different amine/carbonyl molar ratios. The molar ratio is defined as follows:

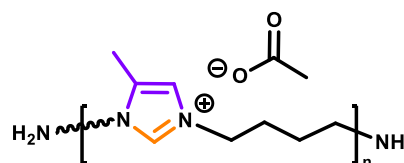
$$\text{Molar ratio} = n_{\text{diamine}} / [(n_{\text{glyoxal}} + n_{\text{formaldehyde}}) \times 0.5]$$

Table 3.1 Exact amounts of precursors required for preparing PIM C4 AcO with varying amine/carbonyl molar ratios.

Compound	BDA	Acetic acid	UP water	Glyoxal 40%	Formalde hyde 37%
PIM C4 AcO 0.8	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	8.728 g	1.25 eq., 25 mmol, 3.628 g	1.25 eq., 25 mmol, 2.029 g
PIM C4 AcO 1.0	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	7.03 g	1.0 eq., 20 mmol, 2.902 g	1.0 eq., 20 mmol, 1.623 g
PIM C4 AcO 1.2	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	5.876 g	0.83 eq., 16.6 mmol, 2.409 g	0.83 eq., 16.6 mmol, 1.347 g
PIM C4 AcO 1.4	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	5.062 g	0.71 eq., 14.2 mmol, 2.06 g	0.71 eq., 14.2 mmol, 1.153 g
PIM C4 AcO 1.6	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	4.486 g	0.625 eq., 12.5 mmol, 1.814 g	0.625 eq., 12.5 mmol, 1.015 g
PIM C4 AcO 1.8	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	3.976 g	0.55 eq., 11 mmol, 1.596 g	0.55 eq., 11 mmol, 0.893 g
PIM C4 AcO 2.0	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	3.637 g	0.5 eq., 10 mmol, 1.451 g	0.5 eq., 10 mmol, 0.812 g
PIM C4 AcO 2.2	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	3.297 g	0.45 eq., 9 mmol, 1.306 g	0.45 eq., 9 mmol, 0.73 g
PIM C4 AcO 2.5	1.0 eq., 20 mmol, 1.763 g	2.0 eq., 40 mmol, 2.402 g	2.927 g	0.4 eq., 8 mmol, 1.161 g	0.4 eq., 8 mmol, 0.649 g

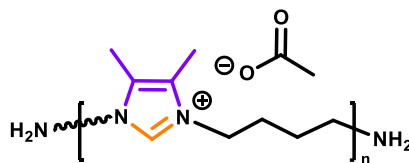
PIM C4b AcO-1.0: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing 1,4-butanediamine (1.0 eq., 20

mmol, 1.763 g) and ultrapure water (8.081 g). Subsequently, a premixed solution of carbonyl components, comprising methylglyoxal 35-45% (1.0 eq., 20 mmol, 3.603 g) and formaldehyde 37 wt.% (1.0 eq., 20 mmol, 1.623 g), was added dropwise to

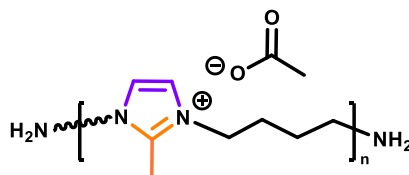


the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution.

PIM C4c AcO-1.0: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing 1,4-butanedi-amine (1.0 eq., 20 mmol, 1.763 g) and ultrapure water (5.260 g). Subsequently, a premixed solution of carbonyl components, comprising dimethyl glyoxal (1.0 eq., 20 mmol, 1.722 g) and formaldehyde 37 wt.% (1.0 eq., 20 mmol, 1.623 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution.



PIM C4d AcO-1.0: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing 1,4-butanedi-amine (1.0 eq., 20 mmol, 1.763 g) and ultrapure water (5.917 g). Subsequently, a premixed solution of carbonyl components, comprising glyoxal 40 wt.% (1.0 eq., 20 mmol, 2.902 g) and acetaldehyde (1.0 eq., 20 mmol, 0.881 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution.



PIM C6 AcO: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing 1,6-hexanedi-amine (HDA) (1.0 eq., 20 mmol, 2.324 g) and ultrapure water. Subsequently, a premixed solution of carbonyl components, comprising glyoxal 40 wt.% and formaldehyde 37 wt.%, was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution. **Table 3.2** represents the exact amounts of required precursors for preparing PIMC6 AcO with 9 different amine/carbonyl molar ratios.

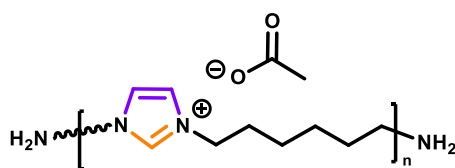


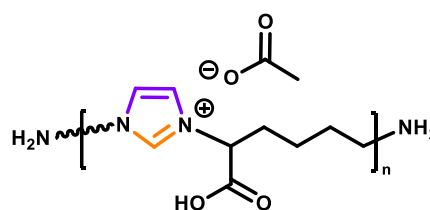
Table 3.2 Exact amounts of precursors required for preparing PIM C6 AcO with varying amine/carbonyl molar ratios.

Compound	HDA	Acetic acid	UP water	Glyoxal 40%	Formalde hyde 37%
PIM C6 AcO 0.8	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	9.57 g	1.25 eq., 25 mmol, 3.628 g	1.25 eq., 25 mmol, 2.029 g
PIM C6 AcO 1.0	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	7.872 g	1.0 eq., 20 mmol, 2.902 g	1.0 eq., 20 mmol, 1.623 g
PIM C6 AcO 1.2	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	6.718 g	0.83 eq., 16.6 mmol, 2.409 g	0.83 eq., 16.6 mmol, 1.347 g
PIM C6 AcO 1.4	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	5.904 g	0.71 eq., 14.2 mmol, 2.06 g	0.71 eq., 14.2 mmol, 1.153 g
PIM C6 AcO 1.6	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	5.328 g	0.625 eq., 12.5 mmol, 1.814 g	0.625 eq., 12.5 mmol, 1.015 g
PIM C6 AcO 1.8	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	4.818 g	0.55 eq., 11 mmol, 1.596 g	0.55 eq., 11 mmol, 0.893 g
PIM C6 AcO 2.0	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	4.479 g	0.5 eq., 10 mmol, 1.451 g	0.5 eq., 10 mmol, 0.812 g
PIM C6 AcO 2.2	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	4.138 g	0.45 eq., 9 mmol, 1.306 g	0.45 eq., 9 mmol, 0.73 g
PIM C6 AcO 2.5	1.0 eq., 20 mmol, 2.324 g	2.0 eq., 40 mmol, 2.402 g	3.799 g	0.4 eq., 8 mmol, 1.161 g	0.4 eq., 8 mmol, 0.649 g

PIM Lys AcO: According to the general reaction

procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing L-lysine (1.0 eq., 20 mmol, 2.924 g) and ultrapure water. Subsequently, a premixed solution of carbonyl

components, comprising glyoxal 40 wt.% and formaldehyde 37 wt.%, was added dropwise to the diamine mixture. Following complete addition, the reaction mixture

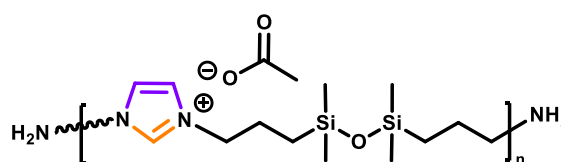


was heated at 100 °C for 1 h, resulting in a dark aqueous solution. **Table 3.3** represents the exact amounts of required precursors for preparing PIM Lys AcO with 4 different amine/carbonyl molar ratios.

Table 3.3 Exact amounts of precursors required for preparing PIM Lys AcO with varying amine/carbonyl molar ratios.

Compound	L-lysine	Acetic acid	UP water	Glyoxal 40%	Formalde hyde 37%
PIM Lys AcO 1.0	1.0 eq., 20 mmol, 2.924 g	2.0 eq., 40 mmol, 2.402 g	8.772 g	1.0 eq., 20 mmol, 2.902 g	1.0 eq., 20 mmol, 1.623 g
PIM Lys AcO 1.6	1.0 eq., 20 mmol, 2.924 g	2.0 eq., 40 mmol, 2.402 g	6.226 g	0.625 eq., 12.5 mmol, 1.814 g	0.625 eq., 12.5 mmol, 1.015 g
PIM Lys AcO 2.2	1.0 eq., 20 mmol, 2.924 g	2.0 eq., 40 mmol, 2.402 g	5.039 g	0.45 eq., 9.0 mmol, 1.306 g	0.45 eq., 9.0 mmol, 0.730 g
PIM Lys AcO 2.5	1.0 eq., 20 mmol, 2.924 g	2.0 eq., 40 mmol, 2.402 g	4.699 g	0.4 eq., 8.0 mmol, 1.161 g	0.4 eq., 8.0 mmol, 0.649 g

PIM Si AcO: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to a solution of 1,3-bis(3-

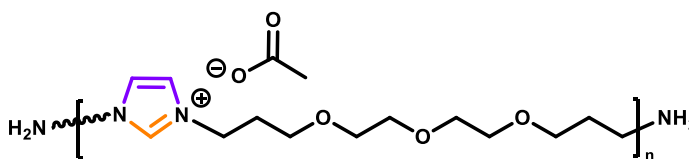


aminopropyl)tetramethyldisiloxane (TMDS^{NH2}) (1.0 eq., 20 mmol, 4.970 g) and 40 mL ethanol. Subsequently, a premixed solution of carbonyl components, comprising glyoxal 40 wt.% and formaldehyde 37 wt.%, was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h, resulting in a dark aqueous solution. **Table 3.4** represents the exact amounts of required precursors for preparing PIM Si AcO with 4 different amine/carbonyl molar ratios.

Table 3.4 Exact amounts of precursors required for preparing PIM Si AcO with varying amine/carbonyl molar ratios.

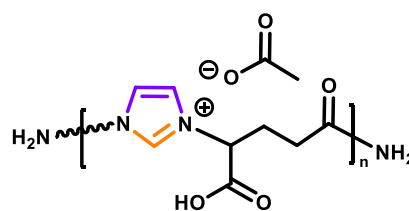
Compound	TMDS ^{NH2}	Acetic acid	Ethanol	Glyoxal 40%	Formalde hyde 37%
PIM Si AcO 1.0	1.0 eq., 20 mmol, 4.970 g	2.0 eq., 40 mmol, 2.402 g	40 mL	1.0 eq., 20 mmol, 2.902 g	1.0 eq., 20 mmol, 1.623 g
PIM Si AcO 1.6	1.0 eq., 20 mmol, 4.970 g	2.0 eq., 40 mmol, 2.402 g	40 mL	0.625 eq., 12.5 mmol, 1.814 g	0.625 eq., 12.5 mmol, 1.015 g
PIM Si AcO 2.2	1.0 eq., 20 mmol, 4.970 g	2.0 eq., 40 mmol, 2.402 g	40 mL	0.45 eq., 9.0 mmol, 1.306 g	0.45 eq., 9.0 mmol, 0.730 g
PIM Si AcO 2.5	1.0 eq., 20 mmol, 4.970 g	2.0 eq., 40 mmol, 2.402 g	40 mL	0.4 eq., 8.0 mmol, 1.161 g	0.4 eq., 8.0 mmol, 0.649 g

PIM E AcO-1.0: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g)



was added dropwise to an aqueous solution containing diethylene glycol bis(3-aminopropyl) ether (1.0 eq., 20 mmol, 4.406 g) and ultrapure water (10.994 g). Subsequently, a premixed solution of carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 20 mmol, 1.623 g) and glyoxal 40 wt.% (1.0 eq., 20 mmol, 2.902 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.

PIM Gln AcO-1.0: According to the general reaction procedure, glacial acetic acid (2.0 eq., 40 mmol, 2.402 g) was added dropwise to an aqueous solution containing L-glutamine (1.0 eq., 20 mmol, 2.923 g) and ultrapure water (8.769 g).



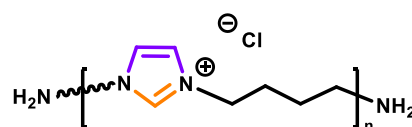
Subsequently, a premixed solution of carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 20 mmol, 1.623 g) and glyoxal 40 wt.% (1.0 eq., 20

mmol, 2.902 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.

PIM C4 Cl-1.0: According to the general reaction

procedure, hydrochloric acid 37 wt.% (2.0 eq., 100 mmol, 10.0 g) was added dropwise to an aqueous

solution containing 1,4-butanediamine (1.0 eq., 50 mmol, 4.408 g) and ultrapure water (10 g). Subsequently, a premixed solution of carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 50 mmol, 4.058 g) and glyoxal 40 wt.% (1.0 eq., 50 mmol, 7.255 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.



PIM C6 Cl-1.0: According to the general

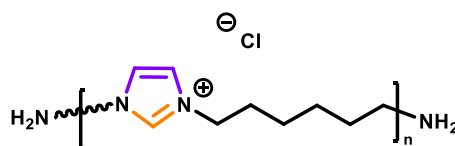
reaction procedure, hydrochloric acid 37 wt.%

(2.0 eq., 100 mmol, 10.0 g) was added dropwise

to an aqueous solution containing 1,6-

hexanediamine (1.0 eq., 50 mmol, 5.811 g) and ultrapure water (10 g).

Subsequently, a premixed solution of carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 50 mmol, 4.058 g) and glyoxal 40 wt.% (1.0 eq., 50 mmol, 7.255 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.



PIM Lys Cl-1.0: According to the general reaction

procedure, hydrochloric acid 37 wt.% (2.0 eq.,

100 mmol, 10.0 g) was added dropwise to an

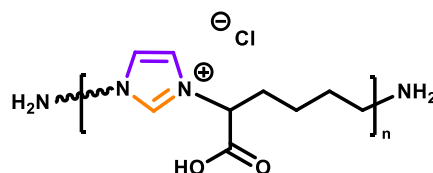
aqueous solution containing L-lysine (1.0 eq., 50

mmol, 7.310 g) and ultrapure water (10 g). Subsequently, a premixed solution of

carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 50 mmol, 4.058

g) and glyoxal 40 wt.% (1.0 eq., 50 mmol, 7.255 g), was added dropwise to the

diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.

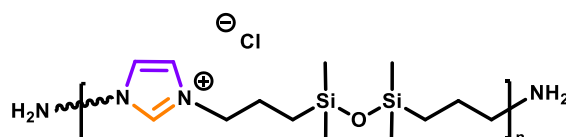


PIM Si Cl-1.0: According to the general

reaction procedure, hydrochloric acid

37 wt.% (2.0 eq., 100 mmol, 10.0 g) was

added dropwise to an aqueous solution



containing 1,3-bis(3-aminopropyl) tetramethyldisiloxane (1.0 eq., 50 mmol, 12.426 g) and ultrapure water (10 g). Subsequently, a premixed solution of carbonyl components, comprising formaldehyde 37 wt.% (1.0 eq., 50 mmol, 4.058 g) and glyoxal 40 wt.% (1.0 eq., 50 mmol, 7.255 g), was added dropwise to the diamine mixture. Following complete addition, the reaction mixture was heated at 100 °C for 1 h.

3.2.3 Synthesis of non-isocyanate polyurethanes (NIPUs)

As previously described, one of the most sustainable methods for preparing non-isocyanate polyurethanes (NIPUs) involves the reaction of cyclic carbonates with amine components that serve as curing agents. In this study, cyclic carbonated soybean oil (CSBO) was reacted with imidazolium-based poly(ionic liquids) (PIMs) to produce NIPU products. This reaction utilizes the amine functionalities present in PIMs to facilitate the ring-opening aminolysis of the cyclic carbonates, resulting in the formation of hydroxyurethane linkages, as illustrated in **Figure 3.4**.

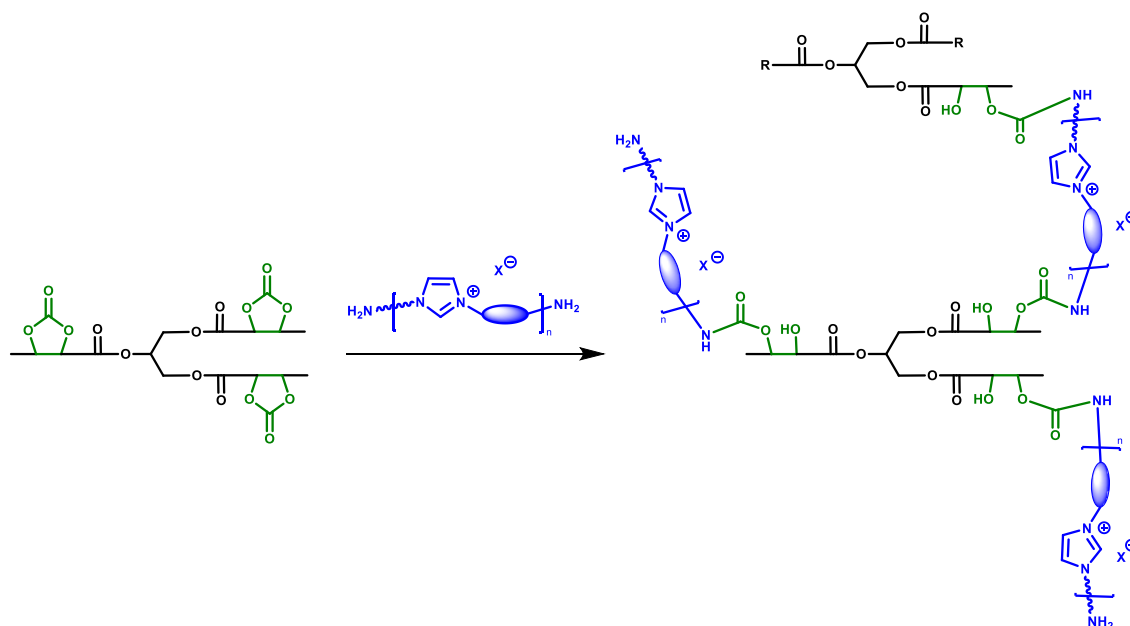


Figure 3.4 Synthesis route for the preparation of NIPU *via* the reaction between cyclic carbonated compounds and PIMs.

In a typical experiment, a two-necked round-bottom flask equipped with a condenser, an inert gas inlet (argon), an oil bath, and a magnetic stirrer was charged

with CSBO and stoichiometric amounts of amine curing agents, as specified in **Tables 3.5** and **3.6** for NIPU synthesized with PIM C4 AcO and PIM C6 AcO, respectively.

To this mixture, 5 mL of *N,N*-dimethylformamide (DMF) was added as a solvent to ensure thorough homogenization and uniform distribution of the reactants, along with 20 μ L of triethylamine (TEA) as a catalyst.

The reaction mixture was stirred and heated to 70 °C, maintaining this temperature for 12 hours under an inert argon atmosphere. Following this period, the DMF solvent was removed under vacuum. The resulting products were then cast into molds and cured in a vacuum oven using a two-step process: first at 70 °C for 10 hours, followed by 100 °C for 3 hours.

The progress of the polymerization reaction was monitored using FT-IR and NMR spectroscopy, observing the disappearance of the characteristic cyclic carbonate spectral features and the emergence of signals corresponding to urethane linkages.

Table 3.5 Composition and stoichiometry of NIPU formulations using CSBO with varying ratios of BDA and PIMC4 curing agents.

Lab code	CSBO			Curing agent					
				BDA			PIM C4 AcO		
	eq.	n (mmol)	m (g)	eq.	n (mmol)	m (g)	eq.	n (mmol)	m (g)
NIPU-SB-0	1.0	2.14	1.000	1.00	2.14	0.189	0.0	0.00	0.000
NIPU-SB-5	1.0	2.14	1.000	0.95	2.03	0.179	0.05	0.11	0.255
NIPU-SB-10	1.0	2.14	1.000	0.90	1.93	0.170	0.1	0.21	0.510
NIPU-SB-25	1.0	2.14	1.000	0.75	1.61	0.142	0.25	0.54	1.275
NIPU-SB-50	1.0	2.14	1.000	0.50	1.07	0.094	0.5	1.07	2.550

NIPU-SB-75	1.0	2.14	1.000	0.25	0.54	0.047	0.75	1.61	3.825
NIPU-SB-100	1.0	2.14	1.000	0.00	0.00	0.000	1.0	2.14	5.100

Table 3.6 Composition and stoichiometry of NIPU formulations using CSBO with varying ratios of HDA and PIMC6 curing agents.

Lab code	CSBO			Curing agent					
				HDA			PIM C6 AcO		
	eq.	n (mmol)	m (g)	eq.	n (mmol)	m (g)	eq.	n (mmol)	m (g)
NIPU-SH-0	1.0	2.14	1.000	1.00	2.14	0.249	0.0	0.00	0.000
NIPU-SH-5	1.0	2.14	1.000	0.95	2.03	0.236	0.05	0.11	0.285
NIPU-SH-10	1.0	2.14	1.000	0.90	1.93	0.224	0.1	0.21	0.570
NIPU-SH-25	1.0	2.14	1.000	0.75	1.61	0.187	0.25	0.54	1.425
NIPU-SH-50	1.0	2.14	1.000	0.50	1.07	0.124	0.5	1.07	2.849
NIPU-SH-75	1.0	2.14	1.000	0.25	0.54	0.062	0.75	1.61	4.274
NIPU-SH-100	1.0	2.14	1.000	0.00	0.00	0.000	1.0	2.14	5.699

3.2.4 Synthesis of polysuccinimide (PSI)

The synthesis of polysuccinimide (PSI) was carried out in a newly developed 100 mL reactor designed by JOHANNA ROMISCHKE in our group, under reflux conditions with continuous stirring, according to the method described by SZILÁGYI *et al.*¹²⁹ For this purpose, 20 g L-aspartic acid and 60 g of a mesitylene/sulfolane mixture (7:3

ratio by volume) were placed in the reactor and homogenized using a magnetic stirrer. Then, 1.7 mL of phosphoric acid (85%) was added as a catalyst. The reaction mixture was heated to 160 °C in an oil bath under reflux condition and remained for 7 hours.

For purification, the resulting white solid was initially dissolved in *N,N*-dimethylformamide (DMF) and then precipitated by adding an excess amount of water. The precipitate was collected by filtration and washed thoroughly with methanol followed by ultrapure water until the pH of the filtrate became neutral. Finally, the obtained product was dried under vacuum to remove any residual solvents.

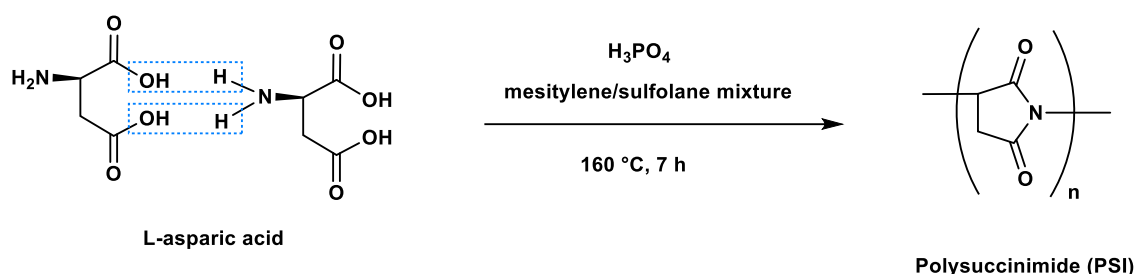


Figure 3.5 Synthesis route of polysuccinimide from L-aspartic acid using phosphoric acid as a catalyst.

3.2.5 Synthesis of PSI-based hydrogel

PSI-based hydrogels were prepared by crosslinking polysuccinimide (PSI) monomers with various diamine crosslinkers, including both non-polymeric and polymeric diamines. The synthesis was based on the procedure developed by SZILÁGYI *et al.* In this process, 1.07 mmol (0.104 g) of PSI was dissolved in 713 μL of DMSO using ultrasonication. For non-polymeric commercially available diamines (such as BDA and HDA), 0.18 mmol of the crosslinker was added to the PSI solution. However, for synthesized polymeric crosslinkers (PIMs), due to their high molecular weights, different amounts (0.1, 0.2, and 0.3 g) were added and investigated. To initiate gelation, 0.45 mmol (75.3 μL) of dibutylamine (DBA) was added to the mixture. The mixture was then allowed to proceed for 24 hours to ensure complete polymerization.

For the preparation of poly(aspartic acid) (PASP) hydrogels, the resulting PSI-based hydrogel was hydrolyzed by immersion in an imidazolium buffer (pH 8; 0.15 M) for three days, with daily buffer exchanges.

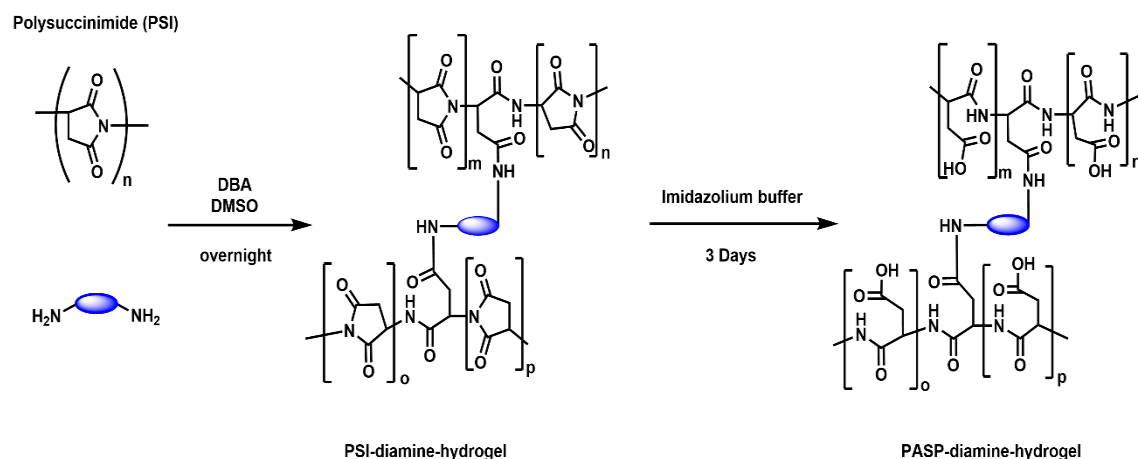


Figure 3.6 Schematic representation of the synthesis of PSI / PASP hydrogels in the presence of different diamines.

3.2.6 Synthesis of Chitosan-based hydrogel

In a typical experiment, a 5% (w/v) chitosan solution was first prepared by dissolving 1.0 g of chitosan (either low or medium molecular weight) in 20 mL of 50% (v/v) acetic acid solution in ultrapure water. The mixture was stirred until complete dissolution of chitosan was achieved, ensuring no precipitate remained.

1 g of the prepared chitosan solution was then diluted in a mixture of 1.2 g H₂O and 0.3 g glacial acetic acid. Simultaneously, a pre-diluted diamine solution (in 0.8 g H₂O) was added to the chitosan solution. The mixture was allowed to homogenize for 1 hour. Subsequently, to initiate the Debus-Radziszewski reaction, 0.363 g (2.5 mmol) of 40% glyoxal solution and 0.203 g (2.5 mmol) of 37% formaldehyde solution were added to the chitosan-amine mixture. The reaction mixture was then left undisturbed to allow the gelation process to proceed to completion.

For the incorporation of commercially available diamines, 2.5 mmol of each diamine was added to the reaction mixture. The specific quantities for each diamine were as follows:

- 1,4-butanediamine (BDA): 0.220 g
- 1,6-hexanediamine (HDA): 0.291 g
- Diethylene glycol bis(3-aminopropyl) ether (E): 0.551 g
- L-lysine (Lys): 0.365 g
- L-glutamine (Gln): 0.365 g
- 1,3-bis(aminopropyl)tetramethyldisiloxane (Si): 0.621 g

In contrast, for polymeric amines, a fixed mass of 0.3 g was added to the reaction mixture, regardless of the molar quantity.

The resulting hydrogels were characterized for their swelling behavior, dye adsorption capacity, and rheological properties. For swelling behavior analysis, hydrogel samples were dried in a convection oven at 40°C for 72 hours. The dried samples were then immersed in appropriate media (water and PBS) to measure their swelling ratios over time. The hydrogels' capacity to adsorb various dyes was evaluated using standard adsorption protocols. Rheological analysis, including amplitude sweep and creep recovery tests, was performed using a rheometer to assess the viscoelastic properties of the hydrogels.

This procedure allows for the systematic preparation and characterization of chitosan-based hydrogels modified via the Debus-Radziszewski reaction, incorporating various amine components to tailor the hydrogel properties.

3.3 Characterization techniques

3.3.1 Fourier transform infrared spectroscopy (FT-IR)

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was performed at room temperature using two different instruments: a Nicolet 380 spectrometer (Thermo Fisher Scientific) and a Bruker ALPHA II FTIR spectrometer. All samples were analyzed over a wavenumber range of 4000 to 400 cm⁻¹.

3.3.2 Nuclear magnetic resonance spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy was performed using Bruker AVANCE spectrometers (Bruker, USA) operating at 250, 300, 400, and 500 MHz. All spectra were recorded at room temperature (298 K) using deuterated solvents. Tetramethylsilane (TMS) served as an internal standard for chemical shift referencing. Chemical shifts (δ) are reported in ppm relative to TMS, and coupling constants (J) are given in Hertz (Hz).

3.3.3 Gel permeation chromatography (GPC)

The molecular weight distributions of the polymers were determined using gel permeation chromatography (GPC) with different systems:

- i. Organic-solvent GPC was performed on an Agilent 1260 Infinity GPC/SEC system (Agilent Technologies, USA) equipped with a refractive index (RI) detector. The system utilized three columns: a pre-column, a 1000 Å column, and a 10000 Å column. Polystyrene standards were used for calibration, providing a molecular weight measurement range of 500 to 2,460,000 Da. Tetrahydrofuran (THF) served as the mobile phase at 25 °C with a flow rate of 1.0 mL/min.
- ii. Aqueous GPC measurements were conducted using two columns in series (PSS, Germany): a PSS-Novema Max analytical linear XL 10 µm column and a PSS-Novema S-VS pre-column. The system was calibrated using pullulan and dextran standards and equipped with both refractive index (RI) and UV detectors. The eluent consisted of 80% aqueous acetate buffer (pH 4.5) and 20% methanol, with a flow rate of 1.0 mL/min at 25 °C.
- iii. The molecular weight distributions of NIPU products were analyzed using a combination of PSS-GRAM 7µ VS, 100, and 1000 columns. The system was calibrated using polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(ethylene oxide) (PEO) standards, and equipped with both RI and UV detectors. N-methylpyrrolidone (NMP) containing 0.5 g/L LiBr served as the eluent at 25 °C with a flow rate of 0.8 mL/min.

3.3.4 Epoxy content determination

The progression of the CO₂ cycloaddition reaction was monitored through quantitative determination of oxirane oxygen content (OOC%) via titration, following the American Society for Testing and Materials (ASTM) D1652 standard protocol. The experimental procedure was as follows:

A precisely weighed 1.50 g aliquot of the oil product was combined with 25 mL of n-propanol in a 100 mL two-necked round-bottomed flask equipped with a condenser, thermometer, and magnetic stirrer. The mixture was refluxed at 95°C for 60 minutes. Subsequently, a freshly prepared potassium iodide solution (3.0 g KI in 5.0 g deionized water) was added to the reaction. 20 drops of bromophenol blue indicator were then introduced to the reaction mixture. The resulting solution was titrated with 1.00 N HCl under reflux condition until a persistent yellow color was observed, indicating the endpoint of the titration.

The epoxy contents were calculated using the following equation:

$$\text{Epoxy content (mol/kg oil)} = \frac{N(\text{HCl}) \times V(\text{HCl})}{W}$$

Where:

N_{HCl} = Normality of HCl solution (mol/L)

V_{HCl} = Volume of HCl solution consumed (mL)

W = Weight of oil sample (g)

3.3.5 High-resolution mass spectroscopy (HRMS)

High-resolution mass spectrometry (HRMS) was performed using an electrospray ionization (ESI) mass spectrometer (Waters Acquity UPLC H-Class/Xevo G2-XS TOF LC-MS). Sample solutions were prepared at 20 mg/mL in acetonitrile with 20 µL of a 2 mg/mL NaI solution, which enhanced ionization by facilitating the formation of [analyte + Na⁺] cations. ESI conditions included a capillary voltage of 1.5 kV, sampling cone voltage of 40 V, and source offset voltage of 80 V, with source and desolvation temperatures set at 120 °C and 300 °C, respectively. Gas flows were maintained at 50 L/h for cone gas and 850 L/h for desolvation gas, using dry

nitrogen as the ESI gas. These optimized conditions resulted in the efficient generation of abundant cations for analysis.

3.3.6 Rheological analysis

Viscosity measurements were conducted using the Rheo Stress 1 from Thermo Scientific Haake, equipped with a 1° cone-plate geometry featuring a 35 mm diameter cone. Analyses were performed at a controlled temperature of 25 °C, with shear rates set from 1 to 100 (1/s). The rotational viscometer calculated viscosity based on the measured torque and rotational speed, along with the specific dimensions of the measuring geometry. The Rheowin Job Manager software facilitated data acquisition and analysis, ensuring precise and reproducible results.

Additionally, rheological analyses were conducted using the same rheometer at a controlled temperature of 25 °C. This involved applying a logarithmically increasing shear stress, ranging from 10^1 to 10^4 μNm while measuring key rheological parameters. The logarithmic ramping of shear stress allowed for a comprehensive assessment of the material's response to varying stress levels, providing valuable insights into its flow characteristics and structural integrity under different conditions.

4. Results and discussion

This section presents and discusses the results of this research study. The discussion begins with an examination of the synthesis of cyclic carbonate compounds, which serve as key precursors for the production of non-isocyanate polyurethanes (NIPUs). Subsequently, the preparation and characterization of poly(imidazolium)-based ionic liquids (PIMs) are described. These PIMs were employed as novel curing agents in the development of NIPU networks. Furthermore, the study explores the utilization of the synthesized amino-terminated PIMs as crosslinking agents in the preparation of two distinct hydrogel systems: poly(succinimide)-based (PSI) hydrogels and chitosan-based hydrogels. This approach demonstrates the versatility of the synthesized materials and highlights their potential for broader applications in the field of polymer chemistry.

4.1 Cyclic carbonated compounds

As described in previous sections, the preparation of cyclic carbonates represents an effective route aligned with the principles of green chemistry, owing to its potential for cost-effectiveness and high atom economy. This approach contributes to sustainable chemistry by maximizing resource efficiency and minimizing waste generation. Various pathways have been reported for synthesizing cyclic carbonates, employing different substrates and catalysts.¹⁵²

Among these methods, one of the most promising routes involves the cycloaddition reaction of epoxide components with CO₂. This reaction is particularly appealing as it utilizes CO₂, as a C1 building block, effectively converting a greenhouse gas into a valuable chemical feedstock. A diverse array of epoxide components, including those derived from bio-based oils, have been successfully used and reported for the incorporation of CO₂ into epoxide moieties. This reaction can be carried out in the presence of various catalytic systems, which facilitate the reaction under different conditions, ranging from ambient CO₂ pressure to elevated pressures.

Recent research has focused on developing highly efficient and selective catalysts that can operate under mild conditions, further enhancing the sustainability of this process. Additionally, the use of bio-based epoxides as substrates aligns with the principles of renewable feedstocks and biocompatibility.

For this purpose, two types of epoxy components, including epoxidized bio-based oils (such as epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO)) and epoxysiloxane compounds, have been used for synthesizing cyclic carbonates. These reactions were conducted via two different pathways: batch conditions under a reflux condenser at ambient pressure and in an autoclave at higher CO₂ pressure, in the presence of a tetrabutylammonium bromide / calcium chloride (TBAB / CaCl₂) catalytic system (compare 3.2.1).

This dual approach not only demonstrates the versatility of the cycloaddition reaction but also highlights the potential for scalable and sustainable production of cyclic carbonates, leveraging both bio-based and synthetic epoxide substrates.

The progress of CO₂ fixation was tracked using several analytical techniques. **Figure 4.1** presents the stacked FT-IR spectra of epoxidized soybean oil (ESBO), clearly demonstrating epoxide conversion to cyclic carbonate products over time.

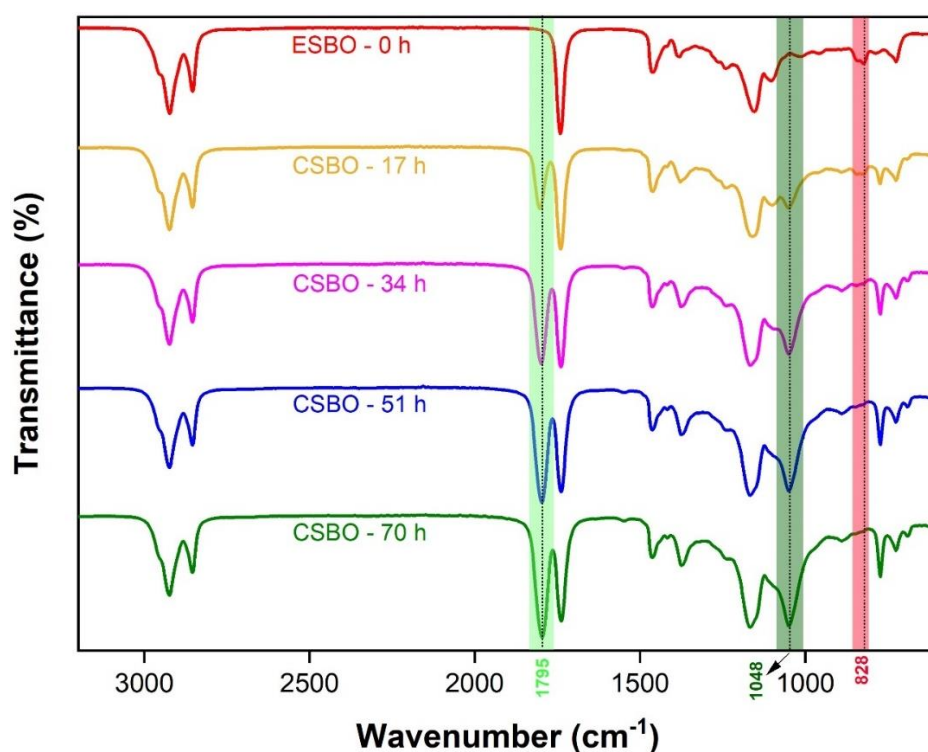


Figure 4.1 Stacked FT-IR spectra of carbonated soybean oil (CSBO) at different reaction times compared with initial epoxidized soybean oil (ESBO).

The oxirane C-O twin bands at 828 and 845 cm^{-1} decreased and eventually disappeared, indicating the consumption of the epoxide. Conversely, a new carbonyl band at 1795 cm^{-1} (C=O stretching) and a new C-O stretching absorbance at 1048 cm^{-1} , assigned to the cyclic carbonate groups, appeared and increased in intensity. These spectral changes confirm the incorporation of CO_2 into the epoxide moiety and the formation of cyclic carbonates.

The conversion of ESBO into CSBO was further confirmed by NMR spectroscopy. As exhibited in **Figure 4.2**, the ^1H NMR spectrum reveals the disappearance of proton signals at 3.0 ppm, corresponding to the oxirane groups, which were no longer evident after the conversion to cyclic carbonate. In contrast, four new characteristic signals attributed to the cyclocarbonate function appeared at 4.3–4.9 ppm, indicating the formation of cyclic carbonates.

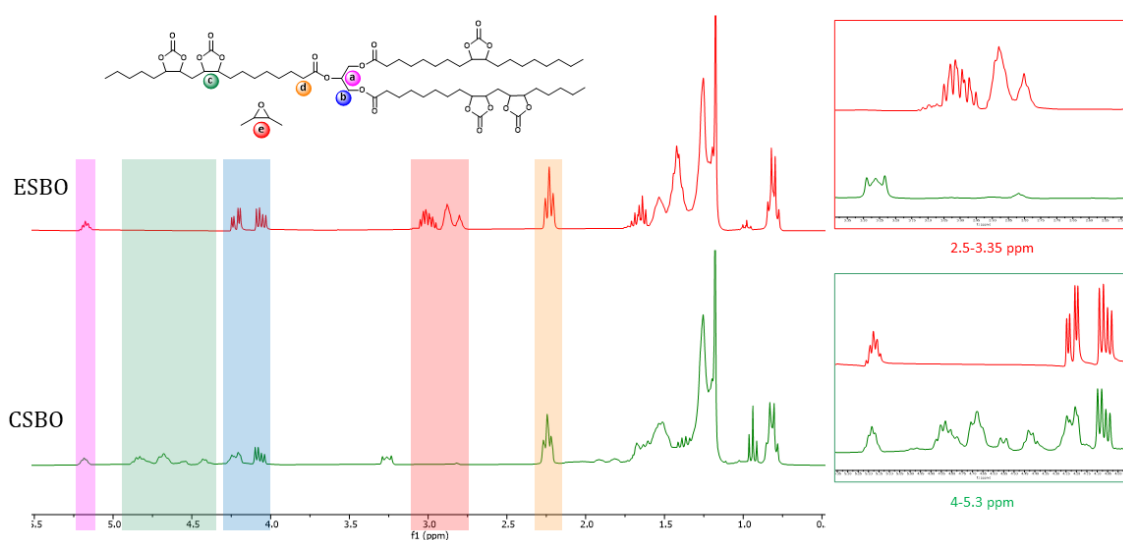


Figure 4.2 ^1H NMR spectra of epoxidized soybean oil (ESBO) and carbonated soybean oil (CSBO).

Likewise, **Figure 4.3** presents a series of stacked ^1H NMR spectra that monitor the progression of the cycloaddition reaction, tracking the conversion of ESBO to CSBO over time. The spectral changes mentioned above are clearly observable in this figure. Specifically, there is a notable decrease and eventual disappearance of the signal at 3.0 ppm, which is assigned to the epoxide moiety, confirming its consumption during the CO_2 utilization reaction. Conversely, the formation and

increasing intensity of characteristic signals around 4.2 ppm, corresponding to the protons of the cyclic carbonate, become evident as the reaction proceeds, highlighting the incorporation of CO₂.

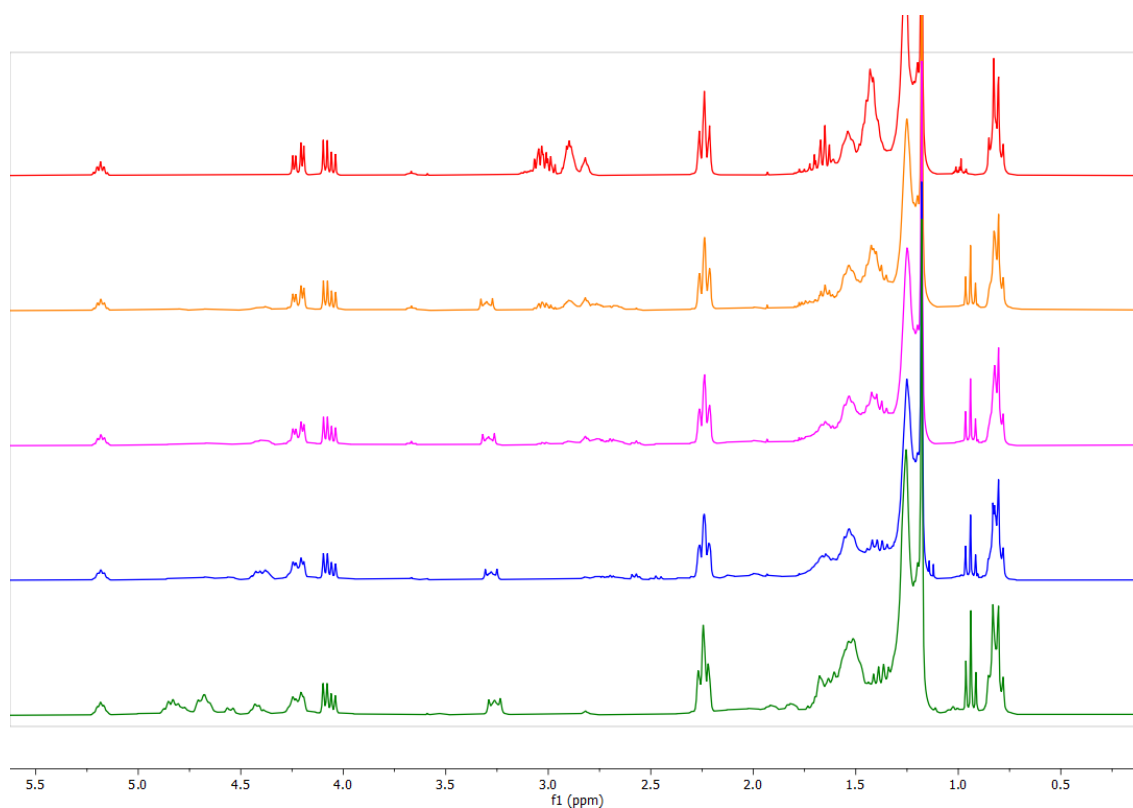


Figure 4.3 Stacked ¹H NMR spectra of ESBO and CSBO during CO₂ fixation reaction.

Moreover, ¹³C NMR spectroscopy was performed, and the spectra are shown in **Figure 4.4**. A new signal detected at 153.8 ppm is ascribed to the carbonyl carbon in the cyclic carbonate. Additionally, the signals at 53 ppm in the ESBO spectrum were shifted to 78–81 ppm in the CSBO spectrum, consistent with the conversion of epoxy groups in ESBO to cyclic carbonate moieties.

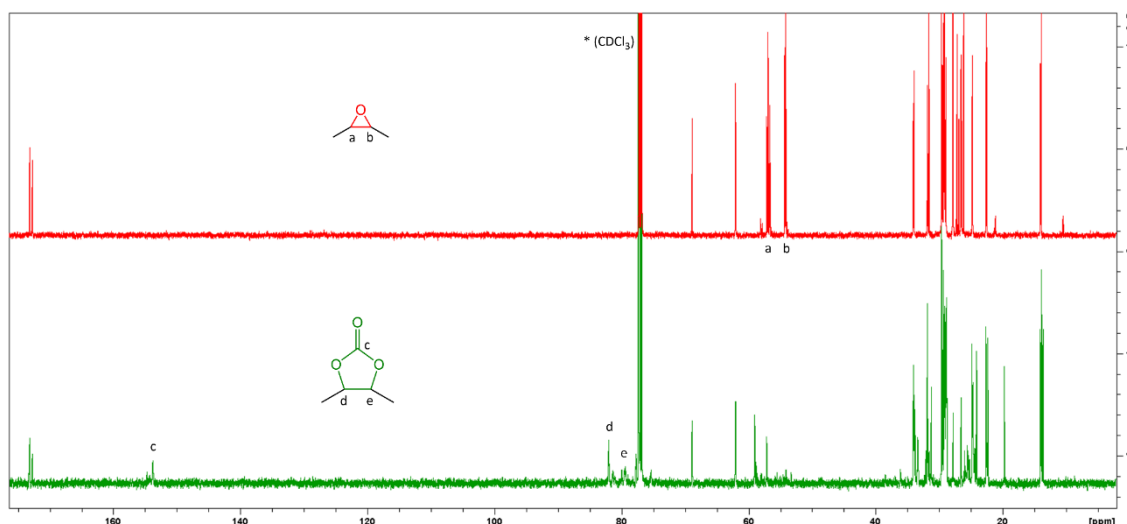


Figure 4.4 ^{13}C NMR spectra of epoxidized soybean oil (ESBO) and carbonated soybean oil (CSBO).

For further investigation, epoxy content, gel permeation chromatography (GPC) measurements, and viscosity analysis, were performed on initial epoxide and carbonated oils at various time points during the cycloaddition procedure, and the results are presented in **Table 4.1**.

The epoxy value of the oils was determined by titration based on the ASTM-D1652 method. The results clearly demonstrate a decrease in epoxy values as the epoxy groups were consumed during the conversion reaction.

GPC measurements (eluent: THF) revealed a slight and continuous increase in the molecular weight of carbonated oils, consistent with the incorporation of CO_2 into the epoxy groups. Additionally, viscosity analysis provided further evidence of the carbonation reaction, showing a significant increase in the product viscosity throughout the fixation of CO_2 into the epoxide moieties. **Figure 4.5** provides a detailed graphical representation of the epoxide group consumption and the subsequent increase in viscosity during the CO_2 cycloaddition reaction.

Table 4.1 Characteristics of carbonated soybean oil (CSBO) at various reaction times compared to initial epoxidized soybean oil (ESBO) during the progress of the CO_2 cycloaddition reaction.

Entry	Reaction time (h)	Epoxy content * (mol/kg)	η ** (Pa.s)	Mw *** (g/mol)	Mn *** (g/mol)	$\bar{D}$ *** (Mw/Mn)
1	0	4.39	0.413	1517	1326	1.144
2	23	2.13	4.627	1588	1380	1.151
3	46	1.66	10.039	1655	1418	1.167
4	70	0.67	16.869	1737	1490	1.166

* Determined by titration (ASTM-D1652)

** Measured by rheometer

*** Obtained by GPC

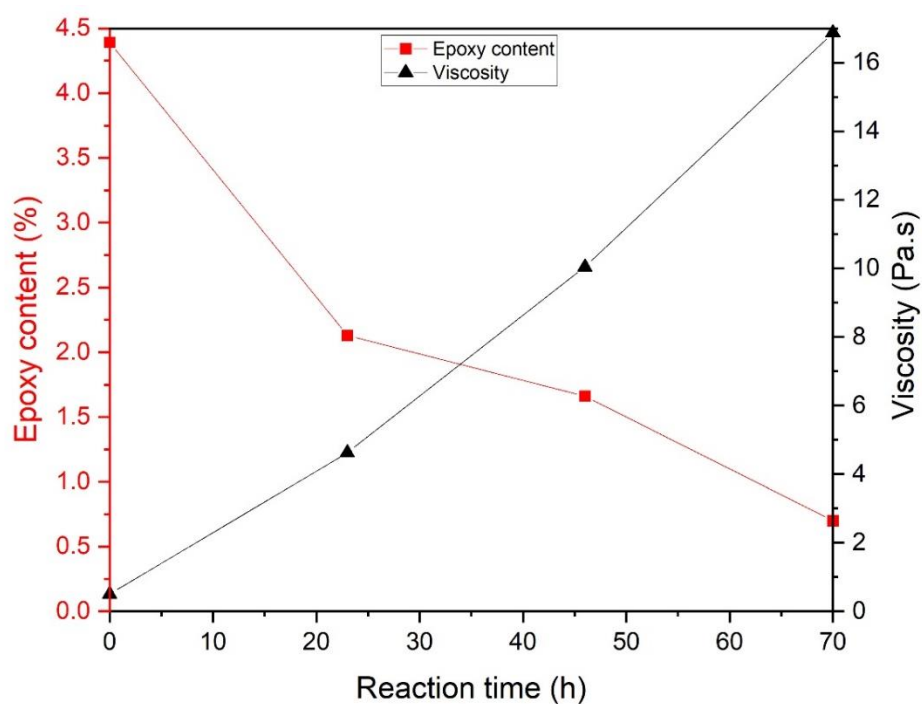


Figure 4.5 Time-dependent variation of epoxy content and viscosity of carbonated soybean oil during the CO₂ cycloaddition reaction.

Finally, the structural changes in the soybean oil compound before and after the CO₂ cycloaddition reaction were further investigated using high-resolution mass spectrometry. As demonstrated in **Figure 4.6**, the ESBO mass spectrum exhibited a characteristic pattern with mass differences of 28 m/z units, corresponding to two methylene groups (-CH₂CH₂-) in the fatty acid chains.

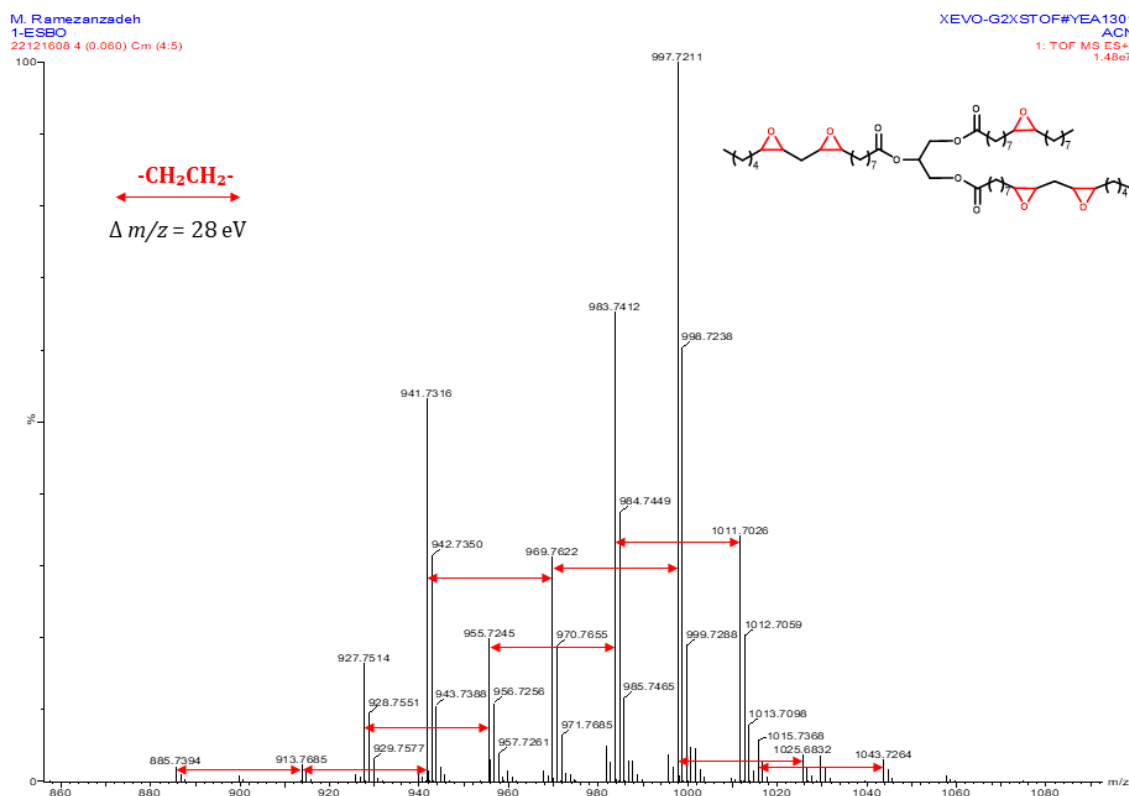


Figure 4.6 ESI-mass spectroscopy of ESBO.

In contrast, the CSBO mass spectrum revealed a shift towards higher m/z values, providing additional evidence for the chemical modification and increased molecular mass resulting from the CO_2 insertion reaction. This observation aligns with the formation of cyclic carbonates through the reaction of CO_2 with the epoxide rings.

Notably, new signals appeared in the CSBO spectrum with mass differences of 44 m/z units, consistent with the incorporation of CO_2 molecules. Simultaneously, several major isomeric signals present in the ESBO spectrum (e.g., m/z 997, 1011, 1025, 1039) were no longer detectable in the CSBO spectrum, indicating their transformation during the reaction (**Figure 4.7**).

These mass spectral changes offer valuable insights into the molecular alterations occurring in soybean oil during the CO_2 cycloaddition reaction. The HRMS results corroborate the findings from previous analytical techniques, providing a

comprehensive understanding of the carbonation process and its effects on the oil's structure.

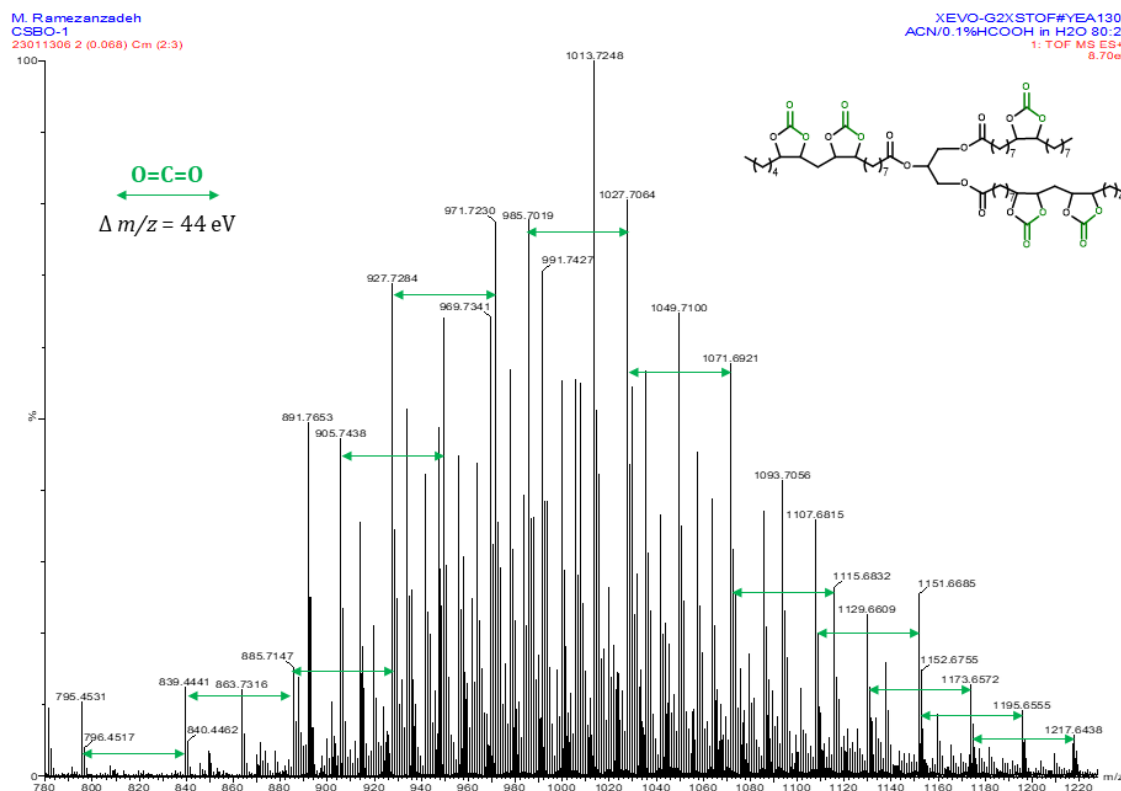


Figure 4.7 ESI-mass spectroscopy of CSBO.

In the batch method under reflux conditions, a substantial quantity (200 g) of epoxide compounds was loaded, yielding 82-91% based on epoxy content titration, with the reaction completing over approximately 70 hours at ambient CO_2 pressure. In contrast, the autoclave method, limited by container capacity, utilized 5 g of epoxide compounds and achieved a 90-95% yield within 24 hours under 20 bar CO_2 pressure. Notably, larger autoclaves have not yet been employed for the synthesis of cyclic products, which may offer opportunities for improved yields and efficiency in future experiments.

Likewise, the cycloaddition reaction was conducted on epoxidized linseed oil (ELO) under the same conditions, and the same characterizations were performed. As both ESBO and ELO are bio-based oils, their fundamental structures share many

similarities. Consequently, the FT-IR and NMR spectroscopic analyses of the cyclic carbonated linseed oil (CLO) yielded results comparable to those observed for CSBO.

The primary distinction between these two oils lies in their fatty acid composition. Linseed oil naturally contains a higher proportion of polyunsaturated fatty acids, particularly α -linolenic acid, compared to soybean oil. This higher degree of unsaturation in linseed oil results in a greater epoxy content per molecule in ELO relative to ESBO following epoxidation. Consequently, ELO possesses more reactive sites per molecule than ESBO, allowing for increased CO_2 incorporation during the cycloaddition reaction.

This increased functionality has notable effects on the product properties. Specifically, the viscosity of CLO is substantially higher than that of CSBO, primarily due to the greater number of cyclic carbonate groups formed per molecule.

Table 4.2 presents comparative data on the epoxy content, molecular weights, and viscosity of CLO at various stages of the reaction. The viscosity of the final cyclic carbonated linseed oil could not be determined due to its extremely high viscosity, which exceeded the measurable range of the available instrumentation. Consequently, this value is reported as "N/A".

Table 4.2 Characteristics of carbonated linseed oil (CLO) at various reaction times compared to initial epoxidized linseed oil (ELO) during the progress of the CO_2 cycloaddition reaction.

Entry	Reaction time (h)	Epoxy content * (mol/kg)	η ** (Pa.s)	Mn *** (g/mol)	Mw *** (g/mol)	$\bar{D}$ *** (Mw/Mn)
1	0	5.52	1.090	1062	1218	1.147
2	23	2.98	11.937	1178	1430	1.215
3	46	1.80	40.837	1276	1537	1.204
4	70	0.80	N/A	1383	1670	1.207

* Determined by titration (ASTM-D1652)

** Measured by rheometer

*** Obtained by GPC

Similarly, CO₂ fixation into the epoxidized oils was conducted using the same catalytic systems in an autoclave reactor, and identical characterizations were performed. The results confirmed the formation of cyclic carbonates. The primary difference in this method was the use of higher CO₂ pressure, which allowed the reaction to proceed in a more controlled system and at a significantly faster rate.

Furthermore, the CO₂ utilization reaction was conducted on an epoxysiloxane compound, specifically epoxypropoxypropyl-terminated polydimethylsiloxane (E-PDMS), which contains siloxane in its backbone and is terminated with epoxy rings. This class of compounds is particularly well-suited for applications such as coatings due to their silicone-derived nature. The schematic representation of this reaction to obtain bis-cyclic carbonate polydimethylsiloxane (CC-PDMS) was previously illustrated in **Figure 3.2**.

Figure 4.8 presents the FT-IR spectra of the initial epoxide-containing component (E-PDMS) and its cyclic carbonate derivative (CC-PDMS) following the incorporation of CO₂. The emergence of a strong, characteristic band at 1787 cm⁻¹, attributable to the C=O stretching vibration of the cyclic carbonate group, provides compelling evidence for the successful formation of cyclic carbonate moieties from the epoxysiloxane compound during the CO₂ utilization reaction.

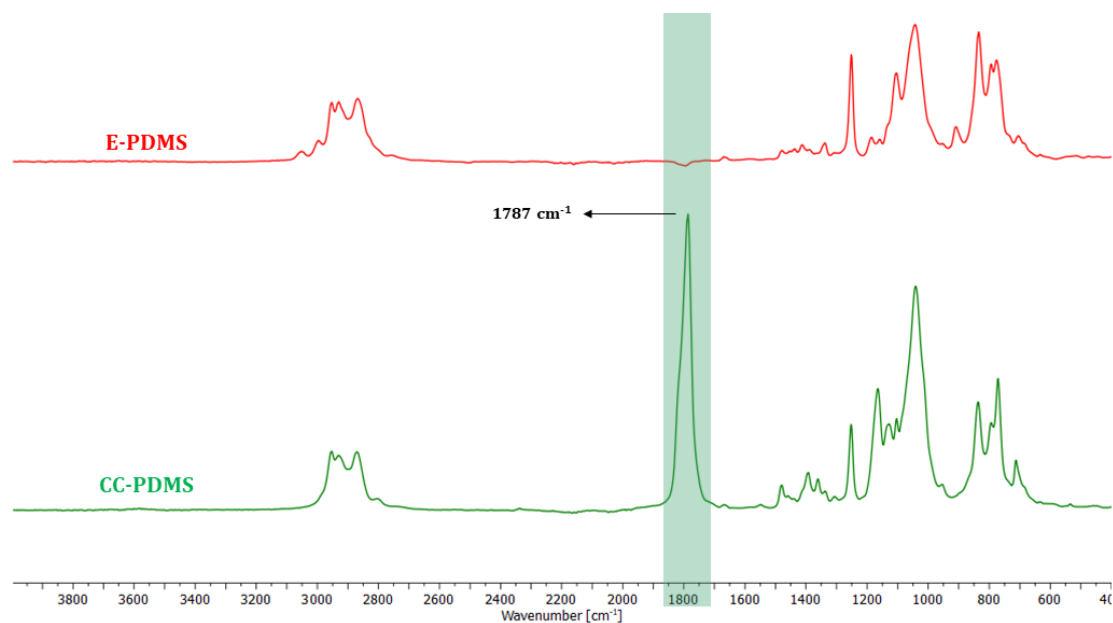


Figure 4.8 FT-IR spectra of E-PDMS and CC-PDMS following CO₂ incorporation.

NMR spectra of the compounds were also recorded, which further confirmed the formation of the cyclic carbonate groups. As illustrated in **Figure 4.9**, the ¹H NMR of the compounds shows the disappearance of signals at 2.5-2.8 ppm corresponding to oxirane moieties and the appearance of new signals at 4.3-4.8 ppm assigned to the cyclic carbonate groups, providing additional evidence for the fixation of CO₂ into the E-PDMS.

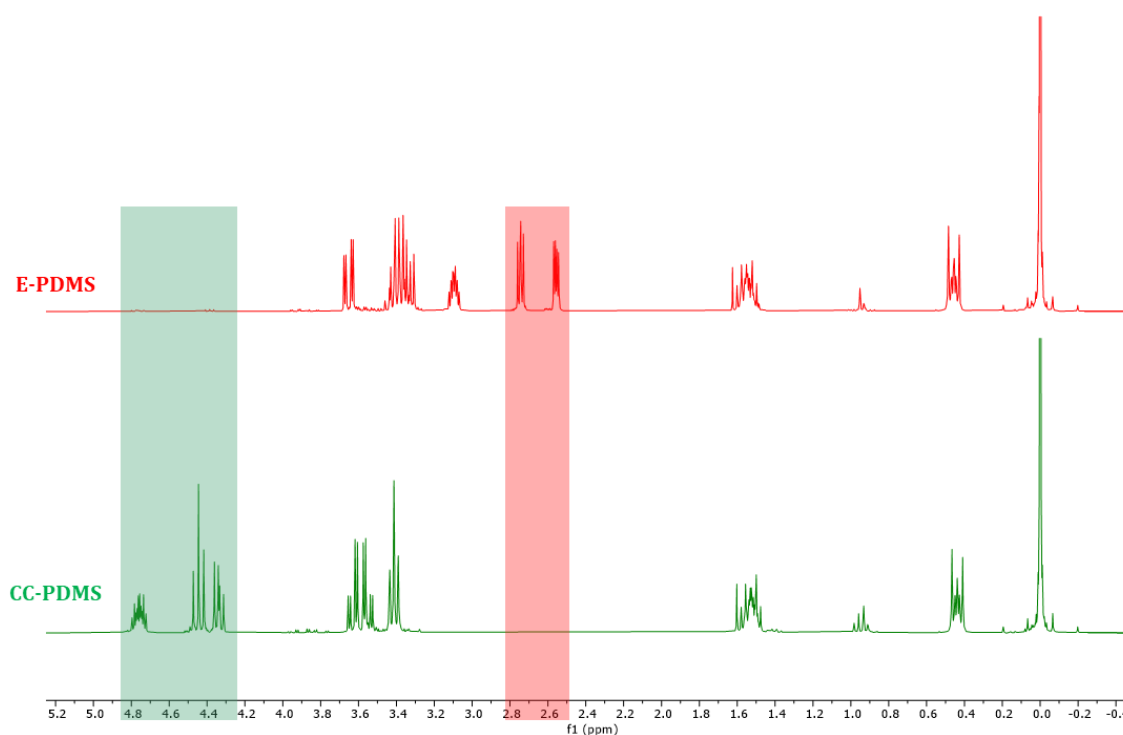


Figure 4.9 ^1H NMR spectra of E-PDMS and CC-PDMS.

Similarly, the ^{13}C NMR spectra reveal a new signal at 155 ppm, which corresponds to the newly formed carbonyl group in CC-PDMS (**Figure 4.10**). In addition, the signals originally observed at 77-80 ppm in E-PDMS shifted to 85-90 ppm in the CC-PDMS spectrum, further corroborating the structural changes resulting from CO_2 incorporation.

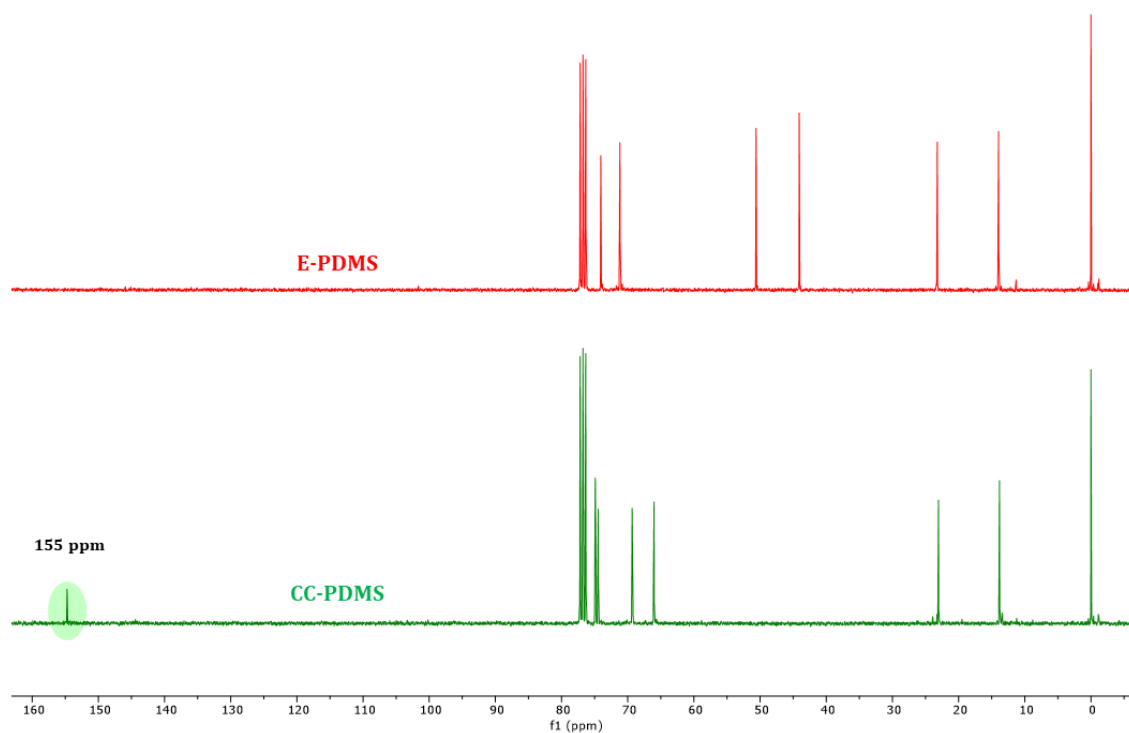


Figure 4.10 ^{13}C NMR spectra of E-PDMS and CC-PDMS.

These spectroscopic analyses collectively provide comprehensive evidence for the successful conversion of E-PDMS to CC-PDMS through CO_2 fixation, demonstrating the efficiency of this approach for CO_2 utilization in epoxy-siloxane compounds.

4.2 Poly imidazolium-based ionic liquids (PIMs)

The Debus-Radziszewski reaction, a well-established multi-component reaction, has gained significant attention in the field of green chemistry due to its potential for synthesizing imidazoles, which are valuable compounds in biomedical applications and pharmaceutical development. This study explores the versatility and eco-friendly aspects of this reaction, with a particular focus on its modified versions that enhance its utility and environmental compatibility.

The classical Debus-Radziszewski reaction involves the condensation of a dicarbonyl compound, an aldehyde, and two equivalents of ammonia to form an imidazole ring. However, recent modifications to this reaction have expanded its scope and improved its efficiency. One notable modification is the use of various amines in place of ammonia, which not only diversifies the range of obtainable imidazole derivatives but also allows for the reaction to proceed in aqueous media. This adaptation aligns well with the principles of green chemistry by reducing the use of organic solvents and improving atom economy.

The ability to perform this reaction in water represents a significant advancement in terms of green chemistry principles. Water as the reaction medium not only reduces the environmental impact of the synthesis but also potentially simplifies purification procedures and improves overall yields. Moreover, since water is the only by-product in this modified reaction, the separation of the desired products from the reaction mixture is facilitated, particularly in the case of polymeric products.

The synthesis procedure for this modified Debus-Radziszewski reaction was previously illustrated in **Figure 3.3**. In this research, a variety of precursors were employed, including diamines, dicarbonyls, aldehydes, and acids, to investigate the reaction's versatility and to optimize the synthesis conditions. The successful formation of the imidazolium ring was effectively confirmed through FT-IR and NMR spectroscopy.

Figure 4.11 displays the FT-IR spectrum of the synthesized PIM C6 AcO, revealing distinct absorption bands characteristic of both the imidazolium cation ring and the acetate counter-anion. The spectrum exhibits a prominent band at 1392 cm^{-1} , which

can be attributed to the C–N stretching vibrations of the imidazolium ring to the symmetric stretching. Additionally, a band observed at 1164 cm^{-1} is likely associated with C–C stretching vibrations in the polymer backbone and alkyl chains. A strong absorption band at 1559 cm^{-1} is noteworthy and can be assigned to the C–O stretching vibration of the acetate counter-anion.

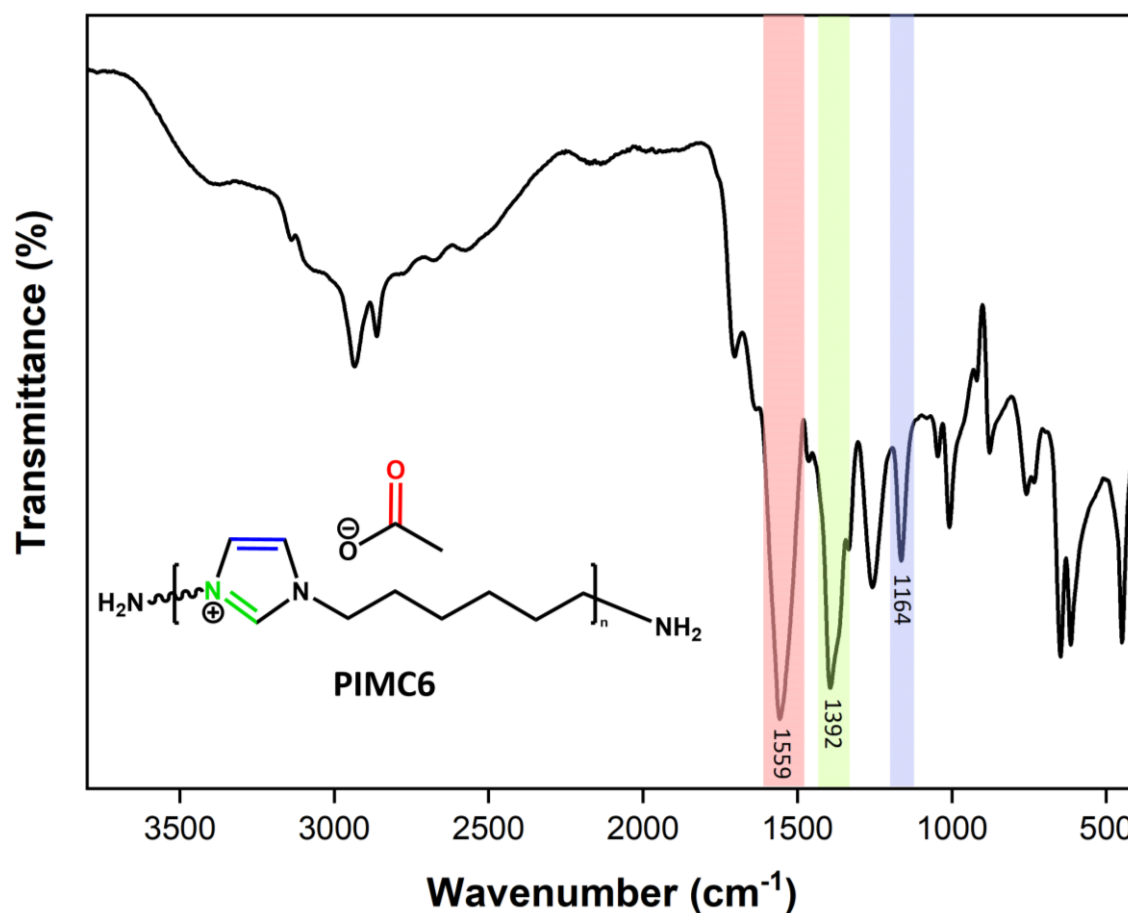


Figure 4.11 FT-IR spectrum of PIM C6 AcO.

These characteristic spectral features were consistently observed across all synthesized PIM products containing acetate counter-anions, confirming the successful formation of imidazolium rings and incorporation of acetate anions in these compounds.

In contrast, the FT-IR spectra of PIMs synthesized with chloride counter-anions exhibited the characteristic imidazolium ring vibrations, but notably lacked the distinctive bands associated with the acetate anion. Specifically, the absence of the

strong carboxylate stretching band around 1557 cm^{-1} provides compelling evidence for the successful incorporation of chloride as the counter-anion in these products.

The consistent presence of imidazolium-related signals across all synthesized PIMs, regardless of the counter-anion, further corroborates the successful implementation of our synthetic strategy in formation a diverse range of poly(imidazolium) based ionic liquids.

Likewise, the formation of the imidazolium ring structure in the synthesized PIM compounds was further confirmed by NMR spectroscopy. As depicted in **Figure 4.12**, the ^1H NMR spectrum of PIM C4 AcO shows characteristic signals corresponding to the imidazolium ring and the acetate counter-anion, consistent with those reported in the literature.

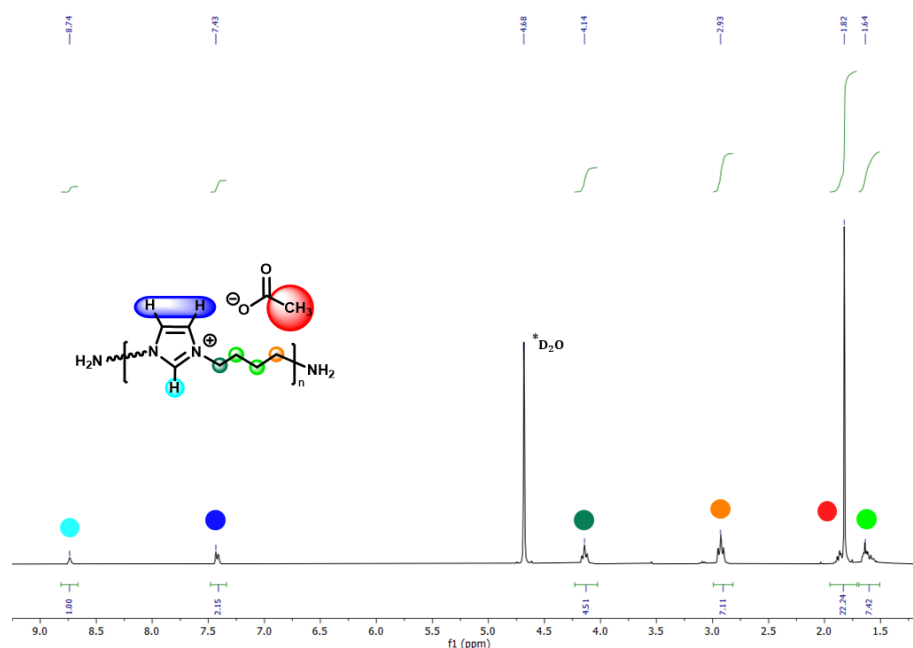


Figure 4.12 ^1H NMR spectroscopy of PIM C4 AcO.

In the ^1H NMR spectra (recorded in D_2O), the PIM compounds, including PIM C4 AcO, PIM C6 AcO, PIM Lys AcO, PIM Si AcO, PIM E AcO, and PIM Gln AcO, signals at approximately 8.7 ppm (1H) and 7.4 ppm (2H) are attributed to the imidazolium ring. Additionally, a signal at 1.9 ppm is assigned to the acetate counter-anion.

Furthermore, the ^{13}C NMR spectra of the aforementioned PIM compounds exhibited signals corresponding to the imidazolium ring carbons at around 135 and 122 ppm,

while the signals for the acetate counter-anion were observed at 180 and 22 ppm. **Figure 4.13** illustrates the ^{13}C NMR spectrum of PIM C4 AcO and PIM C6 AcO. These characteristic signals of the imidazolium ring and acetate counter-anion confirm the successful formation of the mentioned PIMs.

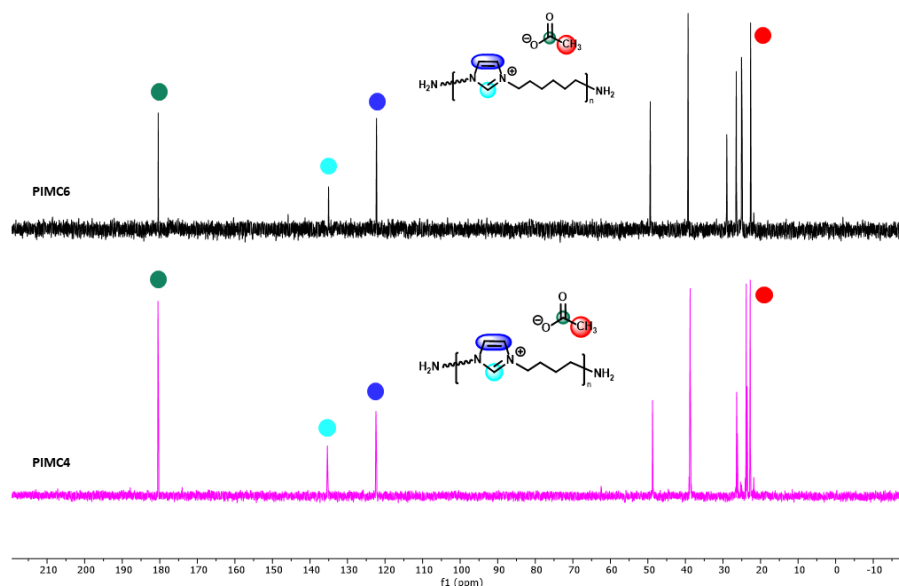


Figure 4.13 ^{13}C NMR spectra of PIMC4 AcO and PIM C6 AcO.

In contrast, for compounds with chloride counter-anions, such as PIM C4 Cl, PIM C6 Cl, PIM Lys Cl, and PIM Si Cl, the signals related to the imidazolium ring were still detectable (8.7 ppm and 7.4 ppm in ^1H NMR, and 135 and 122 ppm in ^{13}C NMR), whereas the absence of signals corresponding to the acetate counter-anion is another indication of the difference in the counter-anion composition.

For the compound PIM C4b AcO, where methyl glyoxal was used instead of glyoxal as the dicarbonyl component in the Debus-Radziszewski reaction to form the imidazolium ring, the characteristic signals of the imidazolium ring and the acetate counter-anion were still detectable, similar to PIM C4 AcO. However, the signal at 7.4 ppm contained 1H, due to the presence of a methyl group in the imidazolium ring, originating from methyl glyoxal, which appears at 2.0 ppm (3H). Additionally, in the ^{13}C NMR, an extra signal related to the methyl group is detectable at 140 ppm.

For the compound PIM C4c AcO, where dimethyl glyoxal was used instead of glyoxal, the signal at 8.7 ppm (1H) assigned to the imidazolium ring remains observable, but the signal at 7.5 ppm was absent due to the presence of two methyl groups from dimethyl glyoxal. Instead, signals corresponding to the methyl groups appeared at 4 ppm (3H) and 5 ppm (3H). Furthermore, in the ^{13}C NMR, compared to PIM C4 AcO, the signal at 130 ppm was no longer present, and two additional signals related to the dimethyl groups were detected at 59 and 64 ppm.

For the compound PIM C4d AcO, where acetaldehyde was used instead of formaldehyde as the aldehyde component in the imidazolium ring formation, the signal at 8.7 ppm (1H) was no longer detectable due to the presence of the methyl group from acetaldehyde. This methyl group's signal was observable at 2.0 ppm (3H). The remaining signals of the imidazolium ring were observable at 7.5 ppm (2H), similar to PIM C4 AcO. Likewise, the signal in the ^{13}C NMR at 135 ppm for the imidazolium ring had shifted to 60 ppm due to the presence of the methyl group from acetaldehyde.

The specific ^1H and ^{13}C NMR spectra for each compound are provided in the Supplementary Information section, supporting the comprehensive characterization of the diverse set of poly(imidazolium) ionic liquid polymers reported in this study.

Moreover, the Debus-Radziszewski reaction, as reported in the literature, adheres to the fundamental principles of A2 + B2 step-growth polymerization. Consequently, alterations in monomer stoichiometry are expected to significantly impact the molecular weight of the resulting polymer. This relationship is rooted in the fact that the balance between the A2 and B2 monomers directly affects the degree of polymerization. An imbalance in the stoichiometry can lead to variations in the molecular weight, as it alters the reactivity of the functional groups involved in the polymerization process.

To investigate this effect, various molar ratios of starting materials, including diamines and carbonyl monomers (glyoxal and formaldehyde), were employed to synthesize PIM C4 AcO and PIM C6 AcO. **Tables 4.3** and **4.4** summarize the number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) for PIM C4 AcO and PIM C6 AcO, respectively, at each

specific amine/carbonyl molar ratio. This analysis was performed using aqueous GPC measurements, with the eluent comprising 80% aqueous acetate buffer (pH 4.5) and 20% methanol.

According to the literature, an excess of the carbonyl-containing component (amine:carbonyl < 1.0) results in an increase in the molecular weight of the PIM compared to the equimolar ratio (amine:carbonyl = 1.0).⁸⁸ For instance, at a molar ratio of 0.8, average Mw of 276,540 and 223,260 g/mol were measured for PIM C4 AcO and PIM C6 AcO, respectively. Likewise, the high polydispersity index (PDI) observed at this molar ratio can be attributed to the lower concentration of the amine precursor compared to the carbonyls present in the formulation.

In contrast, as expected and consistent with reported findings, an excess of diamine (molar ratio > 1.0) leads to a reduction in the molecular weight of the synthesized PIMs. To further explore this relationship, the molecular weights of PIM C4 AcO and PIM C6 AcO with amine:carbonyl molar ratios of 1.2, 1.4, 1.6, 1.8, 2.0, and 2.2 were determined by aqueous GPC.

Table 4.3 Molecular weight characteristics of PIM C4 AcO at various molar ratios.

Entry	Compound	Molar ratio	Mn (g/mol)	Mw (g/mol)	Đ
1	PIM C4 AcO	0.8	27245	276540	10.15
2		1.0	13442	39577	2.94
3		1.2	7982	17007	2.1
4		1.4	6587	12587	1.91
5		1.6	5799	9167	1.58
6		1.8	5411	8410	1.55
7		2.0	5057	7805	1.54

8	2.2	4763	7380	1.54
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Table 4.4 Molecular weight characteristics of PIM C6 AcO at various molar ratios.

Entry	Compound	Molar ratio	Mn (g/mol)	Mw (g/mol)	Đ
1	PIM C6 AcO	0.8	19862	223260	11.24
2		1.0	14725	73404	4.98
3		1.2	8387	18018	2.14
4		1.4	7064	12600	1.78
5		1.6	6114	10344	1.69
6		1.8	5612	8712	1.55
7		2.0	5695	8680	1.52
8		2.2	5322	8261	1.55

Table 4.5 Molecular weight characteristics of various PIMs at a molar ratio of 1.0.

Entry	Compound	Molar ratio	Mn (g/mol)	Mw (g/mol)	Đ
1	PIM E AcO	1.0	14673	43787	2.984
2	PIM Si AcO	1.0	6240	38160	6.116
3	PIM Lys AcO	1.0	3155	4261	1.351
4	PIM Gln AcO	1.0	1710	1932	1.129
5	PIM C4 Cl	1.0	2765	4212	1.523
6	PIM C6 Cl	1.0	2797	4247	1.518

7	PIM Lys Cl	1.0	1683	1743	1.035
8	PIM Si Cl	1.0	2071	2577	1.244
9	PIM C4b AcO	1.0	6956	59105	8.496
10	PIM C4c AcO	1.0	7574	41309	5.453
11	PIM C4d AcO	1.0	7327	92370	12.605

The solubility characteristics of the synthesized poly(imidazolium)-based ionic liquids were investigated in a diverse array of solvents at ambient temperature ($25^{\circ}\text{C} \pm 1^{\circ}\text{C}$). **Table 4.6** summarizes the solubility data for PIMC4 AcO and PIMC6 AcO at a concentration of 0.1 wt%. Both compounds demonstrated significant solubility in protic polar solvents, including water and lower alcohols such as ethanol (EtOH) and 1-propanol (1-PrOH), with rapid dissolution kinetics. Additionally, solubility was observed in ethylene glycol (EG). In contrast, in aprotic polar solvents such as *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), the dissolution process occurred at a notably slower rate; however, complete solubility was achieved without the necessity for elevated temperatures. The compounds exhibited insolubility in a range of less polar and non-polar solvents, including acetone, acetonitrile (MeCN), tetrahydrofuran (THF), 1,4-dioxane, diethyl ether (Et₂O), ethyl acetate (EtOAc), chloroform (CHCl₃), benzene, toluene, and pyridine. This solubility profile strongly suggests that the ionic character of the poly(imidazolium) compounds significantly influences their solvation behavior, favoring interactions with solvents of high polarity and hydrogen-bonding capability.

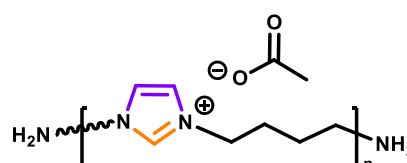
Table 4.6 Solubility profile of PIM C4 AcO and PIM C6 AcO in various solvents.

Compound	H ₂ O	EtOH	1-PrOH	EG	Acetone	MeCN	THF	Dioxane	Et ₂ O	EtOAc	CHCl ₃	DMF	DMSO	Benzene	Toluene	Pyridine
PIMC4 AcO	+	+	+	+	-	-	-	-	-	-	-	+	+	-	-	-
PIMC6 AcO	+	+	+	+	-	-	-	-	-	-	-	+	+	-	-	-

(+) Soluble at 0.1 wt%; (-) Insoluble at 0.1 wt%

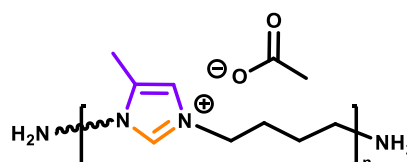
PIM C4 AcO:

¹H NMR (300 MHz, Deuterium Oxide) δ 8.84 (s, 1H), 7.54 (s, 2H), 4.30 – 4.19 (m, 4H), 3.06 – 3.01 (m, 4H), 1.93 (s, 14H), 1.87 – 1.62 (m, 8H). **¹³C NMR** (75 MHz, Deuterium Oxide) δ 180.48, 135.36, 122.43, 48.78, 38.75, 26.37, 23.82, 22.76. **FT-IR** 3099.30, 2962.69, 1559.85 (C=O acetate), 1394.69 (C-N imidazolium ring), 1258.07 (C-O acetate), 1160.20 (C=C imidazolium), 1009.31, 750.36, 644.33, 613.74, 448.58.



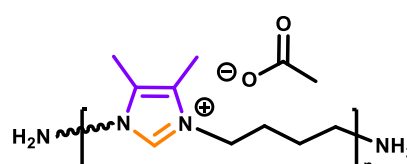
PIM C4b AcO-1.0:

¹H NMR (500 MHz, Deuterium Oxide) δ 8.72 (s, 1H), 7.26 (s, 1H), 4.20 – 4.14 (m, 4H), 3.16 – 2.79 (m, 4H), 2.33 – 2.27 (m, 3H), 1.95 (s, 14H), 1.93 – 1.81 (m, 4H), 1.79 – 1.65 (m, 4H). **¹³C NMR** (126 MHz, D₂O) δ 179.6, 134.6, 132.0, 119.2, 48.6, 45.9, 38.8, 26.1, 23.8, 22.2, 8.1. **FT-IR** 3138.04, 2962.69, 1557.81 (C=O acetate), 1398.76 (C-N imidazolium ring), 1262.15 (C-O acetate), 1154.08 (C=C imidazolium), 1046.01, 1013.39, 654.52, 619.86.



PIM C4c AcO-1.0:

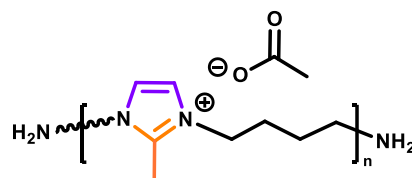
¹H NMR (500 MHz, Deuterium Oxide) δ 8.63 (s, 1H), 4.25 – 3.98 (m, 4H), 3.08 – 2.97 (m, 3H), 2.23 (d, J =



9.5 Hz, 7H), 1.94 (s, 10H), 1.91 – 1.79 (m, 4H), 1.78 – 1.60 (m, 4H). **¹³C NMR** (126 MHz, D₂O) δ 179.9, 133.1, 127.2, 72.0, 62.5, 46.0, 38.8, 26.1, 23.8, 22.4, 7.4. **FT-IR** 3152.32, 2930.06, 1631.21, 1557.81 (C=O acetate), 1398.76 (C-N imidazolium ring), 1262.15 (C-O acetate), 1200.98, 1046.01, 1011.35, 654.52, 619.86.

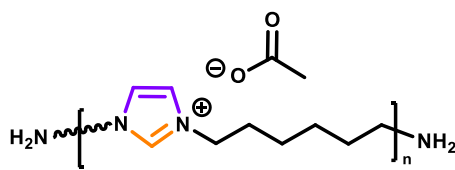
PIM C4d AcO-1.0:

¹H NMR (500 MHz, Deuterium Oxide) δ 7.54 (s, 1H), 7.42 (s, 1H), 4.28 – 4.22 (m, 2H), 4.20 – 4.15 (m, 2H), 3.04 (s, 3H), 2.78 – 2.52 (m, 4H), 1.94 (s, 36H), 1.76 – 1.74 (m, 8H). **¹³C NMR** (126 MHz, D₂O) δ 180.0, 170.7, 135.4, 122.4, 121.1, 49.1, 48.8, 47.3, 46.6, 38.8, 26.4, 26.0, 23.8, 22.5, 8.8. **FT-IR** 2934.14, 1637.33, 1543.53 (C=O acetate), 1398.76 (C-N imidazolium ring), 1268.27 (C-O acetate), 1168.36 (C=C imidazolium), 1046.01, 1013.39, 744.24, 654.52, 619.86.



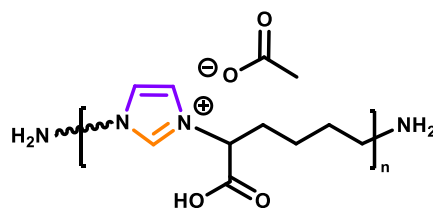
PIM C6 AcO:

¹H NMR (500 MHz, Deuterium Oxide) δ 8.72 (s, 1H), 7.60 – 6.90 (m, 2H), 4.21 – 4.12 (m, 4H), 3.07 – 2.99 (m, 3H), 2.33 – 2.26 (m, 3H), 1.95 (s, 16H), 1.88 – 1.82 (m, 2H), 1.80 – 1.63 (m, 4H). **¹³C NMR** (126 MHz, D₂O) δ 179.6, 134.6, 132.0, 119.2, 48.6, 45.9, 38.7, 26.1, 23.8, 22.2, 8.1. **FT-IR** 2936.18, 2862.78, 1559.85 (C=O acetate), 1390.61 (C-N imidazolium ring), 1258.07 (C-O acetate), 1162.24 (C=C imidazolium), 1007.27, 736.08, 644.33, 611.70, 446.54.



PIM Lys AcO:

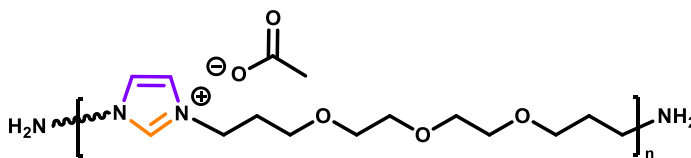
¹H NMR (500 MHz, Deuterium Oxide) δ 8.55 (s, 1H), 7.20 (s, 2H), 4.07 – 3.66 (m, 4H), 1.98 – 1.89 (m, 2H), 1.75 (s, 5H), 1.64 – 1.57 (m, 3H), 1.03 (s, 1H), 0.94 (s, 1H). **¹³C NMR** (126 MHz, D₂O) δ 176.8, 173.9, 135.6, 122.0, 90.5, 64.8, 62.5, 49.2, 31.3, 28.6, 22.1, 20.5. **FT-IR** 3099.30, 2930.06, 1727.04, 1618.98 (C=O



Lysine), 1561.88 (C=O acetate), 1508.87, 1390.61 (C-N imidazolium ring), 1211.17, 1162.24, 1054.17, 823.76, 736.08, 424.11.

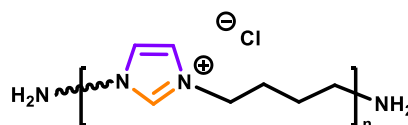
PIM E AcO-1.0:

¹H NMR (300 MHz, Deuterium Oxide) δ 8.85 (s, 1H), 7.54 (s, 2H), 4.41 – 4.26 (m, 4H), 3.68 (d, J = 8.4 Hz, 16H), 3.64 – 3.53 (m, 8H), 3.13 – 3.08 (m, 4H), 2.16 (t, J = 6.5 Hz, 3H), 1.94 (s, 14H). **¹³C NMR** (75 MHz, D₂O) δ 180.3, 135.5, 122.6, 69.3, 68.2, 67.0, 46.7, 37.5, 36.4, 29.1, 28.1, 26.5, 22.7, 21.8. **FT-IR** 3101.34, 2870.93, 1561.88 (C=O acetate), 1396.72 (C-N imidazolium ring), 1251.95 (C-O acetate), 1164.28 (C=C imidazolium), 1092.91 (C-O ether), 876.78, 760.55, 652.48, 617.82, 452.66.



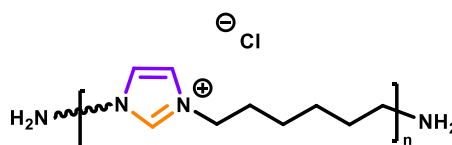
PIM C4 Cl-1.0:

¹H NMR (300 MHz, Deuterium Oxide) δ 8.84 (s, 1H), 7.49 (s, 2H), 4.26 – 4.21 (m, 4H), 3.03 (t, J = 7.8 Hz, 4H), 2.06 – 1.89 (m, 4H), 1.89 – 1.49 (m, 4H). **¹³C NMR** (75 MHz, D₂O) δ 135.4, 122.5, 90.4, 81.7, 71.3, 48.8, 42.5, 38.8, 26.4, 23.6, 22.3. **FT-IR** 3360.30, 2932.10, 1733.16, 1610.82, 1561.88, 1510.91, 1451.78, 1360.02, 1335.55, 1160.20, 1088.83, 838.03, 752.40, 634.13, 483.25.



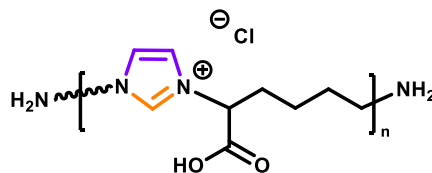
PIM C6 Cl-1.0:

¹H NMR (300 MHz, Deuterium Oxide) δ 8.77 (s, 1H), 7.48 (s, 2H), 4.63 (s, 2H), 4.17 (s, 2H), 2.98 (d, J = 7.4 Hz, 4H), 1.84 (q, J = 7.2 Hz, 4H), 1.68 – 1.59 (m, 8H), 1.41 – 1.34 (m, 8H). **¹³C NMR** (75 MHz, D₂O) δ 135.1, 122.3, 104.3, 99.0, 98.4, 90.4, 81.7, 71.2, 49.4, 43.1, 39.4, 29.0, 26.4, 25.0. **FT-IR** 2932.10, 2860.74, 1735.20, 1610.82, 1561.88, 1508.87, 1459.93, 1357.98, 1333.52, 1160.20, 1088.83, 840.07, 734.05, 636.17, 493.44.

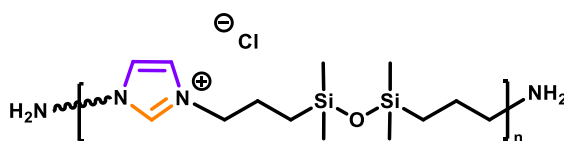


PIM Lys Cl-1.0:

¹H NMR (400 MHz, Deuterium Oxide) δ 9.04 (s, 1H), 7.70 – 7.62 (m, 1H), 7.56 (s, 1H), 4.25 (s, 2H), 3.06 (t, J = 7.7 Hz, 4H), 2.02 (dd, J = 10.1, 5.9 Hz, 6H), 1.80 – 1.76 (m, 4H), 1.58 – 1.52 (m, 4H). **¹³C NMR** (101 MHz, D₂O) δ 172.2, 169.1, 122.5, 90.5, 60.3, 59.4, 52.9, 49.1, 46.6, 39.1, 31.1, 29.4, 26.4, 21.5. **FT-IR** 2925.99, 1731.12, 1606.74, 1502.75, 1211.17, 1166.32, 1058.25, 999.12, 734.05, 534.22.

**PIM Si Cl-1.0:**

¹H NMR (400 MHz, Deuterium Oxide) δ 8.82 (s, 1H), 7.55 – 7.50 (m, 2H), 4.24 – 4.20 (m, 4H), 3.15 (s, 0H), 3.02 (t, J = 7.4 Hz, 2H), 1.98 – 1.91 (m, 4H), 1.86 – 1.68 (m, 2H), 0.73 – 0.46 (m, 8H), 0.34 – -0.03 (m, 24H). **¹³C NMR** (101 MHz, D₂O) δ 176.3, 169.0, 135.3, 122.5, 90.6, 59.4, 52.3, 50.3, 47.2, 42.2, 23.6, 20.9, 19.6, 13.2. **FT-IR** 3350.10, 2954.53, 1627.13, 1561.88, 1445.66, 1413.04, 1349.83, 1251.95, 1164.28, 1043.98, 836.00, 787.06, 703.46, 632.09, 458.78.



4.3 Non-isocyanate polyurethanes (NIPUs)

The development of Non-Isocyanate Polyurethanes (NIPUs) represents a significant advancement in polymer science, offering an effective and promising route to generate urethane linkages without relying on traditional, potentially harmful precursors. This approach addresses several critical challenges associated with conventional polyurethane (PU) synthesis, positioning NIPUs as a green alternative with considerable potential for industrial application and environmental benefit.

In classical PU synthesis, the use of toxic isocyanates and phosgene has been a longstanding concern due to their hazardous nature. The NIPU methodology effectively eliminates the need for these hazardous compounds, representing a substantial enhancement in the safety profile of urethane production. Additionally, the NIPU approach aligns with the principles of green chemistry by reducing reliance on petroleum-derived feedstocks. By incorporating renewable resource-based materials, NIPU synthesis contributes to the broader goal of sustainability in polymer production. This transition from fossil fuel-dependent processes to more sustainable alternatives is essential in the context of global efforts to reduce carbon footprints and mitigate climate change.

Various pathways for the synthesis of NIPUs have been explored by researchers, as detailed in **Section 1.1** of this dissertation. Among these methods, the step-growth polyaddition reaction involving cyclic carbonates and amines as curing agents to produce polyhydroxyurethanes has emerged as a particularly efficient technique. This reaction pathway offers several advantages:

- 1. Reaction Efficiency:** The ring-opening reaction of cyclic carbonates with amines proceeds under milder conditions compared to traditional PU synthesis, often requiring lower temperatures and pressures.
- 2. Structural Diversity:** The variety of available cyclic carbonates and amines allows for the tailoring of NIPU properties to suit specific applications, offering a degree of versatility comparable to traditional PUs.
- 3. Enhanced Functionality:** The resulting polyhydroxyurethanes possess additional hydroxyl groups along the polymer backbone, which can impart

improved adhesion properties and opportunities for further functionalization.

- 4. Reduced Environmental Impact:** The absence of isocyanates and phosgene in this synthetic route significantly reduces the environmental and health risks associated with NIPU production.

During this doctoral study, NIPU products were synthesized through the reaction of carbonated soybean oil (CSBO) with two different amino-terminated poly(imidazolium)-based ionic liquids as curing agents: PIM C4 AcO 2.2 and PIM C6 AcO 2.2. The formation of NIPU compounds was confirmed through FT-IR spectroscopy. As illustrated in **Figure 4.14**, the FT-IR spectra of the NIPU compound demonstrated the consumption of the band associated with cyclic carbonates, typically observed around 1796 cm^{-1} , during the ring-opening of cyclic carbonates *via* reaction with the amine curing agent. The weak band remaining at this wavelength indicates a small portion of unreacted cyclic carbonates.

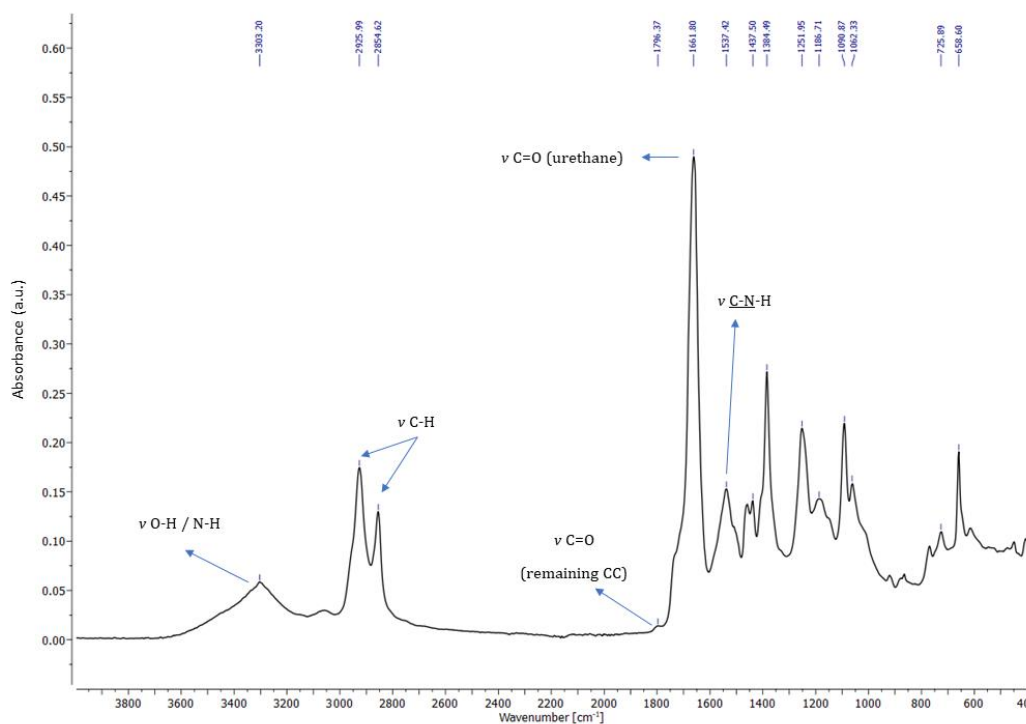


Figure 4.14 FT-IR spectrum of NIPU product.

Additionally, the appearance of a new band in the range of $3200\text{--}3400\text{ cm}^{-1}$, corresponding to the stretching vibrations of urethane O-H and N-H bonds, further confirms the successful reaction. This band was absent in the spectrum of CSBO, indicating the formation of urethane linkages. The stretching of the urethane carbonyl group was observed at 1661 cm^{-1} . Furthermore, the FT-IR spectrum of the NIPUs revealed additional bands indicative of other functionalities, including C-H stretching vibrations ($2800\text{--}3000\text{ cm}^{-1}$), a combination of C-N stretching and N-H out-of-plane bending vibration (1537 cm^{-1}), C-H bending vibrations ($1420\text{--}1450\text{ cm}^{-1}$), C-N stretching vibrations ($1350\text{--}1390\text{ cm}^{-1}$), and C-O stretching vibrations ($1000\text{--}1250\text{ cm}^{-1}$), all of which are related to urethane linkages.

To conduct mechanical stress-strain tests on the non-isocyanate polyurethane (NIPU) films, the films were cast into various molds and placed in an oven for the curing process. Unfortunately, the NIPU films exhibited strong adhesion to the molds, making it difficult to remove them after the curing process and preventing the execution of the mechanical tests. Molds made from PTFE, POM, and silicone, were tested in both dumbbell and rectangular shapes, but the removal of the films after casting remained unsuccessful.

Although the investigation of the adhesive properties of these NIPU films was not within the scope of this dissertation, the promising observations regarding their adhesiveness suggest that conducting such tests may be a valuable direction for future research.

Polyhydroxyurethanes derived from the reaction of CSBO with PIM C4 AcO 2.2 and PIM C6 AcO 2.2 were designated as NIPU-SB and NIPU-SH, respectively. Additionally, the amino-terminated polymeric curing agents (PIM C4 and PIM C6) were combined with commercially available diamines (butanediamine (BDA) and hexanediamine (HDA)) to synthesize the NIPUs, as previously detailed in **Tables 3.5** and **3.6**.

For instance, NIPU-SB25 represents a formulation for synthesizing polyhydroxyurethane through the reaction of CSBO with a combination of curing agents consisting of 25% PIM C4 and 75% BDA. This formulation exemplifies the synthesis of polyhydroxyurethane through the strategic selection of curing agents to achieve desired material properties.

The molecular weight of the synthesized NIPUs was analyzed using GPC. The eluent used for this analysis was N-methylpyrrolidone (NMP) containing 0.5 g/L of lithium bromide (LiBr) to enhance solubility and improve the resolution of the polymer fractions. The molecular weight characteristics of NIPUs are presented in **Table 4.7** for NIPU-SBs and **Table 4.8** for NIPU-SHs.

Table 4.7 Molecular weight characteristics of NIPU-SB compounds with varying ratios of PIM C4 to BDA curing agents.

Entry	Compound	Mn (g/mol)	Mw (g/mol)	Đ
1	NIPU-SB0	2840	5600	1.97
2	NIPU-SB5	1744	2718	1.56
3	NIPU-SB10	1660	2426	1.46
4	NIPU-SB25	1419	1875	1.32
5	NIPU-SB50	1710	2204	1.29
6	NIPU-SB75	1657	1887	1.14
7	NIPU-SB100	1595	1738	1.09

Table 4.8 Molecular weight characteristics of NIPU-SH compounds with varying ratios of PIM C6 to HDA curing agents.

Entry	Compound	Mn (g/mol)	Mw (g/mol)	Đ
1	NIPU-SH0	3526	9280	2.63
2	NIPU-SH5	1815	3090	1.70
3	NIPU-SH10	1539	2542	1.65
4	NIPU-SH25	1103	1591	1.44
5	NIPU-SH50	1358	2336	1.72

6	NIPU-SH75	1074	1446	1.35
7	NIPU-SH100	742	753	1.01

In addition, rheological characterization including amplitude sweep tests was performed on the synthesized NIPU products. For this purpose, the NIPUs were placed on the plate of a rheometer and subjected to controlled strain.

During the amplitude sweep test, the storage modulus (G') and loss modulus (G'') are plotted against strain amplitude at a constant frequency. This test is essential for understanding the viscoelastic properties of materials, as it provides insights into how the material behaves under varying strain conditions. The amplitude sweep allows for the determination of the linear viscoelastic region (LVR), where both G' and G'' remain relatively constant. Beyond this region, as the strain amplitude increases, a transition occurs where G' may begin to decrease while G'' increases, indicating a shift in behavior from solid-like to liquid-like characteristics.

The crossover point is a significant parameter within this context, marking the transition between elastic and viscous behavior of the material. Specifically, it is defined as the point where G' and G'' intersect and become equal at a specific value known as the crossover point. At this crossover point, the material exhibits a balance between its elastic and viscous responses, indicating a shift from predominantly elastic (solid-like) behavior to predominantly viscous (liquid-like) behavior. The strain at which this crossover occurs can provide valuable information about the material's resistance to flow and its structural stability under stress. For NIPUs, the presence and position of the crossover point can offer insights into the degree of crosslinking, the strength of intermolecular interactions, and the overall network structure of the polymer. Materials with a higher crossover point generally exhibit greater structural stability and resistance to flow, which can be beneficial for certain applications requiring enhanced mechanical properties.

The transition point is critical for evaluating the performance of synthesized NIPUs, as it aids in predicting processing behavior and optimizing mechanical properties based on varying curing agent ratios. In several samples, the crossover point was clearly observed within the shear stress range of 10^1 to 10^4 μNm . However, in

instances where the crossover point was not evident due to device limitations, estimates were derived through extrapolation of the G' and G'' curves. The amplitude sweep test results offer valuable insights into the rheological differences among NIPU formulations with varying curing agent ratios, enabling the optimization of mechanical properties for specific applications.

Table 4.9 Rheological properties of various NIPU-SBs at crossover point.

Entry	Compound	$G'=G''$ (Pa)	M (μNm)
1	NIPU-SB0	10300	5900
2	NIPU-SB5	170000	21000
3	NIPU-SB10	70000	18000
4	NIPU-SB25	100000	23000
5	NIPU-SB50	40000	8000
6	NIPU-SB75	91000	16000
7	NIPU-SB100	22000	9000

Table 4.10 Rheological properties of various NIPU-SHs at crossover point.

Entry	Compound	$G'=G''$ (Pa)	M (μNm)
1	NIPU-SH0	13000	6600
2	NIPU-SH5	24000	8400
3	NIPU-SH10	59500	11150
4	NIPU-SH25	27000	3700
5	NIPU-SH50	33400	5000
6	NIPU-SH75	41220	92780
7	NIPU-SH100	15660	6250

4.4 Hydrogels

The synthesized amino-terminated poly(imidazolium)-based ionic liquids (PIMs) have demonstrated remarkable versatility, serving not only as curing agents in the preparation of Non-Isocyanate Polyurethanes (NIPUs) but also as crosslinkers in the synthesis of two distinct types of hydrogels: poly(succinimide) (PSI) hydrogels and chitosan-based hydrogels. This broad applicability highlights the adaptability of these novel materials.

The development of PIM-crosslinked PSI and chitosan-based hydrogels aligns closely with sustainable chemistry principles, offering numerous environmental and practical benefits. By combining the unique properties of PIMs with the versatility of hydrogels, this research demonstrates the integration of sustainable chemistry principles into advanced materials development, potentially leading to eco-friendly, high-performance materials with broad applications in biomedicine and environmental remediation.

4.4.1 PSI Hydrogel

A diverse range of PIMs were employed as crosslinkers in the synthesis of PSI hydrogels, which were subsequently converted to poly(aspartic acid) (PASP) hydrogels through hydrolysis (refer to section 3.2.5 for comparison). The following PIMs were evaluated as potential crosslinkers: PIM C4 AcO, PIM C6 AcO, PIM E AcO, PIM Lys AcO, PIM Si AcO, PIM Gln AcO, PIM C4 Cl, PIMC6 Cl, PIM Lys Cl, PIM Si Cl, PIM C4b AcO, PIM C4c AcO, and PIM C4d AcO. **Table 4.11** provides comprehensive information about the synthesized hydrogels and the precursors of crosslinkers (PIMs). All tested PIMs successfully facilitated the synthesis of PSI hydrogels in a multigram scale, with the exception of the glutamine-based PIM (PIM Gln AcO).

Additionally, blank tests without PIMs were performed to confirm the role of PIMs as crosslinkers in the gelation process; no gel formation was observed in these control experiments, which validates the function of PIMs as essential structural components in the hydrogel network formation.

Table 4.11 Composition and gelation status of poly(succinimide) (PSI) hydrogels crosslinked with various amino-terminated poly(imidazolium)-based ionic liquids (PIMs).

Hydrogel	Crosslinker's ingredients				Status
	Diamine	Dicarbonyl	Aldehyde	Counter-anion	
Gel-1	BDA	Glyoxal	Formald.	AcO ⁻	Gelled
Gel-2	HDA	Glyoxal	Formald.	AcO ⁻	Gelled
Gel-3	E	Glyoxal	Formald.	AcO ⁻	Gelled
Gel-4	Lys	Glyoxal	Formald.	AcO ⁻	Gelled
Gel-5	Si	Glyoxal	Formald.	AcO ⁻	Gelled
Gel-6	Gln	Glyoxal	Formald.	AcO ⁻	NOT Gelled
Gel-7	BDA	Glyoxal	Formald.	Cl ⁻	Gelled
Gel-8	HDA	Glyoxal	Formald.	Cl ⁻	Gelled
Gel-9	Lys	Glyoxal	Formald.	Cl ⁻	Gelled
Gel-10	Si	Glyoxal	Formald.	Cl ⁻	Gelled
Gel-11	BDA	MeGlyoxal	Formald.	AcO ⁻	Gelled
Gel-12	BDA	DiMeGlyoxal	Formald.	AcO ⁻	Gelled
Gel-13	BDA	Glyoxal	Acetald.	AcO ⁻	Gelled

Abbreviations: BDA = 1,4-butanediamine, HDA = 1,6-hexanediamine, E = Diethylene glycol bis(3-aminopropyl) ether, Lys = L-Lysine, Si = 1,3-bis(3-aminopropyl)tetramethyldisiloxane, Gln = L-Glutamine, Formald. = Formaldehyde, Acetald. = Acetaldehyde, MeGlyoxal = methylglyoxal, DiMeGlyoxal = dimethylglyoxal, AcO⁻ = acetate, Cl⁻ = chloride.

The concept of utilizing these novel crosslinkers was initially developed by the author, who synthesized the preliminary PSI hydrogels using diverse PIMs as crosslinkers. Subsequently, in collaboration with JOHANNA ROMISCHKE, a Ph.D. student in Prof. UDO KRAGL's group specializing in hydrogel synthesis, a more comprehensive

and efficient experimental design was implemented to further explore this approach. **Figure 4.15** presents a schematic representation of the synthesized PSI hydrogels crosslinked with amino-terminated poly-imidazolium based ionic liquids.

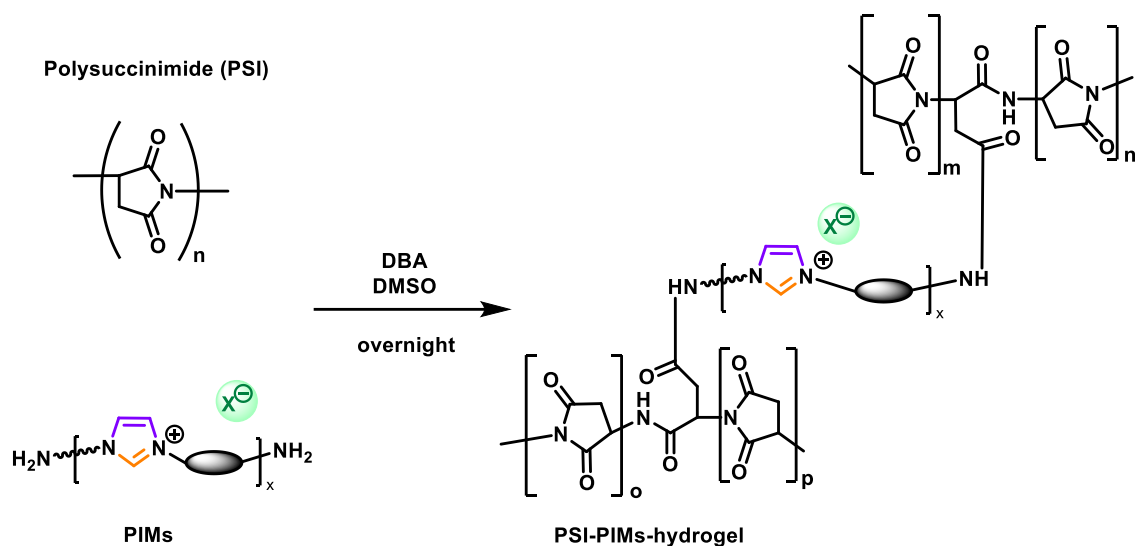


Figure 4.15 Schematic representation of the synthesized PSI hydrogels crosslinked with amino-terminated poly-imidazolium based ionic liquids.

Based on the initial results, four PIM crosslinkers were selected for in-depth investigation:

1. PIM C4 AcO
2. PIM C6 AcO
3. PIM Lys AcO
4. PIM Si AcO

For each of these PIMs, four different amine/carbonyl molar ratios (1.0, 1.6, 2.2, and 2.5) were employed to prepare the corresponding crosslinkers. As discussed in section 4.2, the molecular weight data of synthesized PIMs obtained from Gel Permeation Chromatography (GPC) revealed an inverse relationship between the molar ratio the starting components (amine/carbonyls) and the molecular weight of the PIMs: as the molar ratio increased, the molecular weight of the PIMs

decreased. This observation allows for the systematic investigation of the effect of crosslinker molecular weight on the properties of the resulting hydrogels.

Moreover, one significant advantage of using PIMs as crosslinkers in these PSI hydrogels is the reduced quantity required of crosslinker for gelation. While 180 μmol of non-polymeric commercially available diamines (such as 1,4-butanediamine) are typically required to prepare hydrogels, only 0.1, 0.2, or 0.3 g of PIMs were used, with optimal results obtained using 0.3 g. For example, in the case of PIM C4 AcO, only 7.58 μmol of crosslinker was used instead of 180 μmol , demonstrating the efficiency of this approach.

To the best of our knowledge, this novel method represents the first report of synthesizing PSI hydrogels utilizing amino-terminated poly-imidazolium based ionic liquids derived via the Debus-Radziszewski reaction. This approach offers several advantages:

1. **Tunable crosslinking density:** The ability to control the molar ratio of amine to carbonyl groups allows for precise adjustment of the hydrogel's physical properties, including mechanical strength and swelling behavior.
2. **Ionic conductivity:** The incorporation of imidazolium-based ionic liquids imparts inherent ionic conductivity to the hydrogels, potentially expanding their applications in electrochemical devices and smart materials.
3. **Multifunctionality:** The diverse range of PIMs allows for the introduction of various functional groups, enabling tailored properties for specific applications, such as controlled drug release or stimuli-responsive behavior.

The synthesized hydrogels are currently undergoing comprehensive characterization, including:

- i. **Swelling degree analysis:** To determine the hydrogel's capacity to absorb and retain water, which is crucial for applications in drug delivery and tissue engineering. This analysis involves measuring the weight change of the hydrogel samples when immersed in various aqueous media, such as deionized water and phosphate-buffered saline (PBS), over time.

- ii. **Dye adsorption studies:** To evaluate the hydrogel's potential for environmental remediation and wastewater treatment. These studies involve exposing the hydrogels to model dyes and quantifying the adsorption capacity and kinetics using UV-Vis spectroscopy.
- iii. **Antibacterial activity assessment:** To explore possible biomedical applications, such as wound dressings, contact lenses, or implant coatings. This assessment includes zone of inhibition tests against common pathogens.

These ongoing analyses are being conducted by JOHANNA ROMISCHKE, with assistance from her student, AYNA NAUJACK. The results of these investigations will be compiled and reported in a joint publication, providing a comprehensive understanding of the structure-property relationships in these novel PSI hydrogels.

The results obtained so far indicate that the hydrogels synthesized using PIMs exhibited higher swelling degrees compared to PSI hydrogels crosslinked with ethylenediamine (EDA). Additionally, these PIM-crosslinked hydrogels demonstrated remarkable stability over several weeks when immersed in water. In terms of biocompatibility, the PSI hydrogels with PIM crosslinkers showed similar properties to those with EDA. However, the antibacterial activity of the hydrogels utilizing PIM crosslinkers was higher than that of the EDA-crosslinked variants. Further tests are currently ongoing to determine their precise values, and these experiments will be repeated three times for validation.

4.4.2 Chitosan-based hydrogel

Chitosan-based hydrogels were synthesized using a modified version of the procedure reported by LIEDEL *et al.*¹⁰⁵ This sustainable approach aligns with green chemistry principles in several aspects, including the absence of catalysts and initiators, low-temperature conditions, and the use of water as a reaction medium. This multicomponent approach utilizes Debus-Radziszewski reactions to form 3D network hydrogels through the simultaneous formation of imidazolium rings.

While the original method employed commercially available diamines as crosslinkers in a Debus-Radziszewski reaction with chitosan, our approach utilized

synthesized amino-terminated poly(imidazolium)-based ionic liquids (PIMs) as crosslinkers. This method involves two consecutive Debus-Radziszewski reactions:

1. Synthesis of amino-terminated PIMs
2. Formation of hydrogels in the presence of chitosan, PIMs, glyoxal, formaldehyde, and acetic acid

In our modified approach, we prepared a pre-solution of chitosan dissolved in acetic acid, which was subsequently used for synthesizing all hydrogels. This modification ensures consistency across all synthesized hydrogels and facilitates faster homogenization of all ingredients, preventing the formation of distinct phases which can be attributed to the limited solubility of chitosan and potential inhomogeneity of the mixture due to the generation of different layers.

The concentration of the chitosan solution was optimized to obtain the most homogeneous hydrogels without two-phase color separation. Furthermore, we investigated the effect of chitosan molecular weight (low, medium, and high Mw) on hydrogel preparation, providing insights into the role of polymer chain length in the crosslinking process and final hydrogel properties.

The chitosan-based hydrogels were successfully prepared via this double Debus-Radziszewski reaction approach. To evaluate the efficacy of our method, we also synthesized hydrogels using commercially available diamines, as reported in the literature, for comparison with the PIM-crosslinked hydrogels.^{104-105, 150}

Notable differences were observed between the hydrogels obtained from commercially available diamines (1,4-butanediamine, 1,6-hexanediamine, Diethylene glycol bis(3-aminopropyl) ether, L-Lysine, 1,3-bis(3-aminopropyl) tetramethyl disiloxane, and L-Glutamine) and their corresponding PIMs. These differences were evident in several properties, including:

1. **Color:** Hydrogels obtained from commercially available diamines were predominantly yellowish or pale yellow, while those synthesized using PIMs as crosslinkers exhibited a reddish-brown coloration.
2. **Rate of gelation:** The gelation kinetics differed significantly between the two types of hydrogels. Hydrogels formed with commercially available diamines

(BDA, HDA, E, Lys, Gln, Si) exhibited rapid gelation (less than 2-5 minutes), whereas those with PIMs as crosslinkers demonstrated slower gelation rates (1-24 hours). The gelation rate of hydrogels with PIMs varied depending on the specific PIM used. For samples requiring longer gelation times, they were left at room temperature to complete the gelation process.

These observed differences in hydrogel properties can be attributed to the structural and chemical variations between the commercially available diamines and the synthesized PIMs, particularly the presence of pre-formed imidazolium moieties in the PIMs.

Figure 4.16 illustrates the proposed mechanism for using diamines in the preparation of chitosan-based hydrogels, highlighting the key steps in the crosslinking process and network formation.

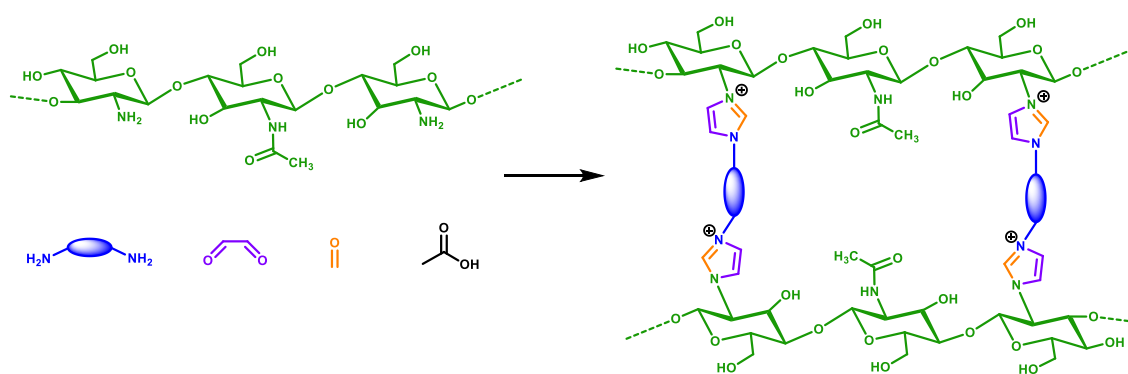


Figure 4.16 Schematic illustration of chitosan-based hydrogel preparation *via* Debus-radziszewski reaction (adapted from ^{105, 150}).

Further characterization of these novel chitosan-based hydrogels is ongoing, focusing on:

1. **Swelling Degree:** Quantitative analysis of the hydrogels' capacity to absorb and retain water under various conditions, in various aqueous media, such as deionized water and phosphate-buffered saline (PBS), over time.
2. **Dye Adsorption:** Investigation of the hydrogels' ability to adsorb various dyes, providing insights into their potential use in environmental remediation and wastewater treatment. Due to the presence of cationic

backbones of imidazolium moieties, the removal of anionic dyes such as Remazol Brilliant Blue was expected and confirmed. Interestingly, our investigations also yielded positive results with cationic dyes such as Malachite Green. Further studies are ongoing to test additional dyes from both cationic and anionic categories.

3. **Rheological Analysis:** Comprehensive rheological characterization, including amplitude sweep and creep recovery tests, to elucidate the viscoelastic properties of the hydrogels. This analysis will provide valuable information on the hydrogels' mechanical behavior, stability, and self-healing potential, which are crucial for various applications.

While the concept and preliminary preparation of chitosan-based hydrogels were developed by the author, the ongoing investigations are currently being pursued by my student, LAUREEN ZSCHÄBITZ, who is completing her Staatsexamen in the group of Prof. UDO KRAGL. These studies will provide a more comprehensive understanding of the structure-property relationships in these novel chitosan-based hydrogels and their potential advantages over conventional diamine-crosslinked systems. The results of these investigations will be reported in due course, offering a thorough evaluation of this novel hydrogel synthesis approach and its implications for various applications in biomedicine, environmental science, and materials engineering.

5. Summary

This PhD study presents an innovative approach to synthesize non-isocyanate polyurethanes (NIPUs) using renewable resource-based cyclic carbonated oils and poly(ionic liquid)s (PIMs) derived from the Debus-Radziszewski reaction. The successful development of these NIPU networks, incorporating imidazolium rings inherited from the PIMs, holds significant potential for enhancing antibacterial properties, making them promising candidates for biomedical applications. Although this study did not explore the antibacterial properties of NIPU products, the synthesized NIPUs demonstrated strong adhesion to molds and exhibited favorable rheological behavior.

The synthesis of cyclic carbonated compounds was accomplished through two distinct methodologies: batch conditions and autoclave reactions. The batch process demonstrated significant advantages for scaling up production, even under ambient CO₂ pressure, while the autoclave method, which employed higher CO₂ pressures, facilitated more rapid product formation.

The batch method allowed for processing of larger quantities, with reactions conducted on 200 g of epoxide precursors. This approach yielded cyclic carbonates with conversions ranging from 82% to 91%, as quantified by epoxy content titration. The reaction proceeded under ambient CO₂ pressure, reaching completion over an extended period of approximately 70 hours. This method's primary advantage lies in its scalability and ability to handle larger quantities.

In contrast, the autoclave method, while limited by reactor volume capacity, demonstrated enhanced reaction kinetics. Using only 5 g of epoxide precursors, this approach achieved higher conversions of up to 95% within a significantly reduced timeframe of 24 hours. The improved efficiency can be attributed to the elevated CO₂ pressure of 20 bar, which likely accelerated the cycloaddition process. Despite the smaller batch size, the autoclave method revealed superior yield and time efficiency.

A diverse range of PIMs was synthesized *via* the Debus-Radziszewski reaction, including 13 different PIMs consisting of various precursors such as diamines (comprising 1,4-butanediamine (BDA), 1,6-hexanediamine (HDA), diethylene

glycol bis(3-aminopropyl) ether (E), L-lysine (Lys), L-glutamine (Gln) and 1,3-bis(aminopropyl)tetramethyldisiloxane (Si)), dicarbonyls (comprising glyoxal, methyl glyoxal and dimethyl glyoxal), aldehydes (comprising formaldehyde and acetaldehyde), and acids (comprising acetic acid and hydrochloric acid). Additionally, the effect of varying starting material molar ratios (amine/carbonyls) on the molecular weight of PIMs was investigated.

These amino-terminated polyimidazolium-based ionic liquids served dual purposes within this study: as curing agents in NIPU preparation and as crosslinkers in hydrogel formulations. This versatility underscores the broad applicability of the synthesized PIMs in polymer chemistry.

Consequently, NIPU compounds were synthesized and designated as NIPU-SB and NIPU-SH, derived from PIM C4 AcO 2.2 and PIM C6 AcO 2.2, respectively. These were formulated with varying combinations of curing agents, including both PIMs and commercially available diamines (BDA and HDA). The prepared NIPUs underwent GPC analysis using NMP as an eluent to investigate their molecular weight distribution. Additionally, rheological characterization was conducted to elucidate their viscoelastic properties and flow behavior. These analyses provided crucial insights into the materials' processability and potential applications in various fields, including coatings, adhesives, and biomedical devices.

Furthermore, all synthesized PIMs were employed as crosslinkers in two distinct types of hydrogels: polysuccinimide (PSI) hydrogels and chitosan-based hydrogels. An innovative concept for synthesizing PSI-PIM hydrogels through the reaction of polysuccinimide with a range of amino-terminated PIMs was also presented by the author of this dissertation. This novel approach opens new avenues for tailoring hydrogel properties through the incorporation of imidazolium-based ionic liquid moieties. Ongoing experiments are focused on evaluating the swelling degree, dye adsorption capabilities, and antibacterial activity of these hydrogels, which will further clarify their potential in environmental and biomedical applications.

Preliminary results indicate that polysuccinimide (PSI) hydrogels crosslinked with polymeric imidazolium-based ionic liquids (PIMs) exhibit superior properties compared to those crosslinked with ethylenediamine (EDA). PIM-crosslinked hydrogels demonstrated higher swelling degrees and maintained stability for

several weeks in aqueous environments. While biocompatibility was comparable to EDA-crosslinked hydrogels, the PIM-crosslinked variants showed enhanced antibacterial properties. Further quantitative analysis is ongoing to determine precise values, with experiments planned for triplicate validation to ensure result reliability and reproducibility.

Moreover, by means of the Debus-Radziszewski reaction, a versatile series of chitosan-based hydrogels was developed incorporating PIMs as crosslinkers, including PIM C4 AcO, PIM C6 AcO, PIM E AcO, PIM Lys AcO, PIM Gln AcO, PIM Si AcO, PIM C4 Cl, PIM C6 Cl, PIM Lys Cl and PIM Si Cl, *via* the Debus-Radziszewski reaction. This method involves two consecutive Debus-Radziszewski reactions: first, the synthesis of PIM crosslinkers, followed by the preparation of chitosan-based hydrogels. This approach capitalizes on the biocompatibility of chitosan while integrating the unique properties of PIMs.

We investigated the impact of chitosan concentration on the final hydrogels. The effects of varying molecular weights of chitosan—low, medium, and high—on the final hydrogels were also examined. Furthermore, experiments were conducted in the presence of commercially available diamines, including 1,4-butanediamine (BDA), 1,6-hexanediamine (HDA), diethylene glycol bis(3-aminopropyl) ether (E), L-lysine (Lys), L-glutamine (Gln) and 1,3-bis(aminopropyl)tetramethyldisiloxane (Si), to enhance our understanding of the effects of PIMs on hydrogels and compare them with their commercially available diamine counterparts.

Ongoing investigations into the swelling behavior, dye adsorption capacity, and rheological analysis—including amplitude sweep and creep recovery—of these hydrogels are expected to reveal their potential applications in areas such as water treatment, drug delivery, and tissue engineering. So far, the swelling degree of hydrogels obtained from PIMs has shown higher values compared to those synthesized with commercially available diamines, particularly for hydrogels derived from PIM E AcO. Additionally, these hydrogels have demonstrated significant dye adsorption capabilities for dyes such as Remazol Brilliant Blue R and Malachite Green.

6. Outlook

The outlook for future research in this field presents several promising avenues for exploration and development. Building upon the current work, there is significant potential in investigating the antibacterial activities of non-isocyanate polyurethanes containing imidazolium-based curing agents, with a particular focus on their application in wound dressing materials. This could lead to the development of advanced, biocompatible wound care solutions. Concurrently, assessing the adhesion properties of NIPUs incorporating siloxanes could open up new possibilities in coatings and adhesives technology, potentially offering improved durability and flexibility in various industrial applications. Importantly, incorporating other synthesized cyclic carbonated oils into these formulations could enhance their properties and broaden their applications, paving the way for innovative materials that leverage renewable resources while addressing critical needs in biomedical and industrial fields.

Future research may also focus on evaluating the swelling degree, dye adsorption, and antibacterial effectiveness of PSI hydrogels crosslinked with PIMs. This line of inquiry could be complemented by a parallel investigation into chitosan-based hydrogels crosslinked with PIMs, focusing on similar properties along with their rheological characteristics. This comprehensive approach to future research aims to advance our understanding of these novel polymer systems and their potential applications across multiple fields, from biomedical engineering to environmental remediation and industrial coatings.

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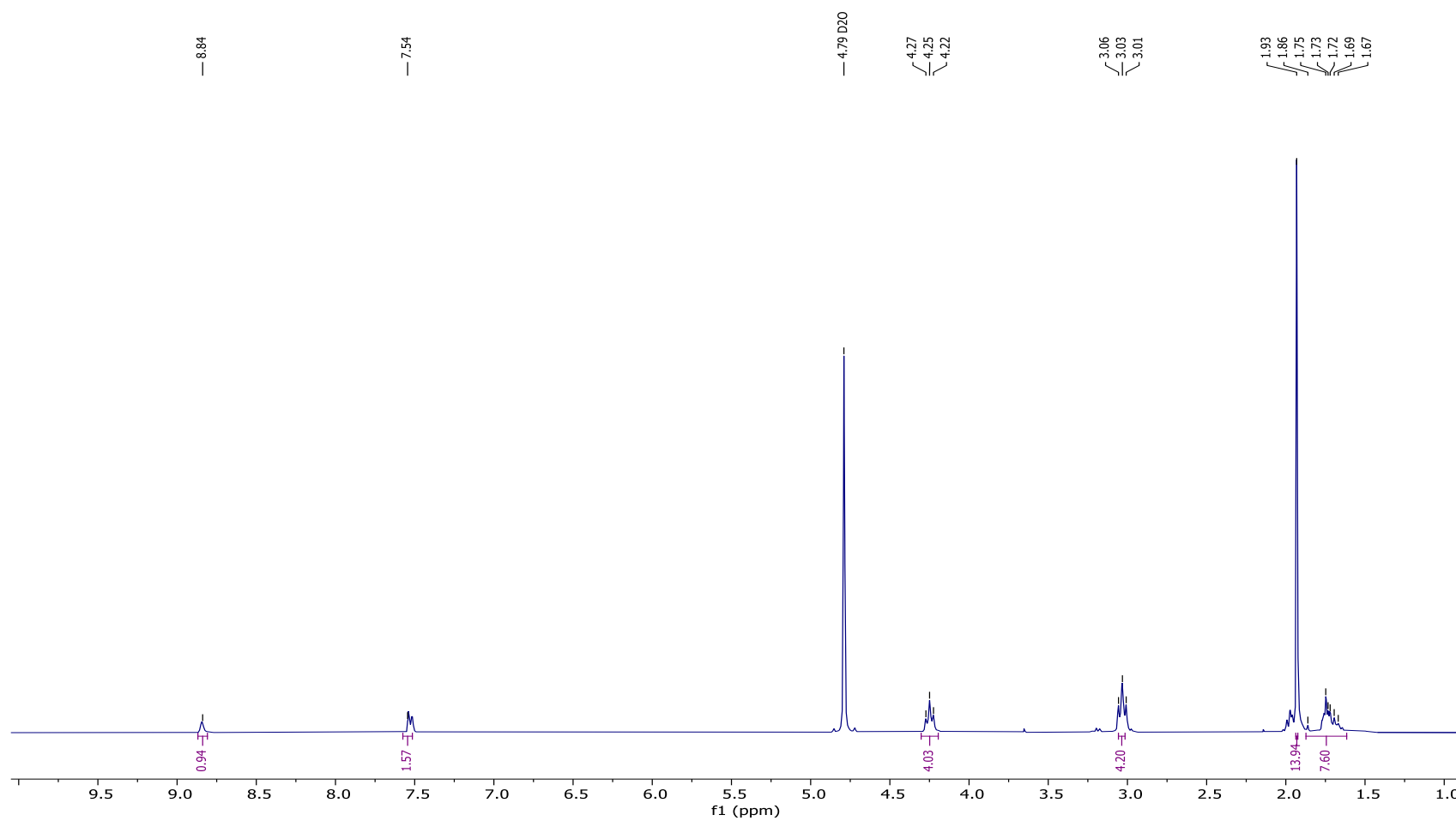
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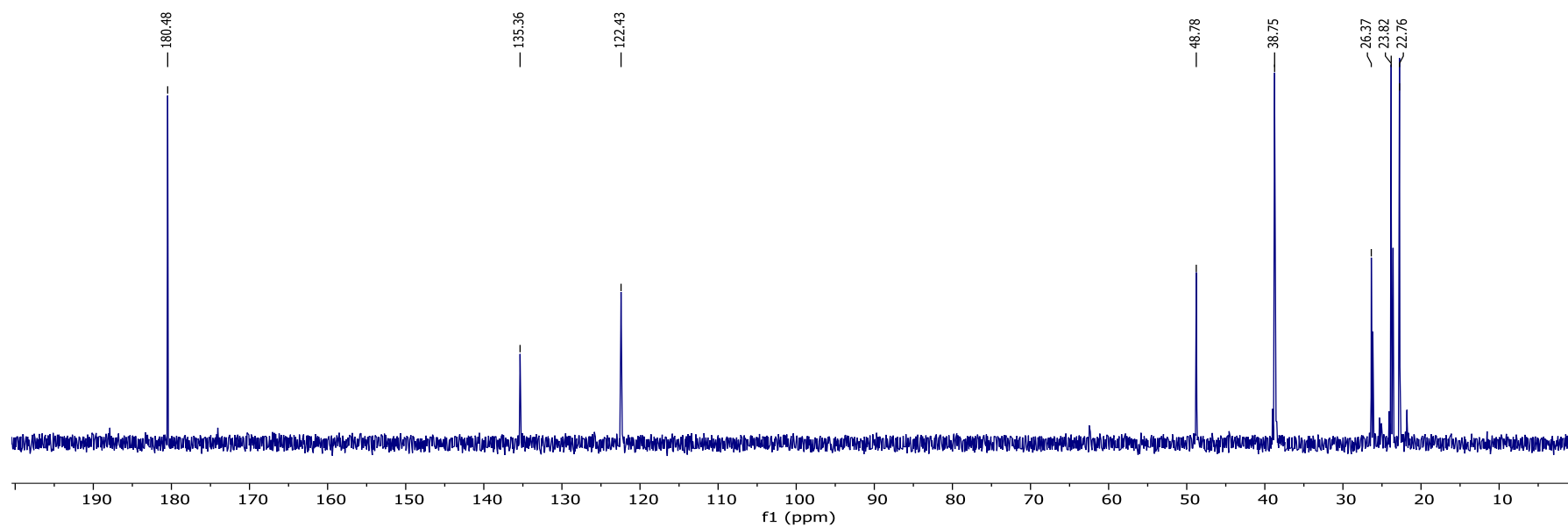
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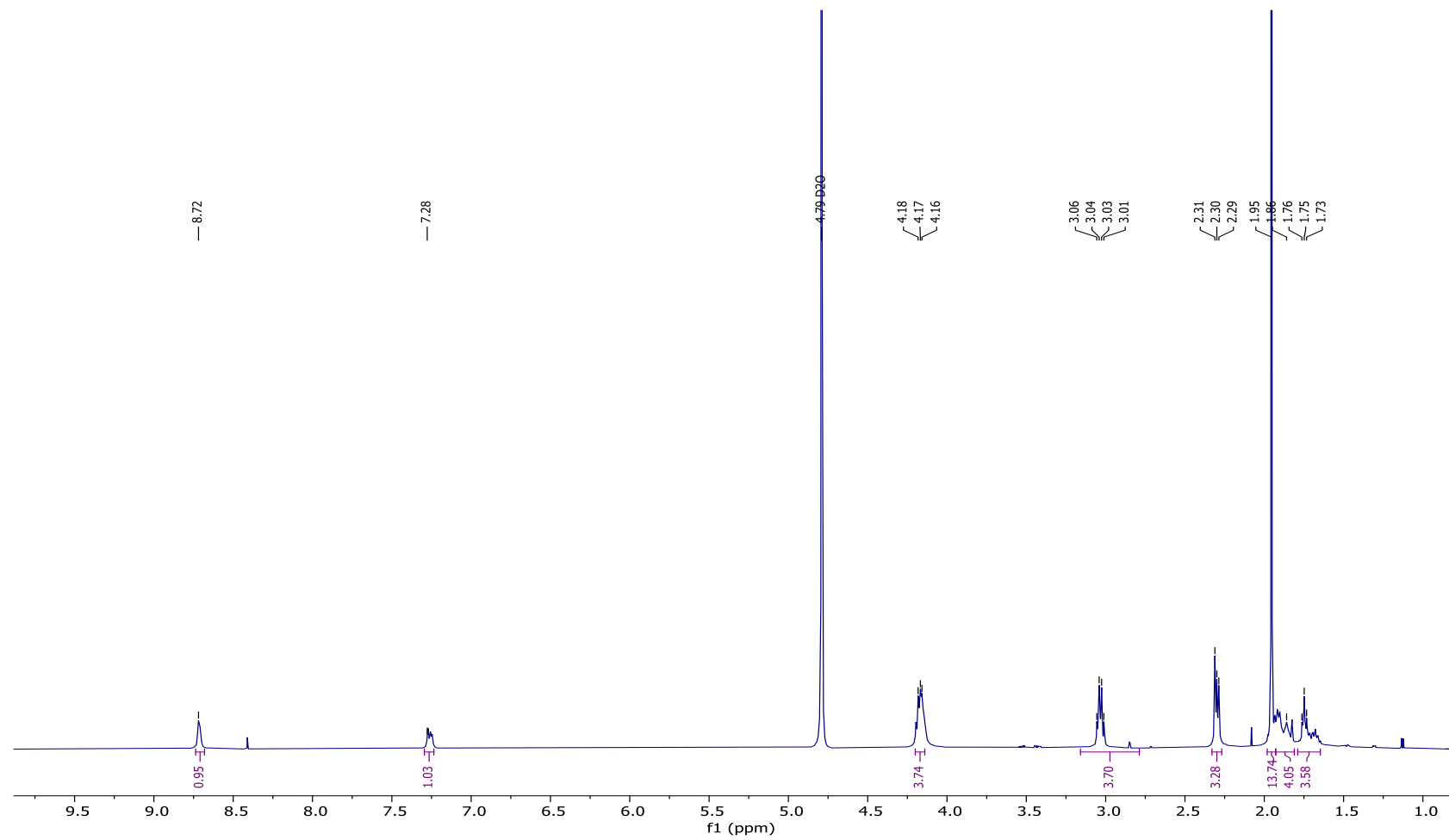
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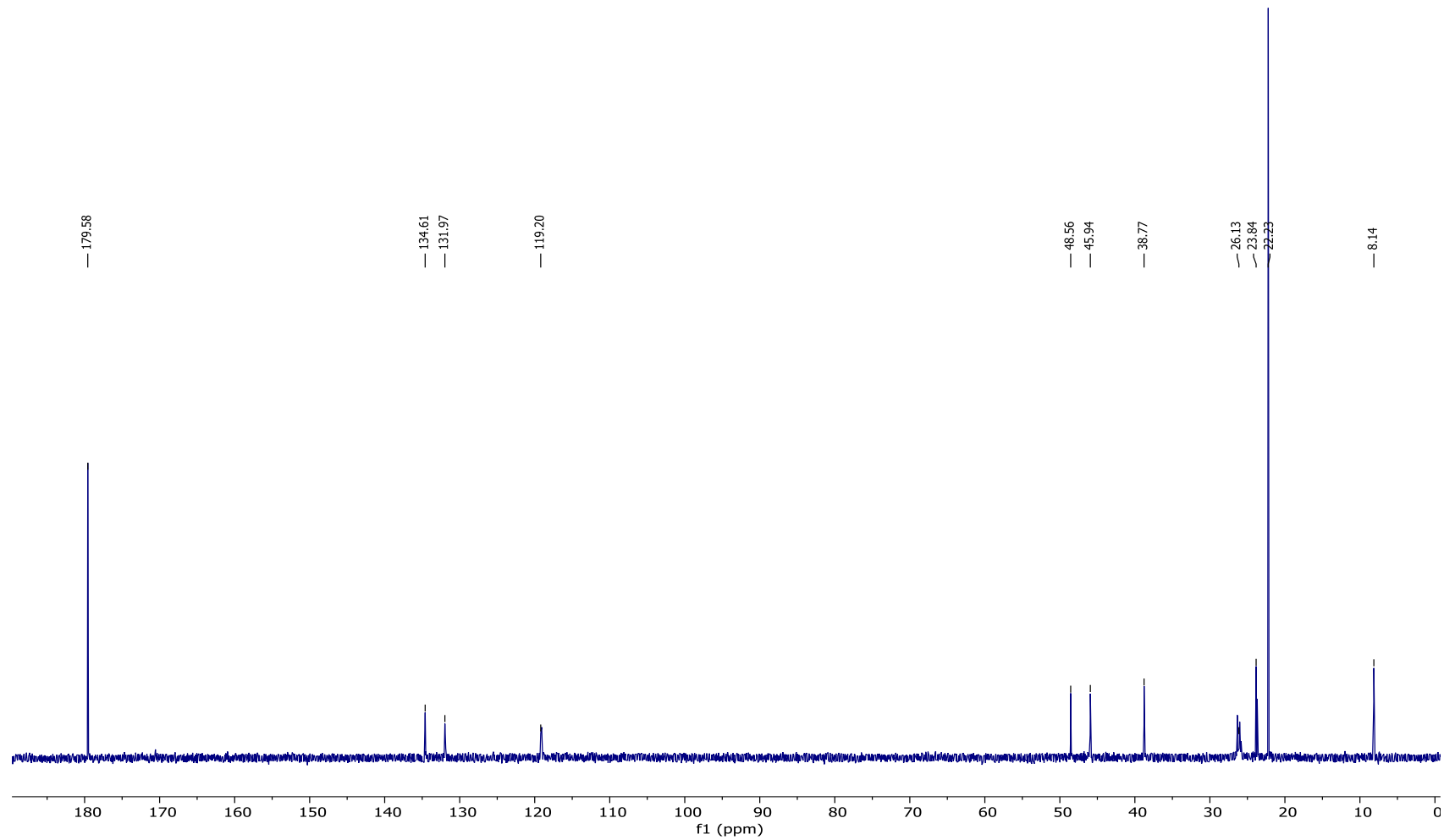
^1H NMR of PIM C4 AcO (300 MHz, D_2O)

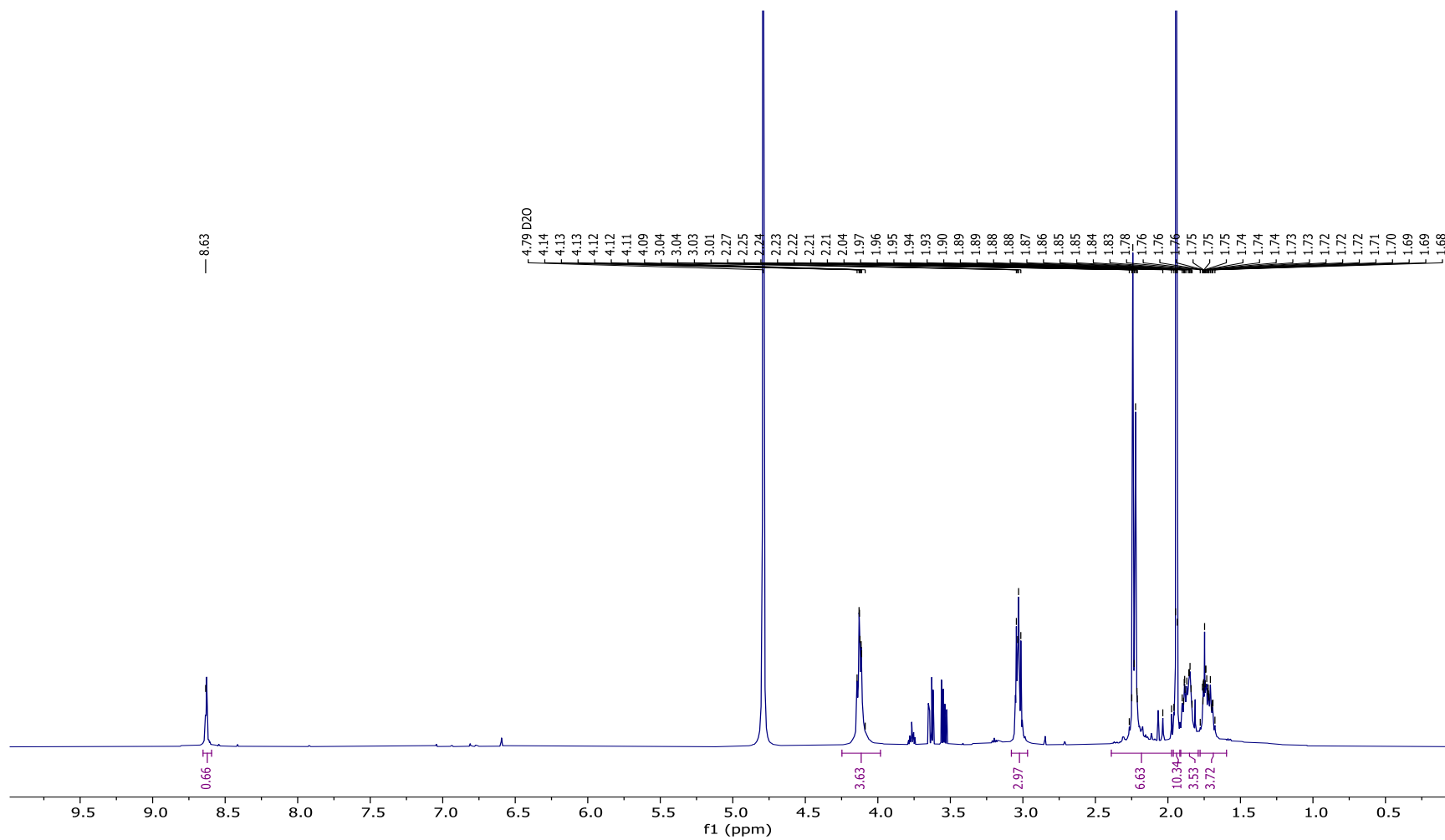


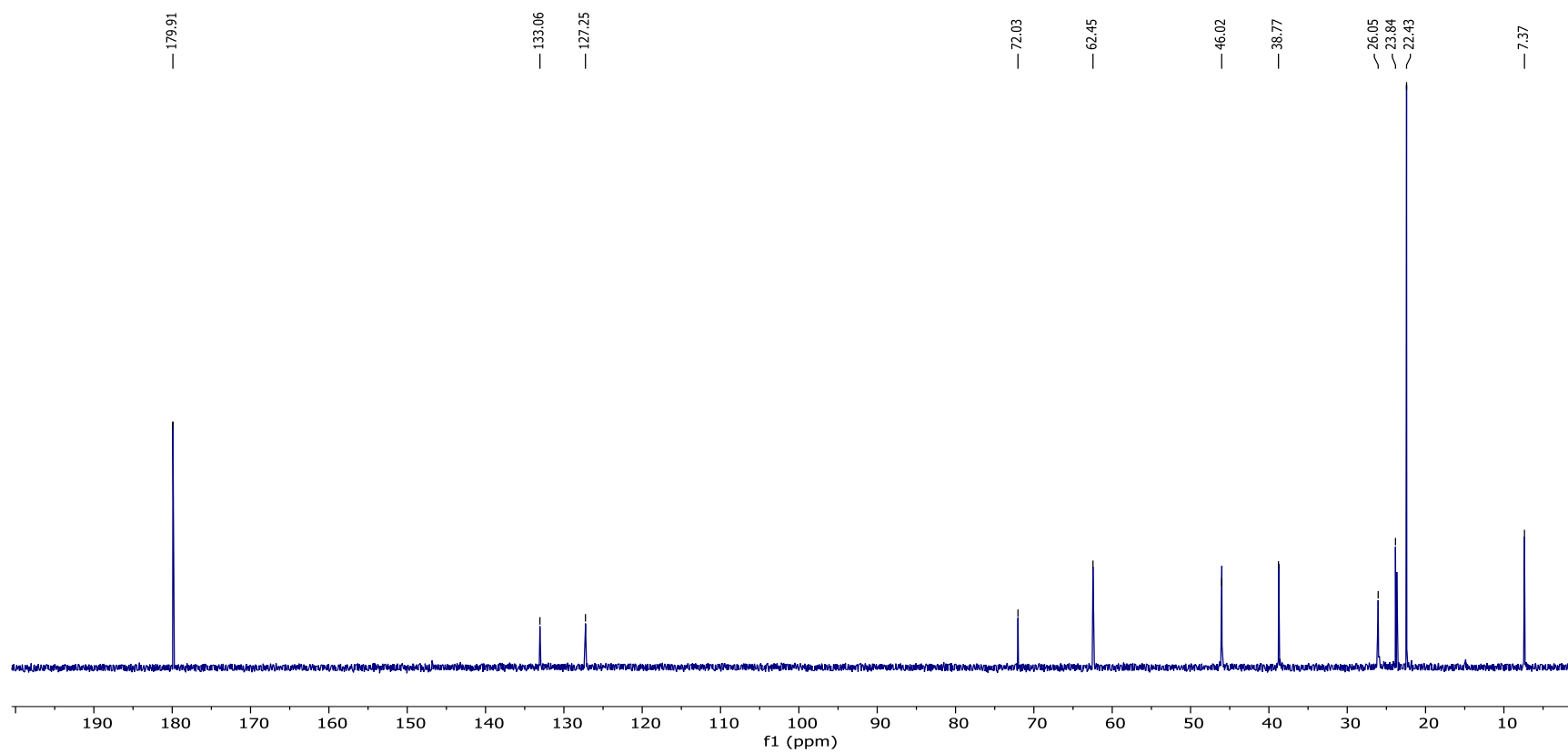
^{13}C NMR of PIM C4 AcO (75 MHz, D_2O)

^1H NMR of PIM C4b AcO (500 MHz, D_2O)

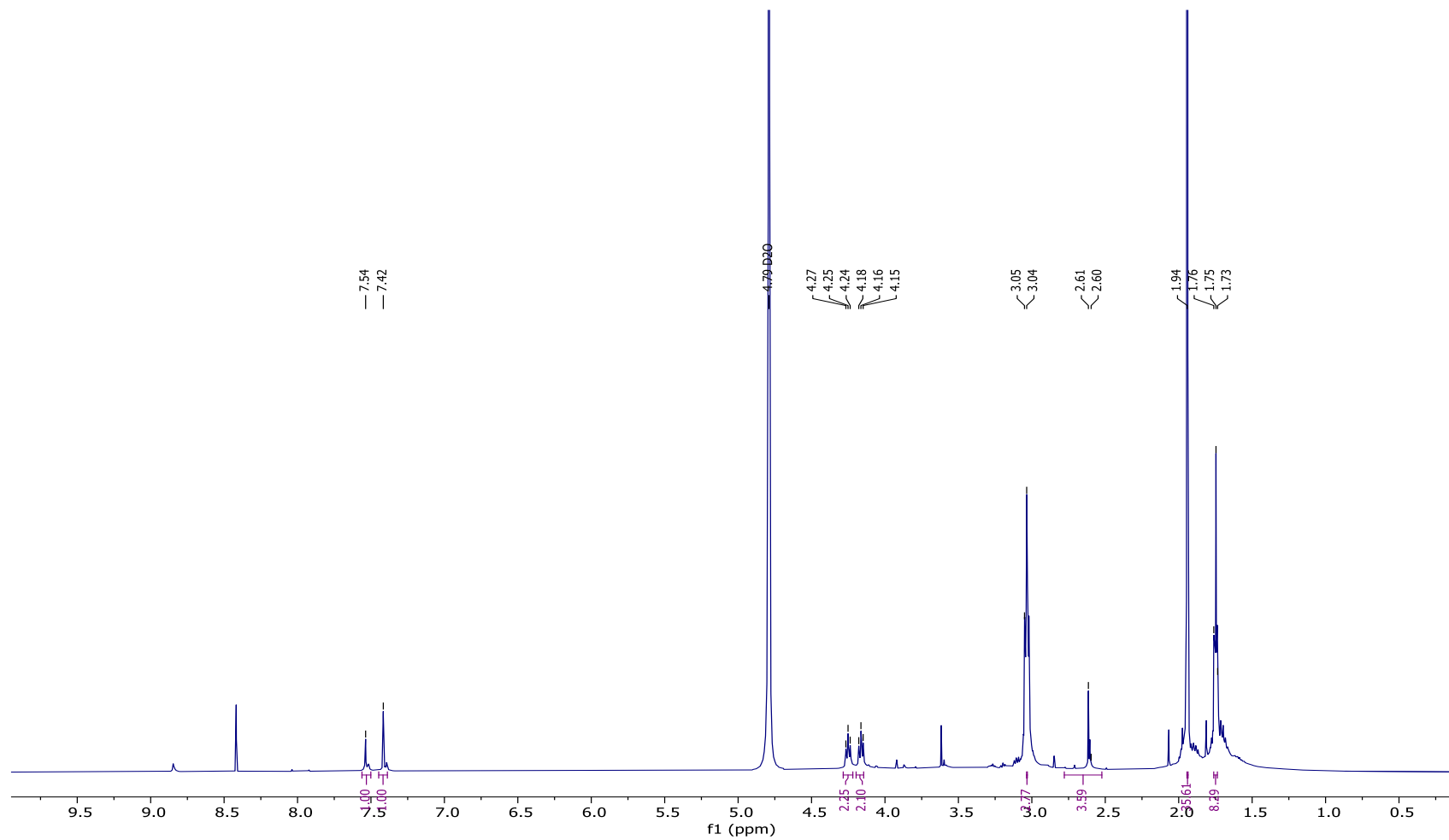


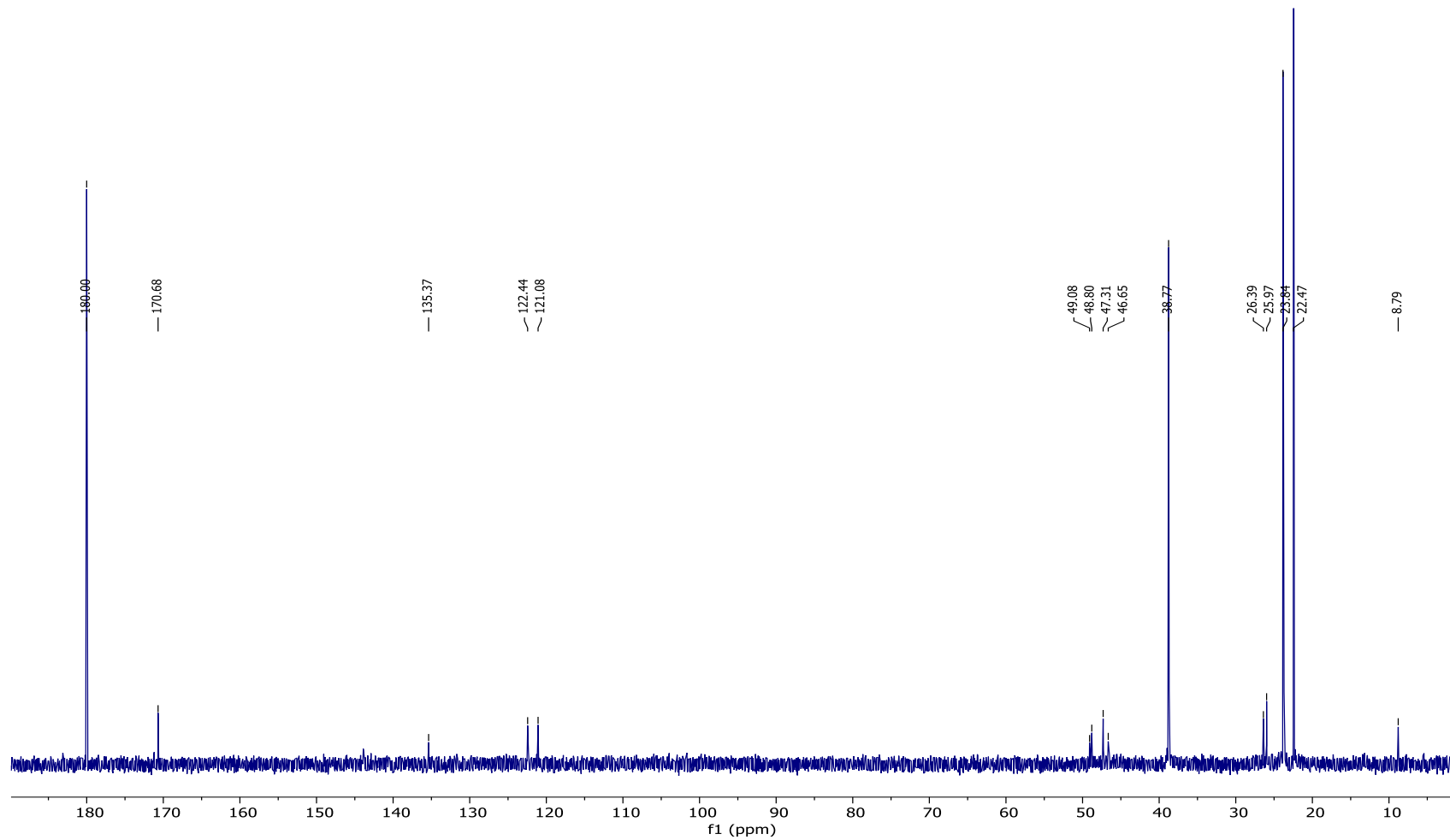
^{13}C NMR of PIM C4b AcO (126 MHz, D_2O)

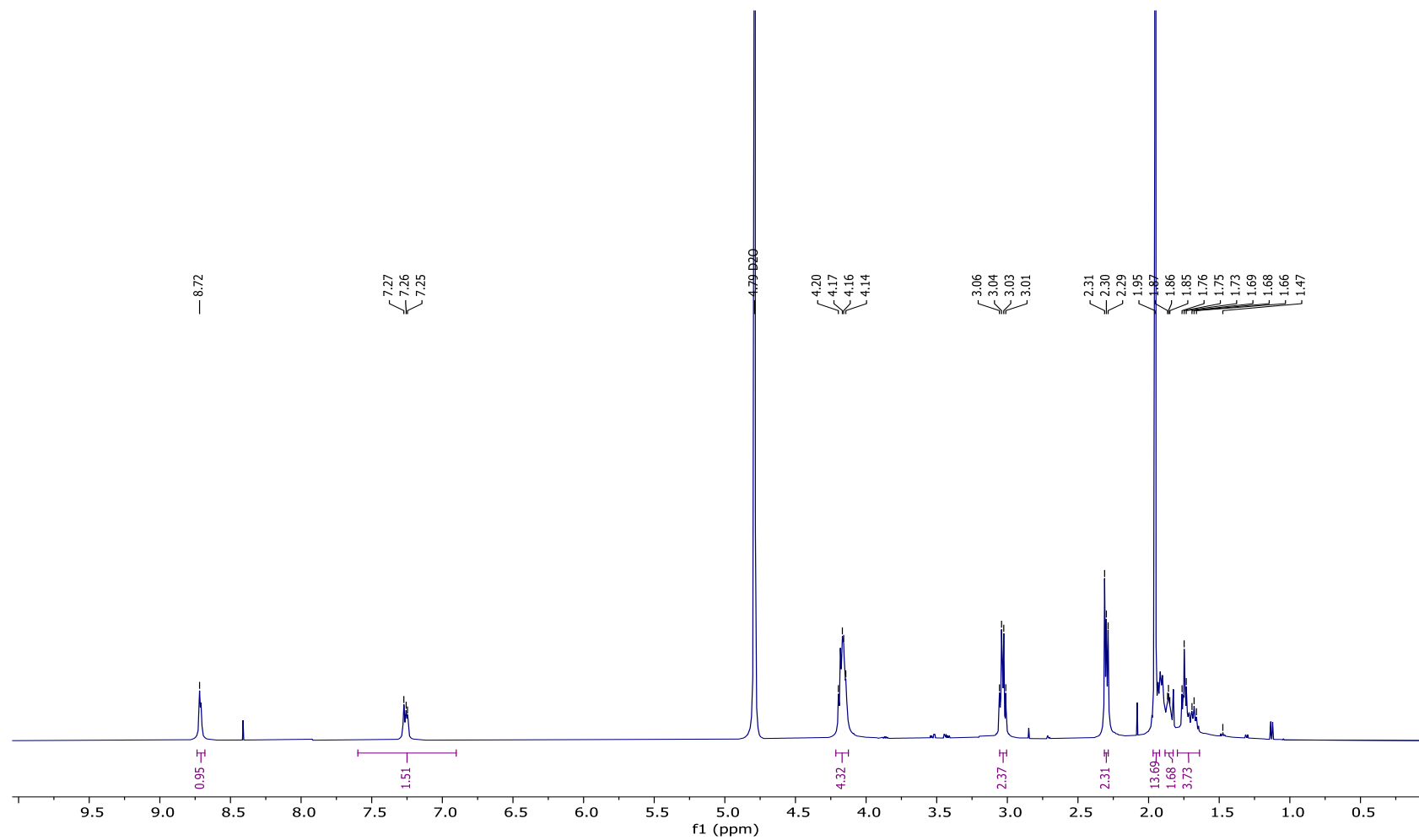
^1H NMR of PIM C4c AcO (500 MHz, D_2O)

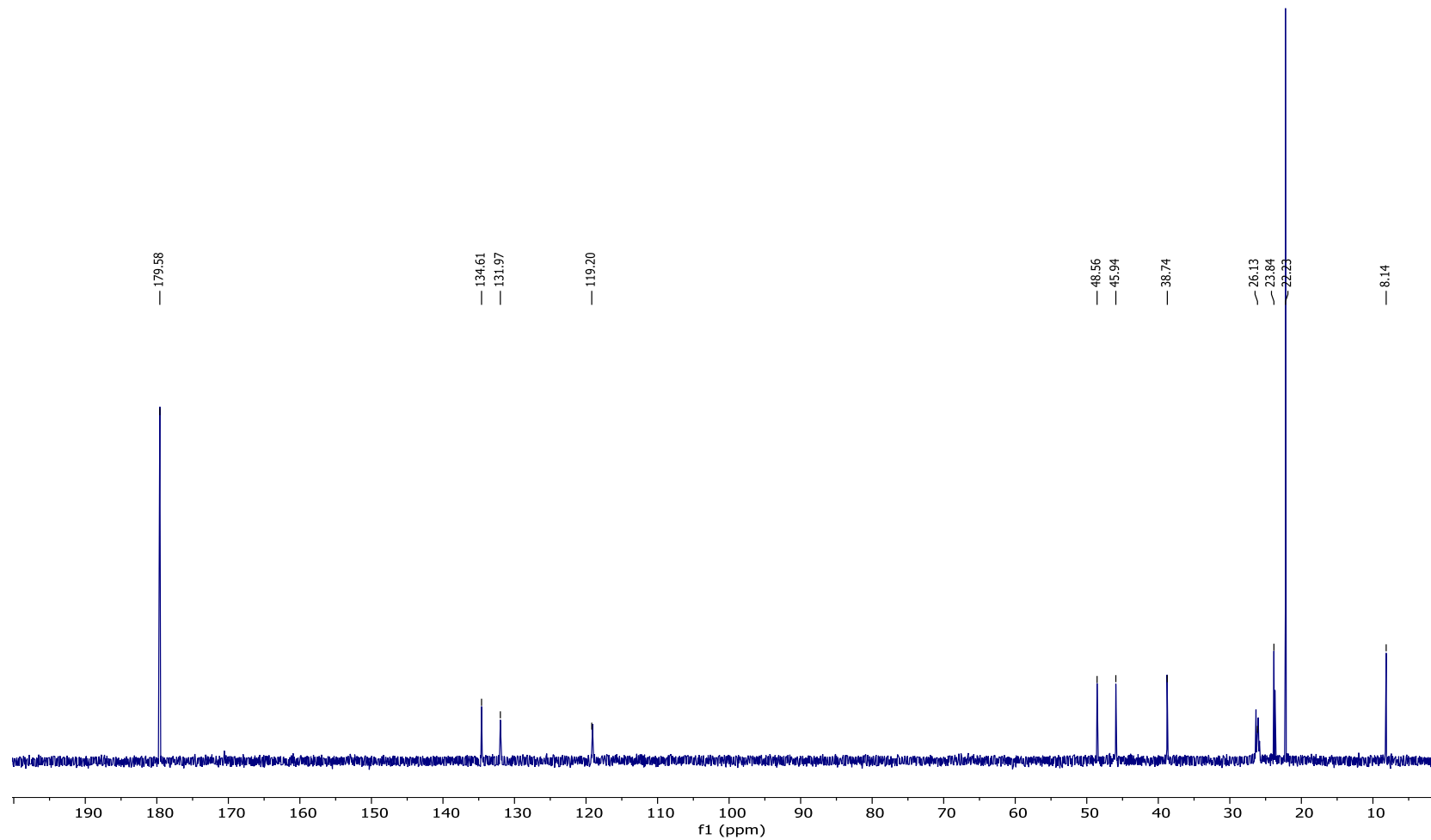
^{13}C NMR of PIM C4c AcO (126 MHz, D_2O)

^1H NMR of PIM C4d AcO (500 MHz, D_2O)

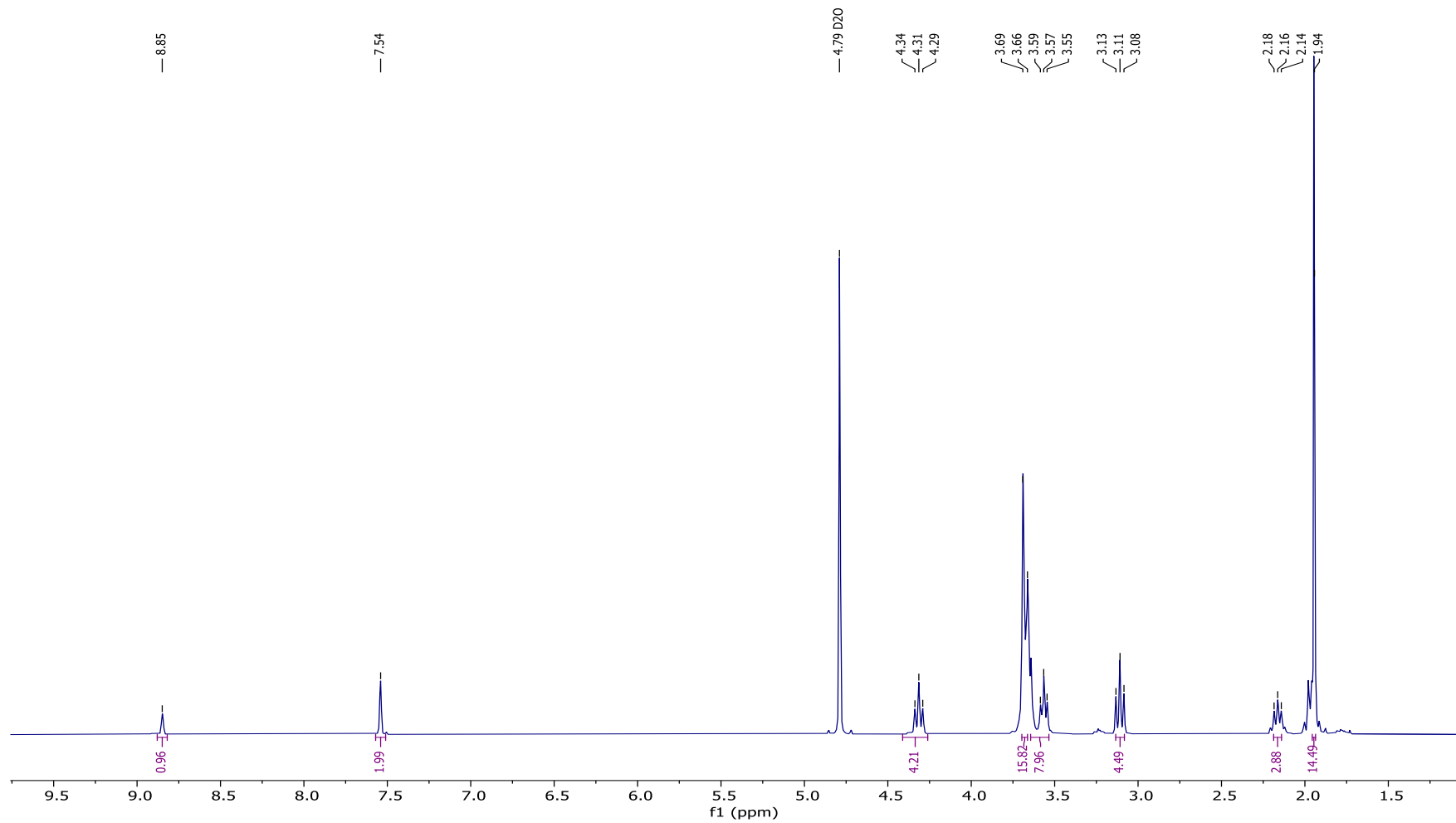


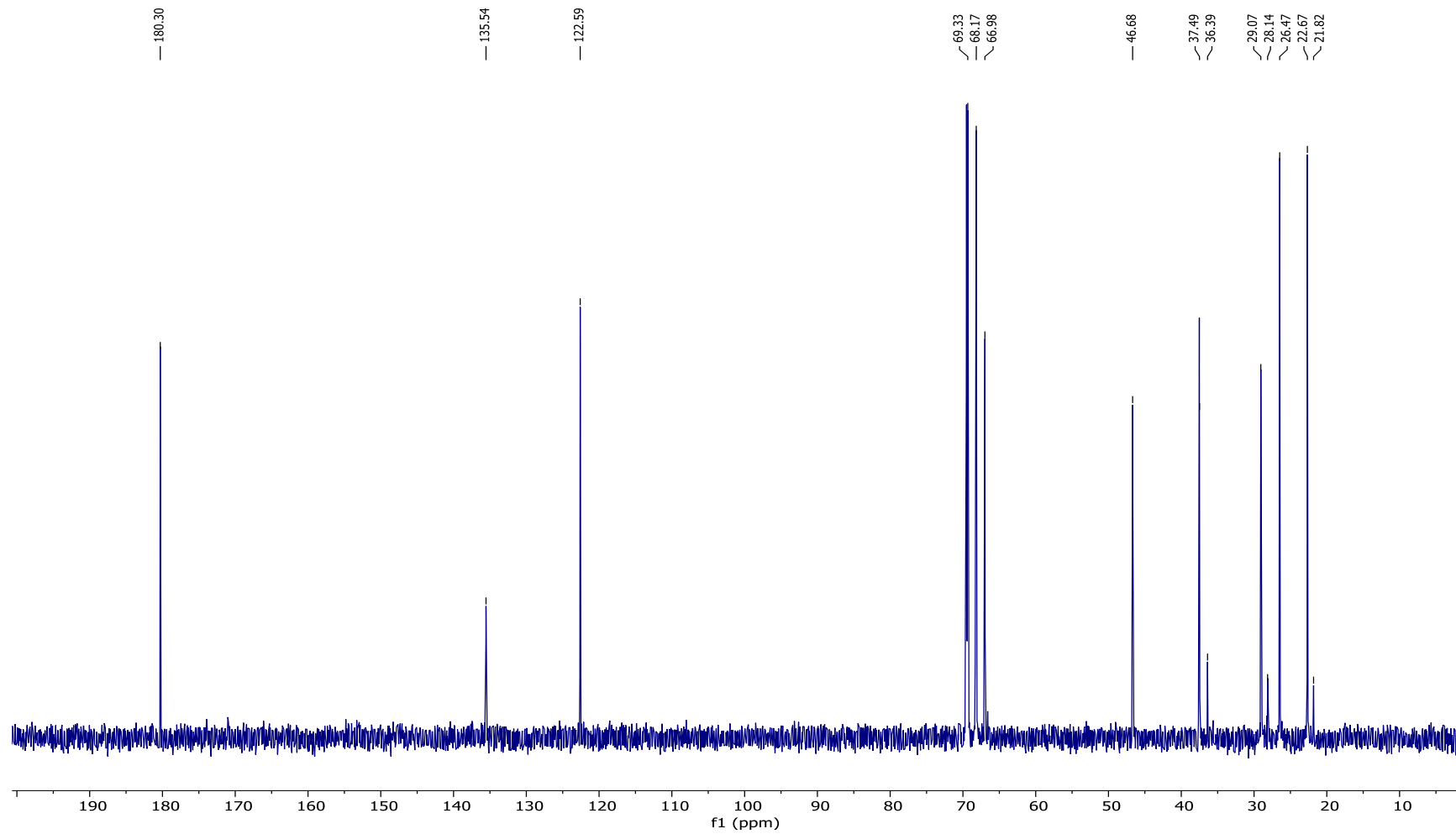
^{13}C NMR of PIM C4d AcO (126 MHz, D_2O)

^1H NMR of PIM C6 AcO (500 MHz, D_2O)

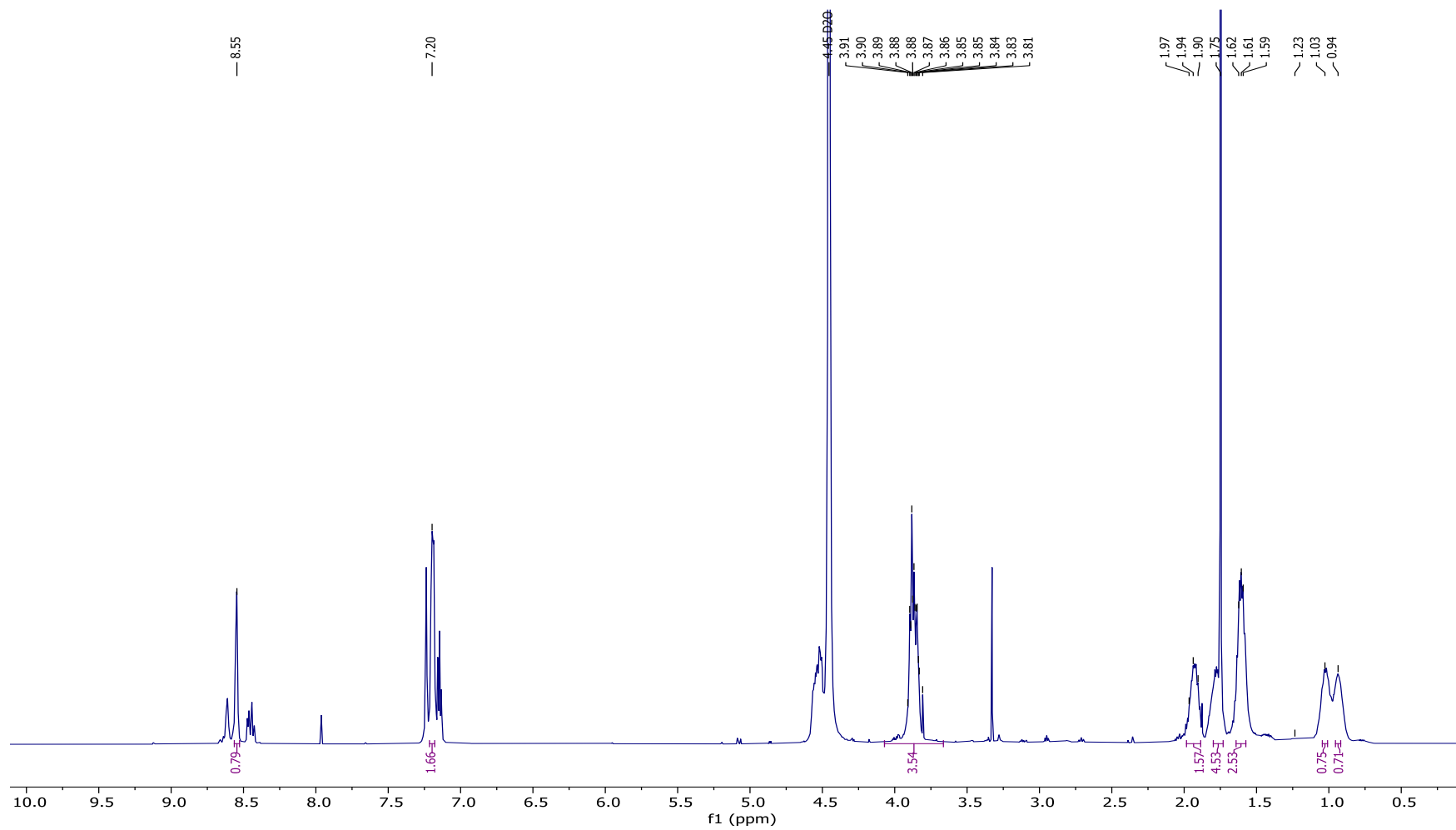
^{13}C NMR of PIM C6 AcO (126 MHz, D_2O)

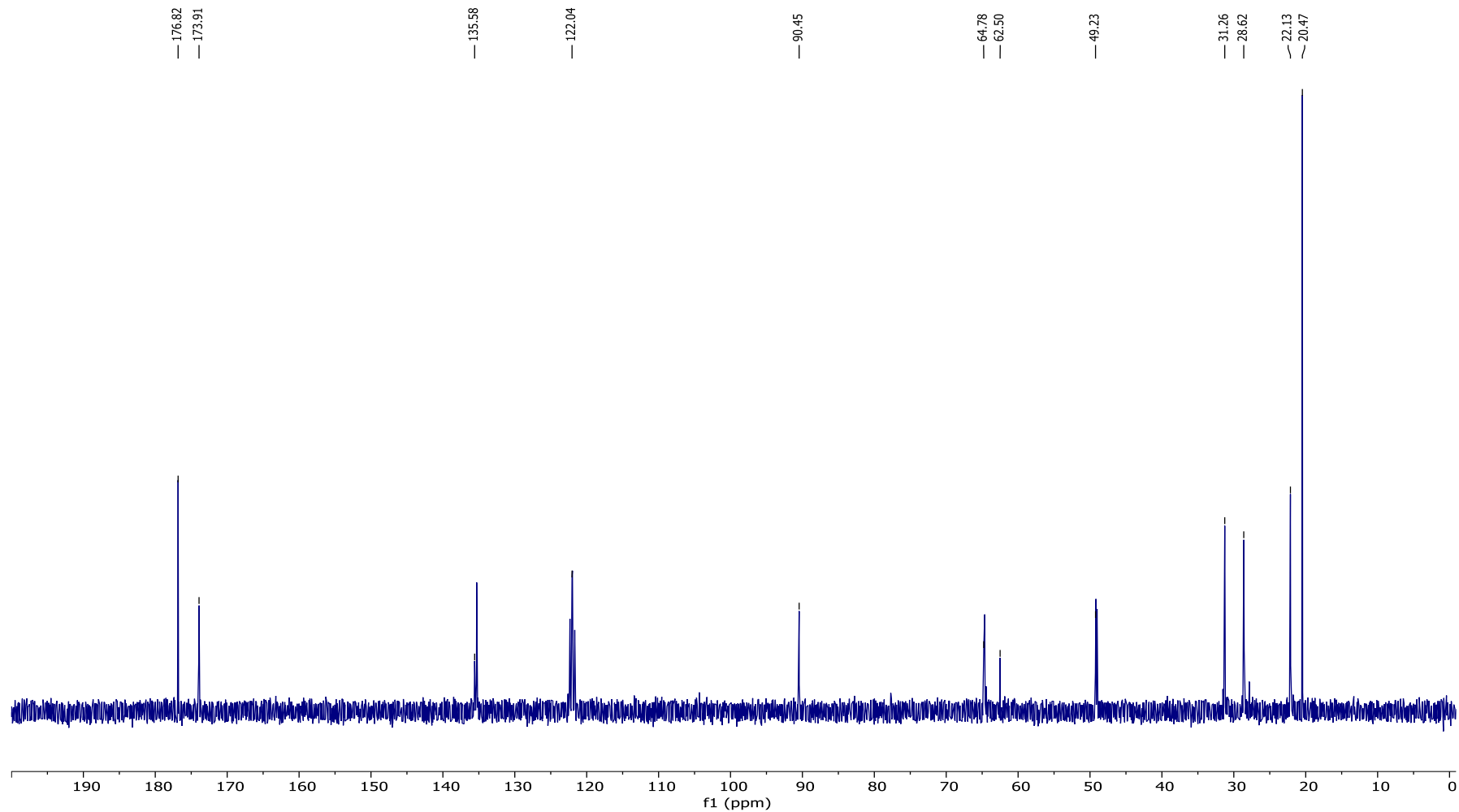
^1H NMR of PIM E AcO (300 MHz, D_2O)



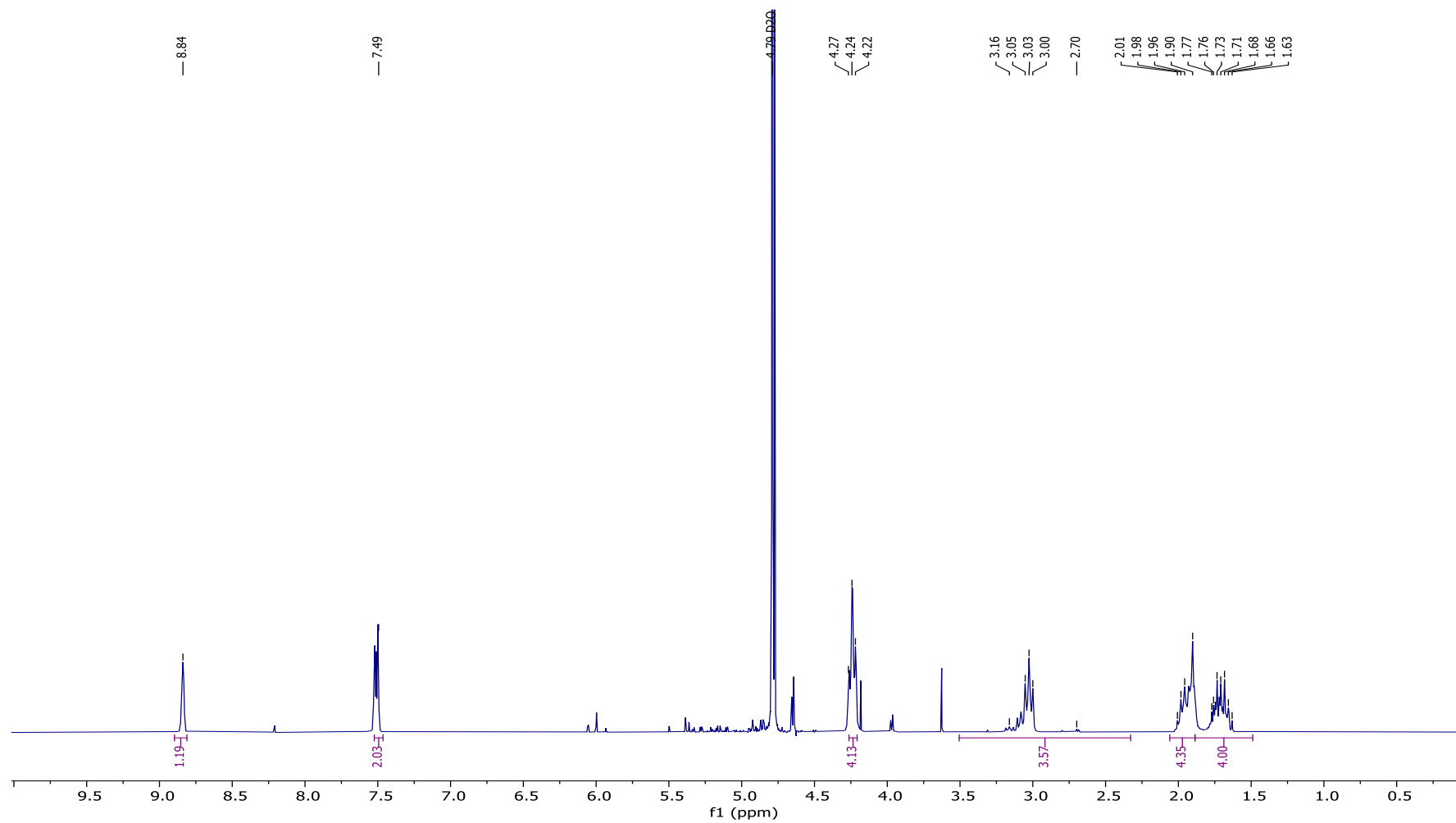
^{13}C NMR of PIM E AcO (75 MHz, D_2O)

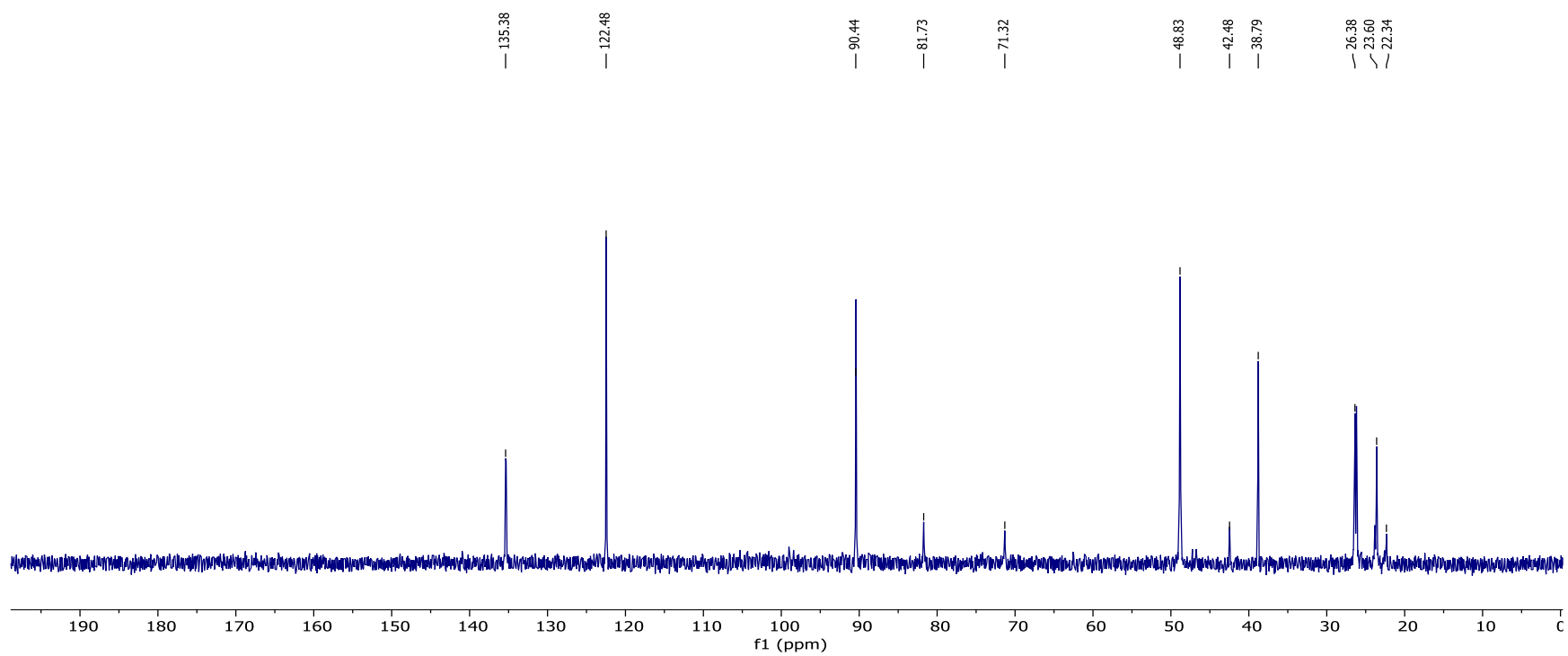
^1H NMR of PIM Lys AcO (500 MHz, D_2O)



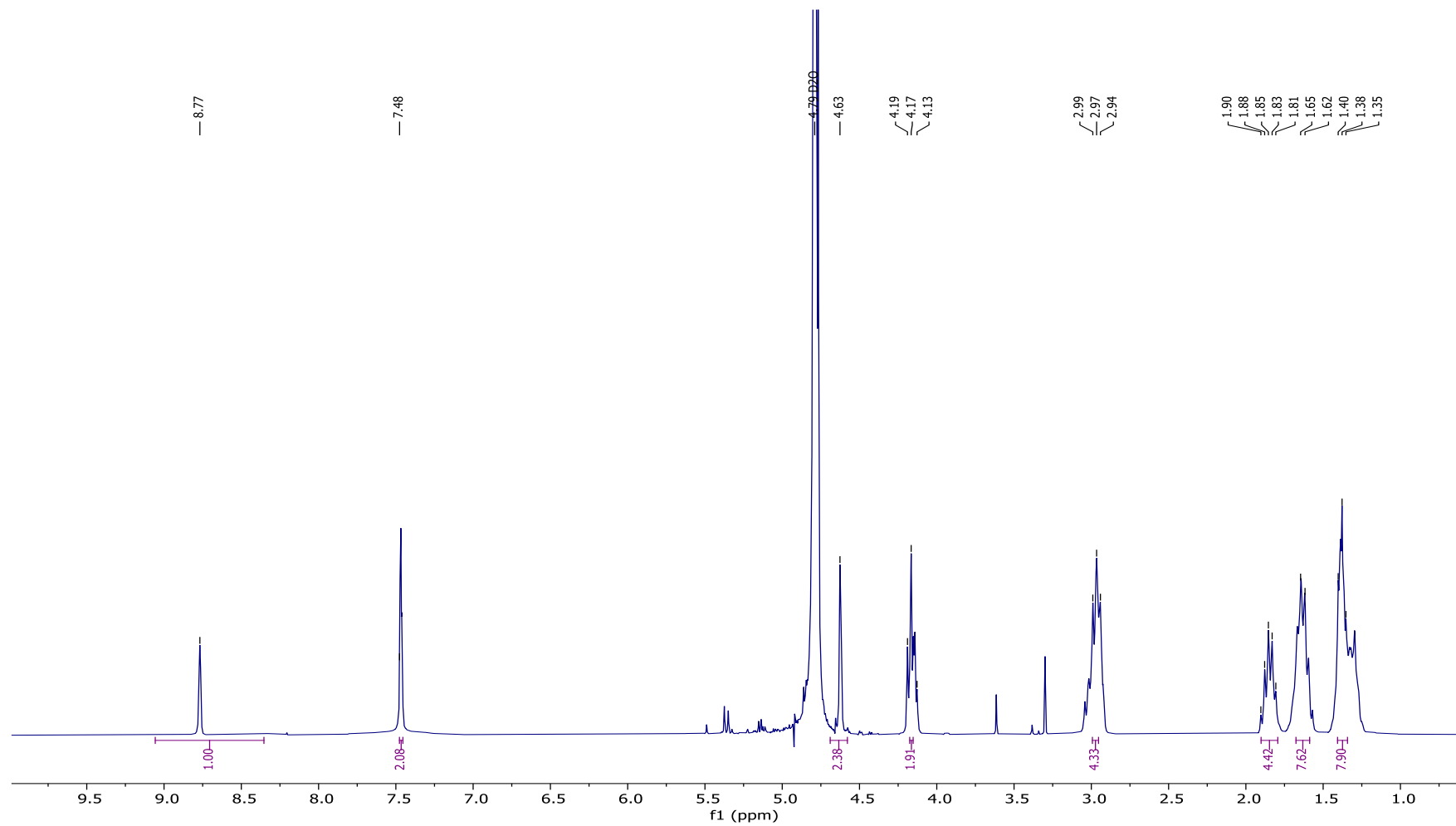
^{13}C NMR of PIM Lys AcO (126MHz, D_2O)

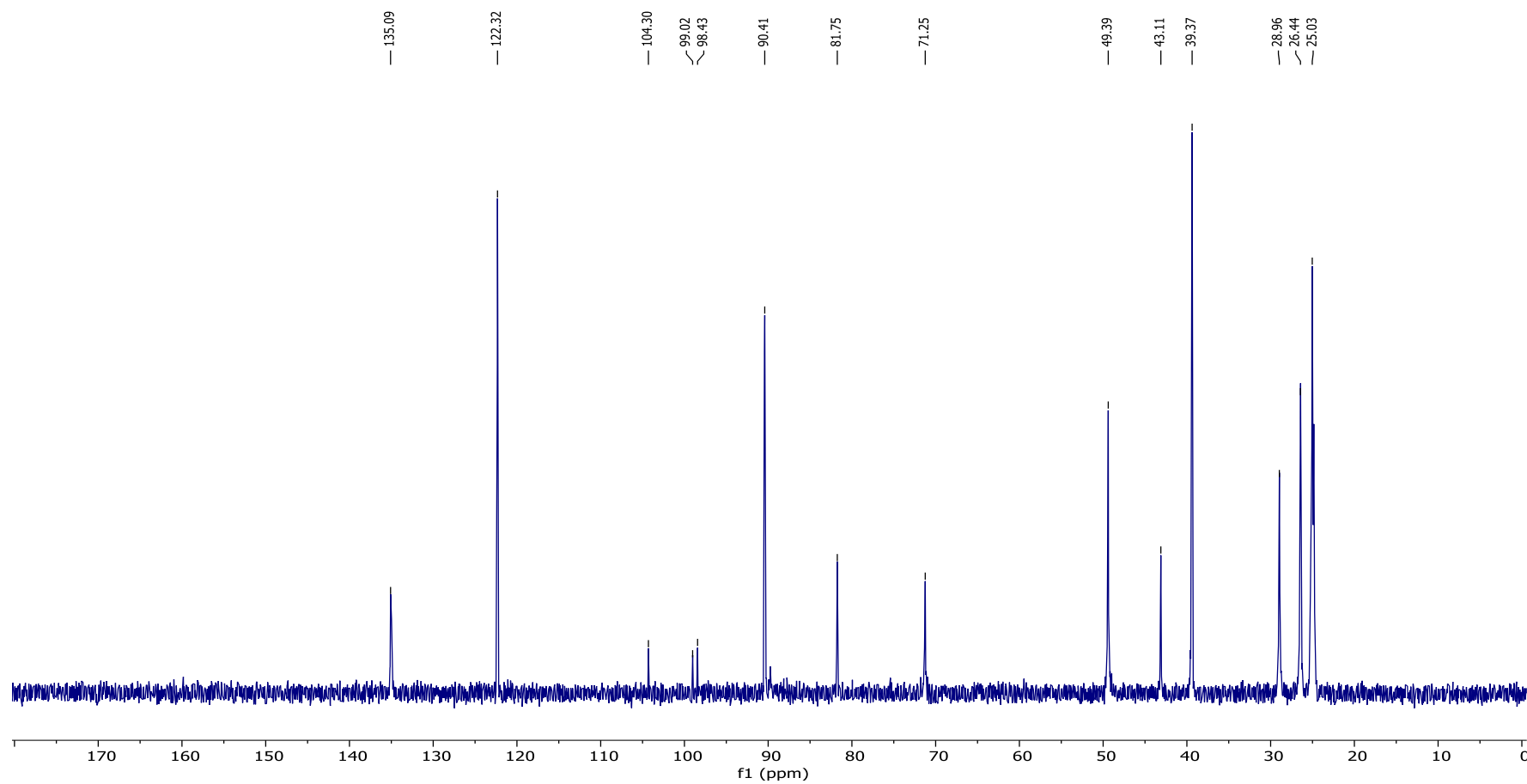
^1H NMR of PIM C4 Cl (300 MHz, D_2O)



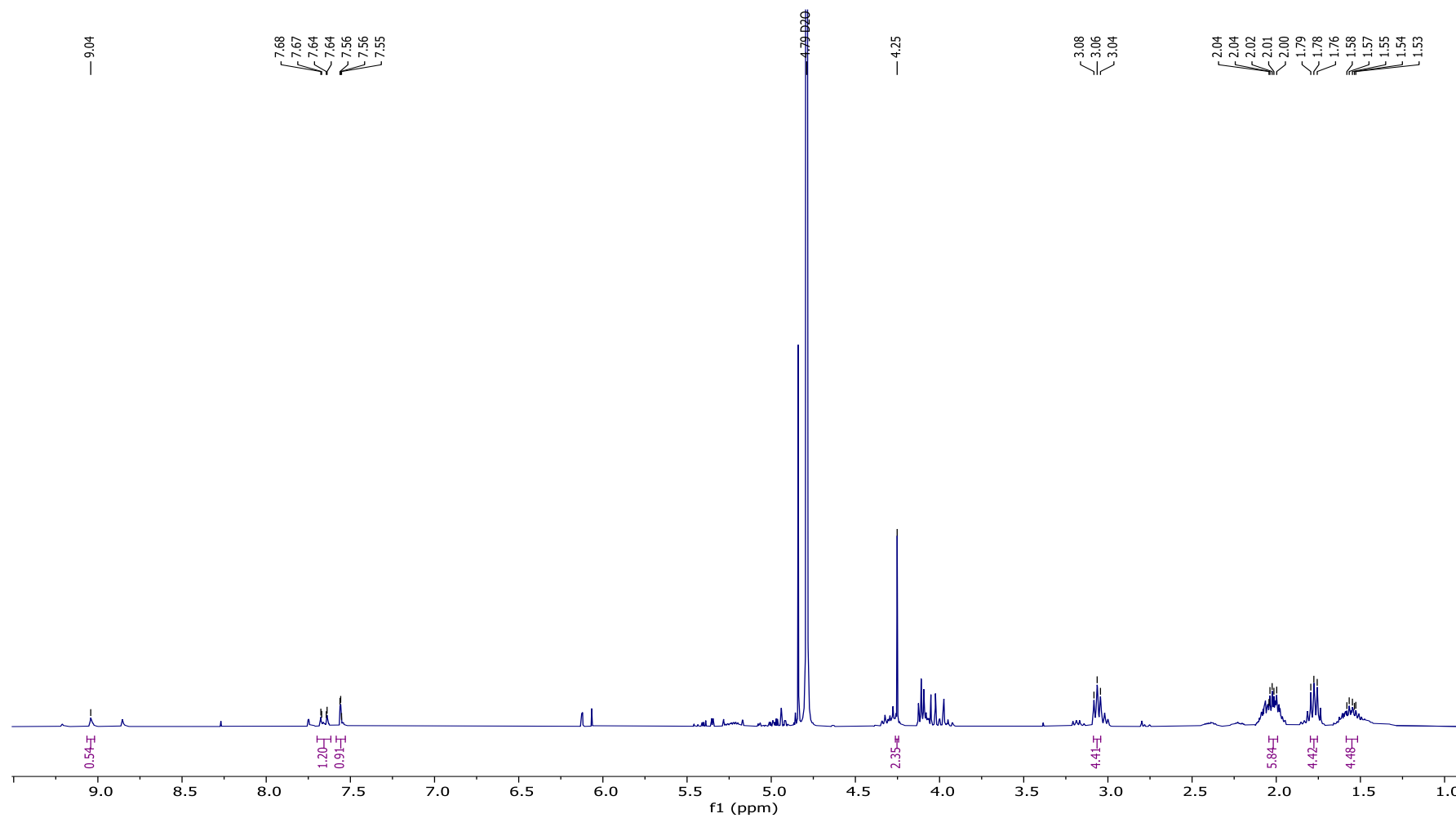
^{13}C NMR of PIM C4 Cl (75 MHz, D_2O)

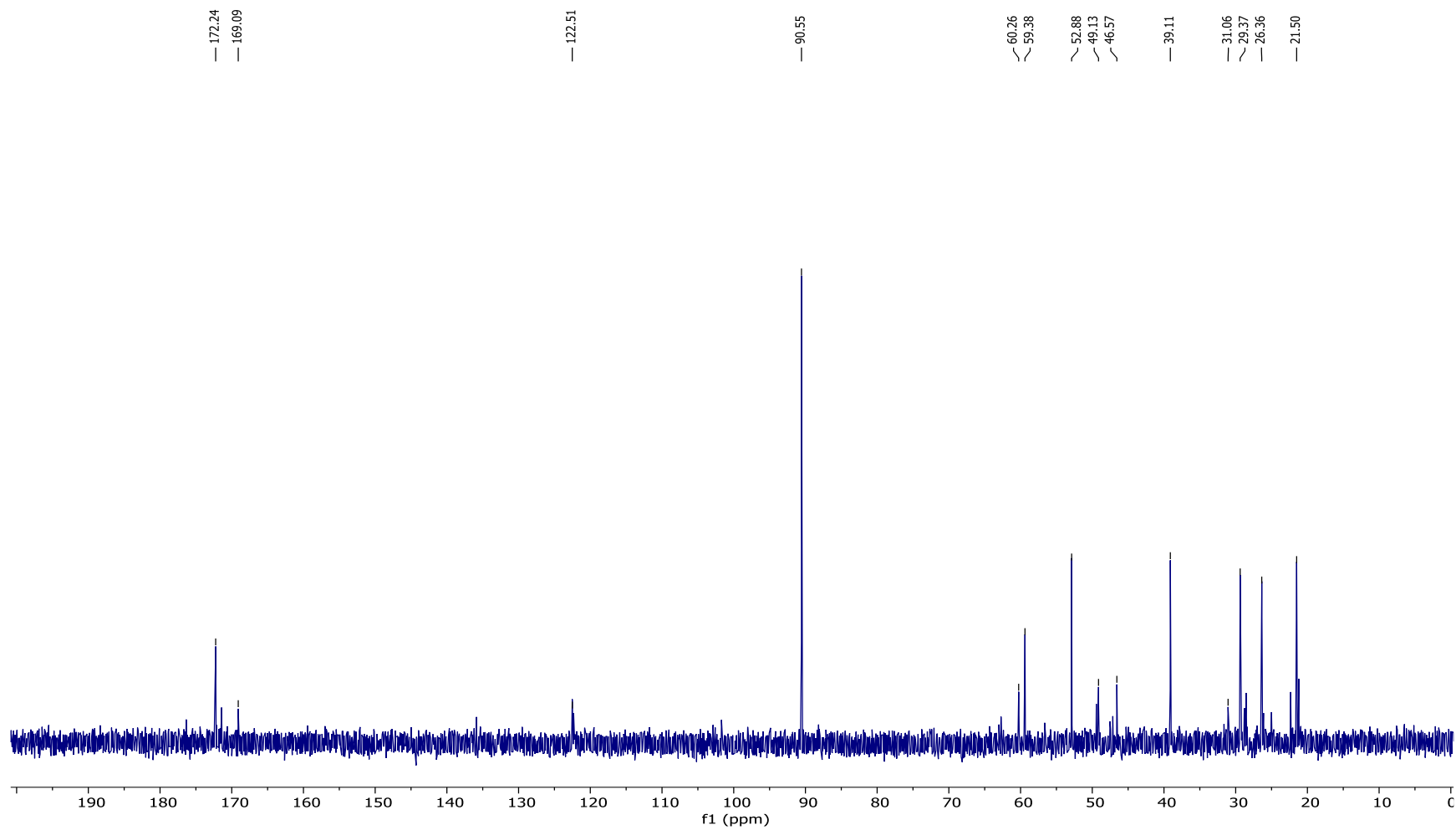
^1H NMR of PIM C6 Cl (300 MHz, D_2O)



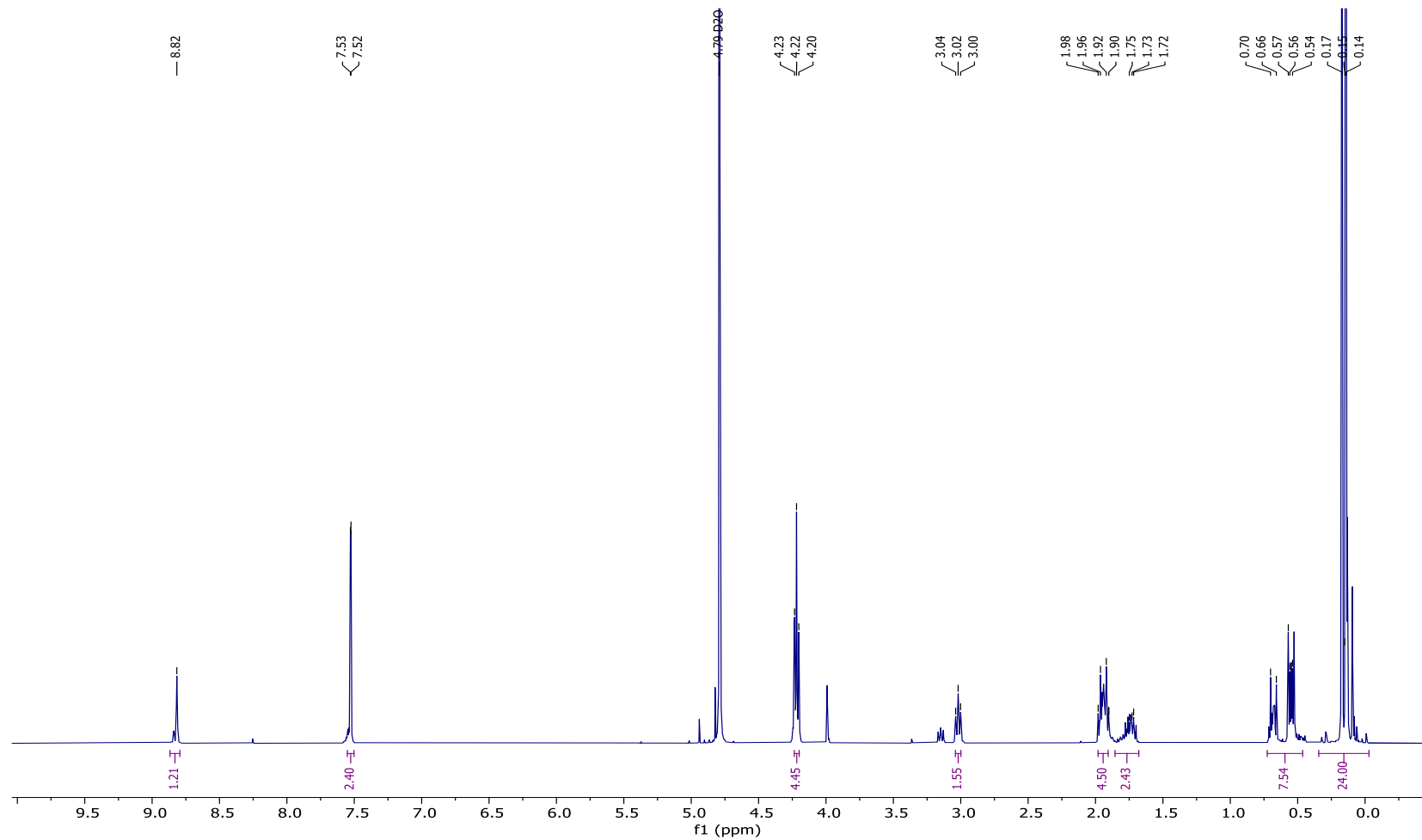
^{13}C NMR of PIM C6 Cl (75 MHz, D_2O)

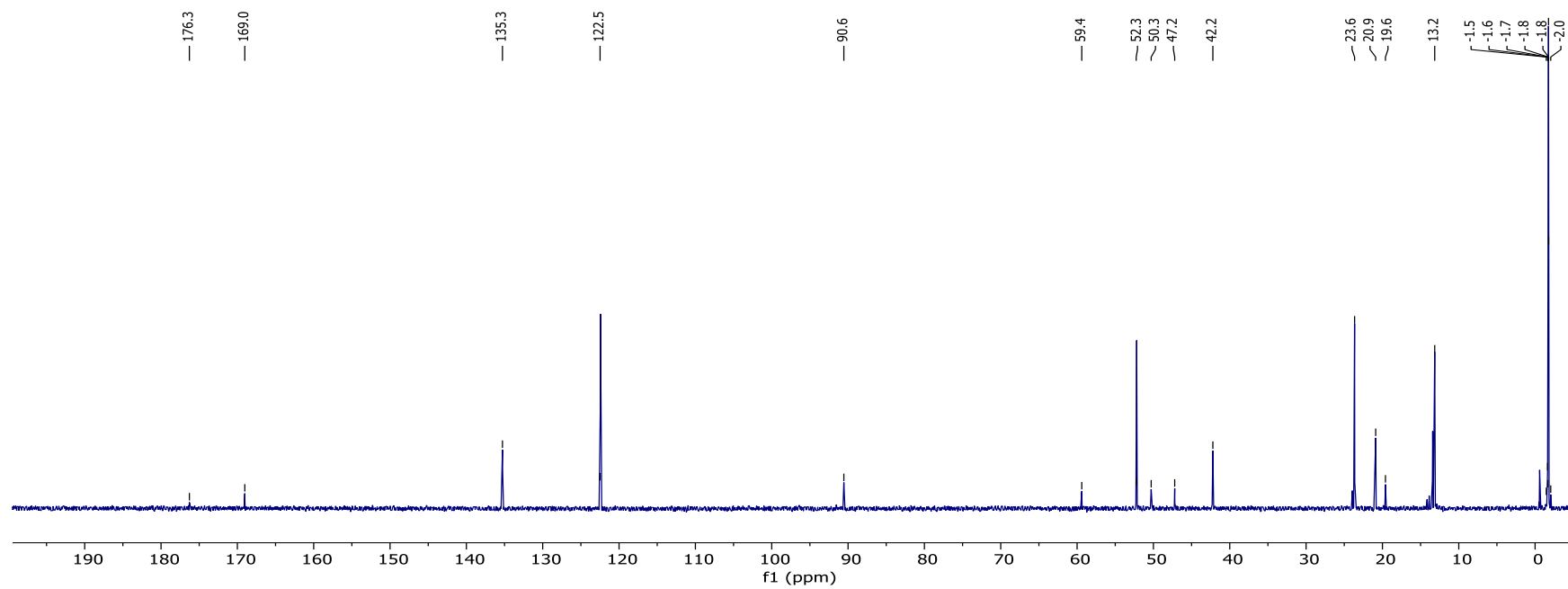
^1H NMR of PIM Lys Cl (400 MHz, D_2O)



^{13}C NMR of PIM Lys Cl (101 MHz, D_2O)

^1H NMR of PIM Si Cl (400 MHz, D_2O)



^{13}C NMR of PIM Si Cl (101 MHz, D_2O)

Curriculum Vitae

Name Masoud Ramezanzadeh

Date and place of birth 26.08.1989, Mashhad, Iran

Professional Career

08.2019 – 06.2024 Research assistant, Technical and Analytical Chemistry, University of Rostock, Germany

06.2023 – 10.2023 Research assistant, Leibniz Institute for Catalysis (LIKAT), Rostock, Germany

02.2015 – 01.2018 Technical assistant, Mashhad Pathobiology Lab, Mashhad, Iran

Education

08.2019 – 06.2024 PhD student in the group of Prof. Dr. Udo Kragl at the University of Rostock, Rostock, Germany

09.2012 – 02.2015 Master of Science in Inorganic Chemistry, Azad University (IAUM), Mashhad, Iran

09.2008 – 08.2012 Bachelor of Science in Applied Chemistry, Azad University (IAUM), Mashhad, Iran

Presentations

Oral

7th RoHan DAAD SDG summer school
06.2023, Rostock, Germany

6th RoHan DAAD SDG winter school
11.2022, Hanoi, Vietnam

Poster

7th RoHan DAAD SDG summer school
06.2023, Rostock, Germany

COIL9 – Congress on Ionic Liquids
04.2023, Lyon, France

3rd ComBioCat Symposium
06.2022, Rostock, Germany

Award

Landesgraduiertenförderung von Mecklenburg-Vorpommern (10.2020 – 05.2023)

Eidesstattliche Erklärung

Doktoranden-Erklärung gemäß § 4 Absatz 1 Buchstaben g und h der Promotionsordnung der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock

Name: Masoud Ramezanzadeh

Anschrift: Wollenweberstr. 8, 18055 Rostock

Ich habe eine Dissertation zum Thema:

Synthesis and Incorporation of Poly(Imidazolium)-based Ionic Liquids in Non-isocyanate Polyurethane Networks and Sustainable Hydrogel Systems

an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock angefertigt. Dabei wurde ich von Herrn Professor Dr. Udo Kragl betreut.

Ich gebe folgende Erklärung ab:

1. Die Gelegenheit zum vorliegenden Promotionsvorhaben ist mir nicht kommerziell vermittelt worden. Insbesondere habe ich keine Organisation eingeschaltet, die gegen Entgelt Betreuerinnen/Betreuer für die Anfertigung von Dissertationen sucht oder die mir obliegenden Pflichten hinsichtlich der Prüfungsleistungen für mich ganz oder teilweise erledigt.

2. Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe. Dazu habe ich keine außer den von mir angegebenen Hilfsmitteln und Quellen verwendet und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen habe ich als solche kenntlich gemacht.

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