

Polar-functionalised polyolefins starting from poly(acrylonitrile-co-butadiene)

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Preface

The past four years as an Engineering Technology student have been quite a journey. They not only introduced me to chemistry, catalysis, and research, but also to many inspiring people who shaped my academic path along the way. After countless lectures, exams, laboratory sessions, and ten months of thesis work, and more than 254 reactions later, it is finally time to write the final chapter of this journey: this master's thesis.

This thesis would not have been possible without the support of several people. I would even dare to say that this research would not have taken the form it has today.

First and foremost, I would like to express my sincere gratitude to my daily supervisor, Jarne Leinders. I could always enter his office for advice, feedback, help, or an in-depth discussion about the experimental results. He was always willing to think problems through with me and supported me with my problems in and outside the lab. Beyond being an excellent supervisor, he was also a very pleasant person to work with, and a chat or a laugh was never uncommon. It is remarkable how much he taught me about catalysis and scientific research over this past year. Without his guidance and support, this thesis would certainly not have been the same.

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In addition, I would like to express my gratitude towards my assessor, Ruth Janssens, for reading and assessing my thesis, as well as her flexibility and support throughout my studies. Thanks to her assistance, I was able to continue my laboratory work during the third year of my bachelor's programme despite a broken hand, allowing me to remain on schedule. I would also like to thank Stijn De Jonge for his valuable guidance and advice concerning my further studies.

Last, but certainly not least, I would like to express my deepest gratitude to my parents for their unconditional support, encouragement, and trust throughout the past years. I am incredibly grateful for the opportunities they gave me and for always providing me with a warm home.

Luka Wouters

Samenvatting

Trefwoorden: poly(acrylonitril-co-butadien), polair-gefunctionaliseerde polyolefinen, oppervlakte-eigenschappen, retro-hydrocyanatie, post-polymerisatie functionalisatie

Jaarlijks wordt meer dan 230 miljoen ton polyolefinen geproduceerd, waarmee ze de meest geproduceerde kunststoffen wereldwijd zijn. Hun populariteit is voornamelijk te danken aan hun lage kost, lichtgewicht, slijtvastheid en goede verwerkbaarheid. Niettemin vertonen polyolefinen belangrijke beperkingen op het vlak van ontwerp vrijheid en compatibiliteit met polaire materialen. Door hun apolaire structuur hebben ze beperkte bedrukbaarheid, adhesie en mechanische performantie. Daardoor worden polyolefinen vaak gecombineerd met potentieel schadelijke additieven of verwerkt in complexe polymeermengsels en multilayerstructuren, wat hun recycleerbaarheid drastisch vermindert. Hierdoor eindigen intrinsiek recycleerbare materialen zoals polyolefinen vaak alsnog in verbrandingsinstallaties of stortplaatsen.

Polair-gefunctionaliseerde polyolefinen vormen een veelbelovend alternatief dat deze beperkingen kan aanpakken zonder de nood aan schadelijke additieven of complexe polymeermengsels. Zelfs een lage functionalisatiegraad kan leiden tot aanzienlijke verbeteringen in compatibiliteit met polaire materialen, adhesie, bedrukbaarheid en taaiheid, terwijl de intrinsiek gunstige eigenschappen van conventionele polyolefinen zoals slijtvastheid en verwerkbaarheid behouden blijven. Huidige synthese strategieën vereisen echter vaak dure monomeren, extreme reactieomstandigheden, en bieden daarenboven weinig controle over het gehalte aan ingebouwde functionele groepen.

Om deze tekortkomingen aan te pakken, ontwikkelden we een nieuwe driestapsmethode voor de synthese van polair-gefunctionaliseerde polyolefinen met nauwkeurige controle over het gehalte aan polaire groepen, zonder gebruik te maken van extreme reactieomstandigheden of dure reagentia. Het commercieel beschikbare poly(acrylonitril-co-butadien) (NBR) werd gekozen als startmateriaal en werd succesvol omgezet in een reeks polair-gefunctionaliseerde polyolefinen. In tegenstelling tot bestaande methoden vertrekt deze synthese van een polymeer dat reeds een hoog gehalte aan functionele groepen (nitrillen) bevat. In een retro-hydrocyanatiestap wordt vervolgens selectief een gecontroleerde fractie nitrilgroepen geëlimineerd tot dubbele bindingen, wat een precieze afstemming van het gehalte aan functionele groepen mogelijk maakt. Een daaropvolgende ruthenium-gekatalyseerde hydrogenering leidt tot de vorming van een amino-gefunctionaliseerde polyolefine. In een derde stap worden de aminogroepen van dit intermediaire polymeer verder gefunctionaliseerd tot diverse stikstofgefunctionaliseerde polyolefinen. In deze studie ligt de focus op de acylatie en ftalimidevorming, hoewel de methode kan worden uitgebreid naar andere functionalisaties.

Samenvattend biedt deze nieuwe methode een flexibele syntheseroute naar stikstofgefunctionaliseerde polyolefinen, die een veelbelovend alternatief vormen voor toepassingen waarin verbeterde eigenschappen zoals taaiheid, bedrukbaarheid, adhesie en compatibiliteit met polaire materialen vereist zijn. Toekomstig onderzoek zal zich richten op een diepgaande karakterisatie van de mechanische eigenschappen en het identificeren van potentiële toepassingen van deze polymeren.

Abstract

Keywords: poly(acrylonitrile-co-butadiene), polar-functionalised polyolefins, surface properties, retro-hydrocyanation, post-polymerisation functionalisation

Yearly, more than 230 million tons of polyolefins are produced, making them the most widely manufactured plastics worldwide. Their popularity stems from their low cost, light weight, durability, and ease of processing. However, they exhibit major shortcomings in terms of designability and compatibility with polar materials. Due to their hydrophobic structure, they suffer from limited printability, dyeability, adhesion, and mechanical performance. Consequently, their applications often rely on harmful chemical additives, complex polymer blends, or multilayer materials, which significantly reduce their recyclability. As a result, these inherently recyclable materials often end up in incineration facilities or landfills.

Polar-functionalised polyolefins offer a promising alternative to address these limitations without requiring harmful additives or complex blends. The incorporation of even small amounts of functional groups can significantly enhance compatibility with polar materials, adhesion, printability, and toughness, while retaining the desirable properties of conventional polyolefins such as durability and processability. However, current synthesis methods typically require expensive monomers and harsh reaction conditions, while offering limited control over functional group incorporation.

To address these limitations, we developed a novel three-step synthesis strategy for polar-functionalised polyolefins that enables precise control over functional group content under mild conditions without the use of expensive reagents. Starting from the commercially available poly(acrylonitrile-co-butadiene) (NBR), a variety of polar-functionalised polyolefins were synthesized. In contrast to other methods, this approach starts with a polymer with a high functional-group content (nitriles), in which a controlled fraction of nitrile groups is selectively converted into C=C bonds via a retro-hydrocyanation step, thereby enabling precise control over the functional-group content. This step is followed by a Ru-catalysed hydrogenation step to yield an amine-functionalised polyethylene-like polymer. Further functionalisation of these amines then provides access to a broad range of N-functionalised polyolefins. As proof of concept, acylation and phthalimide functionalisation are demonstrated in this work. This strategy is readily extendable to a broad range of additional functionalisation pathways.

To conclude, this new approach provides a versatile route towards N-functionalised polyolefins, offering strong potential for high-performance applications in which improved toughness, printability, adhesion, or compatibility with polar materials are required. Future work will focus on comprehensive mechanical characterisation to identify potential application areas for these materials.

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List of symbols

A	Peak surface area	[Area counts]
ECN	Effective Carbon Number	/
$F(R - wt)$	Weight response factor	/
MW	Molar mass	[g/mol]
n	Amount of substance	[mol]
T_b	Boiling point	[°C]
wt	Weight	[g]

List of abbreviations

^1H NMR	Proton Nuclear Magnetic Resonance
2-MeTHF	2-Methyltetrahydrofuran
ABS	Acrylonitrile butadiene styrene
ADMET	Acyclic diene metathesis polycondensation
Ar	Argon
ATR	Attenuated total reflectance
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaftyl
BuOAc	N-butyl acetate
CAGR	Compound annual growth rate
CDCl_3	Deuterated chloroform
cMACS	Centre for membrane separation, adsorption, catalysis, and spectroscopy for sustainable solutions
CPME	Cyclopentyl methyl ether
Cs_2CO_3	Cesium carbonate
DCB	Dichlorobenzene
DCM	Dichloromethane
DMF	Dimethylformamide
ECN	Effective carbon number
EPDM	Ethylene-propylene-diene rubber
Et_3N	Triethylamine
EtOAc	Ethyl acetate
FID	Flame ionisation detector
FTIR	Fourier Transform Infrared Spectroscopy
dHNBR	Defunctionalised hydrogenated nitrile butadiene rubber
dNBR	Defunctionalised nitrile butadiene rubber

dppb	1,4-Bis(diphenylphosphino)butane
dppf	1,1'-Bis(diphenylphosphino)ferrocene
GC	Gas chromatography
H ₂	Hydrogen
HCN	Hydrogen Cyanide
HDPE	High-density polyethylene
HNBR	Hydrogenated nitrile butadiene rubber
KOtBu	Potassium tert-butoxide
LDPE	Low-density polyethylene
LiAlH ₄	Lithium aluminium hydride
LLDPE	Linear low-density polyethylene
MCB	Monochlorobenzene
MeCN	Acetonitrile
MEK	Methyl Ethyl Ketone
Mt	Million tons
N ₂	Nitrogen
NaN ₃	Sodium azide
NaOtBu	Sodium tert-butoxide
NBD	Norbornadiene
NBE	Norbornene
NBR	Nitrile butadiene rubber
NBP	N-Butyl-2-pyrrolidone
N-functionalised	Nitrogen-functionalised
(P(4-F-Ph) ₃	Tris(4-fluorophenyl) phosphine
P(4-MeO-Ph) ₃	Tris(4-methoxyphenyl) phosphine
PB-1	Polybutylene-1
PC	Polycarbonate

PCy ₃	Tricyclohexylphosphine
PE	Polyethylene
PEEK	Polyether ether ketone
PET	Polyethylene terephthalate
PFAS	Per- and polyfluoroalkyl substances
PhCl	Chlorobenzene
PhCN	Benzonitrile
PP	Polypropylene
PPh ₃	Triphenylphosphine
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
ROMP	Ring-opening metathesis polymerisation
TCE	Tetrachloroethane
TMS	Tetramethyl silane
THF	Tetrahydrofuran
UHMWPE	Ultra-high molecular weight polyethylene
UNDP	United Nations Development Programme

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1 INTRODUCTION AND PROBLEM STATEMENT

Synthetic polymer materials have become indispensable in modern life, with polyolefins representing the most significant class among them. Their low cost, high availability, light weight, ease of processing, and good chemical, mechanical, and moisture resistance make them the most produced and consumed plastics worldwide. These polyolefins are used for food packaging, bottles, jugs, containers, pipes, toys, buckets, wire isolation, automotive parts, medical devices, textiles, and many more. A world without these materials is no longer imaginable.

Despite their overall good properties, they exhibit major drawbacks in terms of compatibility and designability. Firstly, because polyolefins are saturated hydrocarbons, they are hydrophobic, posing compatibility challenges with many polar substances, such as dyes, natural fibres, and metal surfaces. Furthermore, in terms of designability, polyolefins face limitations in flame retardancy, oxidative stability, UV resistance, and elasticity. Therefore, these polyolefins are often blended with other plastics or chemical additives to obtain the desired properties. However, this drastically complicates their recycling, thereby losing the inherent good recyclability of polyolefins.

The aim of this thesis project is to investigate the potential of polar-functionalised polyolefins, starting from poly(acrylonitrile-co-butadiene), as an alternative to traditional polyolefins, combining the good properties of conventional polyolefins with improved compatibility and designability through the incorporation of nitrogen functionalities. The N-functionalised polyolefins will be manufactured via sequential chemical reactions known as post-polymerisation functionalisation, which in recent years have become the most important chemical modification leading to new materials.

This way, polar-functionalised polyolefins bypass the need for harmful additives and polymer blends, thereby drastically simplifying their recycling and potentially enabling closed-loop recycling while delivering the same performance as currently used polymer blends.

This thesis aims to answer the following problem statements:

- Is it possible to manufacture various nitrogen-functionalised polyolefins starting from poly(acrylonitrile-co-butadiene)?
- Is it possible to synthesise various nitrogen-functionalised polyolefins with precise control over the functional group content?
- Do the newly nitrogen-functionalised polyolefins have improved dyeability, printability, and elasticity while conserving the good properties of regular polyolefins?

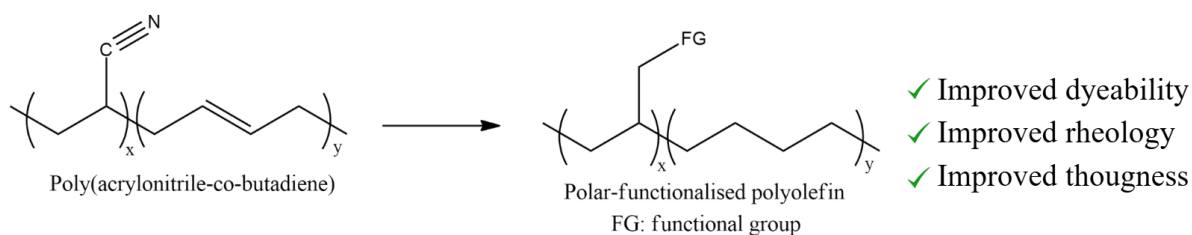


Figure 1: Schematic representation of the strategy investigated in this thesis.

2 LITERATURE REVIEW

2.1 The importance of Plastics

It all started at the beginning of the 20th century when Leo Baekeland mixed phenol and formaldehyde together and created the world's first fully synthetic polymer - Bakelite [1]. This invention opened the door to the age of plastics. Today, plastics are everywhere and have revolutionised our daily lives. From the clothes we wear to the bottles we drink from to the cars we drive, most of our everyday items are made of plastic, either partially or completely. They have even become as familiar to us as woods and metals. Plastics are a category of versatile materials consisting of long chains of repeating molecular units or monomers, most frequently derived from fossil fuels, but can also be based on renewable sources, such as cellulose or starch. Plastics are characterised by their ability to be moulded or shaped while soft and then consolidated upon cooling. Commodity plastics such as polyolefins, including polyethylene (PE) and polypropylene (PP), as well as materials like polyvinyl chloride (PVC) or polystyrene (PS), are widely used because they are inexpensive, lightweight, durable, and easily processable. Due to these properties, they are mass produced, in 2023 around 413.8 million tons of plastics were produced wherefrom 230.7 million tons were polyolefins [2]. The OECD estimates that the total plastic production will reach a volume of 736 million tons by 2040, with current policies [3]. The major demand-driving industry is packaging, which accounts for 40.5% of the produced plastics. Other major demand-driving industries are construction and automotive, which respectively account for 20.4% and 8.8% of the total plastic production [3]. However, for applications that require high performance, these commodity plastics often fall short in terms of chemical, mechanical, or thermal performance.

In recent years, industries have increasingly adopted engineering plastics such as polycarbonate (PC), acrylonitrile butadiene styrene (ABS), polyamides (Nylons), and even some speciality polymers, such as polyether ether ketone (PEEK), polytetrafluorethylene (PTFE), or functionalised polyolefins because of their better chemical, mechanical, and thermal performance compared to commodity plastics. These engineering plastics are mainly used in demanding industries such as aerospace, automotive, and the medical sector, where commodity plastics would fall short, enabling the replacement of metals in situations requiring high strength, heat resistance, or durability. This replacement of metals is desired because the performance of engineering plastics continues to improve, while metal prices and fabrication costs are expected to further increase [4]. Currently, the engineering plastic market size is estimated at 62.3 million tons in 2025 and is expected to grow to 79.83 million tons by 2030. This indicates that a further shift towards engineering plastics is forecasted in the coming years [4].

As a major consequence of the massive global production of plastic, enormous amounts of plastic reach the end of their life each year. From the 400 million tons of plastic waste generated each year, only 9% is recycled [5]. Currently, the most used recycling method is mechanical recycling. This process typically includes collecting, sorting, washing, and grinding plastic waste [6]. Afterwards, the plastic flakes or pellets can be melted and remoulded into new products, such as bottles or containers. Chemical recycling is an alternative recycling process in which plastics are broken down into their building blocks, enabling the production of virgin-quality polymers. Chemical recycling can be done via either pyrolysis,

depolymerisation, or dissolution of the waste plastic [7]. Non-recycled plastic waste is either incinerated, landfilled, or released into the environment due to inadequate waste management. Of all plastic waste generated, 19% is incinerated, most of which is processed in waste-to-energy facilities, recovering electricity and heat. However, when this plastic waste is incinerated, it emits a mixture of harmful chemicals into the air, such as dioxins, furans, and acidic gases. Therefore, incineration of plastic waste requires advanced pollution control and flue gas cleaning. Unfortunately, the biggest part of plastic waste produced, around 50%, is discarded in sanitary landfills, and even worse, another 22% of plastic waste is disposed of in uncontrolled dumpsites, openly burned, or leaks into the environment [3]. Consequently, when these materials enter the environment, they persist for hundreds to thousands of years, gradually breaking down into smaller microplastics that accumulate across ecosystems. This accumulation poses significant threats to wildlife and contributes to global pollution and climate change. Over time, rainwater can also leach toxic additives and microplastics from waste stored in landfills, contaminating groundwater and soil. Even a new study by the U.S. federal government claims that plastic production is a major driver of climate change and that, by 2050, it would account for 21%-31% of the global carbon budget required to keep global warming below 1.5 degrees [8].

Drastically increasing plastic recycling rates can be a major solution. Currently, recycling rates are rather low. One of the main reasons for this problematic low recycling rate is the use of harmful chemicals in plastic production. Conventional plastics are complex blends, and often different chemical additives are added to obtain specific properties for various applications. Many of these substances are harmful to human health. Recycling these can result in long-term negative health impacts for workers, local communities, and end-of-life product users, according to the UNDP [5]. Bypassing the need for these chemical additives in plastic production has great potential to drastically increasing recycling rates and reduce the environmental impact of the plastic industry.

2.2 Polyolefins and their shortcomings

Polyolefins, including PE, PP, polybutylene-1 (PB-1), and synthetic rubbers like ethylene-propylene-diene rubber (EPDM), are the most widely used commercial polymers on the planet and constitute over half of the global plastic production [9], [10]. With a total production of 230.72 million tons (Mt) in 2024 and a forecasted compound annual growth rate (CAGR) of 4.88%, the polyolefin market is expected to reach 371.54 Mt by 2034 [11]. This sustained growth underscores the vital role of polyolefins across global industries.

Polyolefins are a family of polymers produced from simple olefin monomers (alkenes) such as ethylene, propylene, and norbornene. These monomers are typically derived from crude oil and natural gas feedstocks via a process known as steam cracking, in which larger hydrocarbons are converted into smaller, often unsaturated, molecules under the injection of steam at temperatures between 800-870°C [12]. Afterwards, the cracked gas is separated into its valuable fractions according to the requirements of downstream processes.

Once obtained, the olefin monomers are converted into polyolefins via various polymerisation processes. Firstly, free radical polymerisation can be used, but it generally leads to branched structures and is industrially employed exclusively to produce low-density polyethylene (LDPE) [13]. The branched structure of LDPE reduces crystallinity, resulting in a more flexible,

transparent, and processable material, ideal for films, coatings, and packaging applications. In contrast, coordination polymerisation techniques using Ziegler-Natta and metallocene catalysts produce more linear or more stereoregular polymers, such as isotactic PP, high-density polyethylene (HDPE), or linear low-density polyethylene (LLDPE).

The widespread use of polyolefins can be attributed to various factors. Firstly, the olefins used as raw materials are inexpensive and widely available as products of petroleum and natural gas refining. Furthermore, they possess excellent material properties; they are lightweight, chemical- and moisture-resistant, electrically insulating, and durable. Moreover, mechanical and thermal properties can be further tailored by controlling molecular weight and crystallinity during the processing stages, resulting in versatile products such as LLDPE, HDPE, and ultra-high molecular weight polyethylene (UHMWPE) as different versions of PE [9], [14].

In addition, they have a great processability. Polyolefins are easy to melt, mould, extrude, blow into films, or spin into fibres. Moreover, polyolefins are thermoplastics that can be remelted and reshaped, making them easy to recycle. These excellent properties make them popular materials across many industries, such as packaging, textiles, automotive, construction, and consumer goods [9].

However, polyolefins have major limitations in terms of compatibility and designability. These limitations directly come from their molecular structure. Polyolefins consist solely of hydrocarbons, making them hydrophobic and chemically inert, which results in poor interactions with polar substances such as water, dyes, and natural fibres. This translates into low dyeability, weak adhesion, and very limited compatibility with polar substances (e.g., other polymers) in general. Furthermore, the simplicity of the backbone also causes designability limitations. For instance, polyolefins are susceptible to UV degradation, becoming brittle under prolonged exposure to sunlight. Moreover, they exhibit low-temperature embrittlement, which restricts their applications in cold environments. Their limited thermal stability further constrains their use in high-temperature applications. Additionally, their inherent flammability limits their use in applications requiring high fire resistance [10].

Due to these limitations, polyolefins are often blended with other plastics or chemical additives to improve overall performance in applications while keeping costs low. Alternatively, multilayer packaging has become widely used in sectors such as food and cosmetics. These multi-layer packages consist of multiple layers made from different plastics, such as PE, PP, or polyethylene terephthalate (PET). This is done so unique properties of different materials can be combined [15], [16]. However, multilayer packaging and polymer blending pose enormous challenges for both mechanical and chemical recycling, hindering efficient recovery of high-purity polyolefins. The different materials in the blend or multilayer cannot be separated via mechanical recycling. Remelting these incompatible plastics leads to phase separation, resulting in a significant decline in mechanical properties, such as strength and ductility, making preservation of quality almost impossible [16]. Additionally, these plastic mixtures pose challenges for chemical recycling, as such processes are optimised for specific polymers and require precise control of reaction conditions. The various plastics present in blends or multilayers have different melting temperatures and degradation pathways, so only certain polymers can be effectively depolymerised, while others cannot. When relatively pure streams of polyolefins can be obtained for recycling by bypassing the need for chemical additives, polymer blends, or multilayer materials, both mechanical and chemical recycling would become significantly simplified and more efficient, making it possible to recycle much larger quantities [10].

2.3 The need for functionalised polyolefins

Functionalised polyolefins are of great interest because they combine the good material properties of polyolefins with enhanced compatibility and designability properties. Therefore, functionalised polyolefins can reduce the need for polymer blends and additional chemical additives, simplifying material composition and making recycling more efficient [17]. By introducing polar functionalities, typically based on oxygen or nitrogen, into the polymer backbone, structure, properties, and performance can be significantly modified [18]. Even the introduction of small numbers of polar moieties can have a strong impact on bulk and surface properties, improving adhesion, printability, dyeability, and other properties like toughness, miscibility, and rheology of the polyolefin. This concept of polyolefin functionalisation is schematically represented in Figure 2. This enables new applications where the outstanding material properties of polyolefins are retained while new beneficial surface properties are added. Currently, the incorporation of oxygen functionalities into polyolefins is extensively used and well-documented due to their functional diversity and availability [19]. On the other hand, nitrogen-functionalised polyolefins are currently underexplored, despite their great potential to significantly improve bulk and surface properties. This can be attributed to the challenging synthesis of nitrogen-based copolymers due to nitrogen-induced catalyst poisoning. Besides that, N-groups inhibit chain propagation and induce chain transfer far more severely than O-groups. This limits manufacturing to low molecular weight polymers with N-functionalised comonomer content seldom exceeding 5 mol% [19].

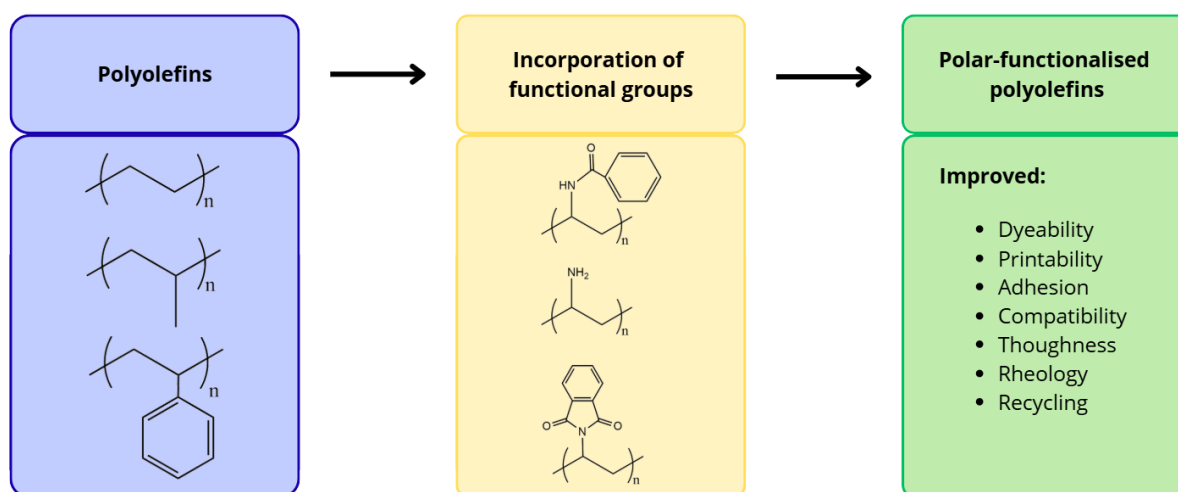


Figure 2: Polar-functionalised polyolefins and resulting improvements in material performance.

Generally, the main challenges faced in current functionalisation strategies are the incorporation of functional groups in a selective, controlled, and mild manner. Having control over the level of incorporated functional groups is highly desired for precise property tailoring of the functionalised polyolefins [19].

The following section reviews the state of the art in polyolefin functionalisation and discusses the most commonly used methods, their advantages, and shortcomings.

In 2013, De Bruin and co-workers published a state-of-the-art paper on polyolefin functionalisation, which greatly classified current functionalisation methods of polyolefins and critically discusses their advantages and shortcomings [18]. Current methods can be subdivided into methods producing randomly functionalised copolymers, Chain-end functionalised copolymers, and methods producing graft or block copolymers.

Currently, post-polymerisation functionalisation is among the most widely adopted approaches for producing random-functionalised polyolefins, as it benefits from the well-established manufacturing processes for non-functionalised polyolefins. A great example of post-polymerisation functionalisation was published by Hong and co-workers [20]. They established a post-polymerisation functionalisation technique based on the non-catalytic C-H insertion of sulfonyl azides, enabling the introduction of a wide range of functional groups, including amino, hydroxyl, acetamide, and carboxyl moieties, into polypropylene. Notably, these functionalities were incorporated without the need for catalysts and with minimal degradation of the polymer backbone [20]. Lastly, some big advancements were made in post-polymerisation of N-functionalised polyolefins by the Hartwig group, from which the chemistry is currently underexplored due to a challenging synthesis via other pathways [17]. They established a novel post-polymerisation strategy based on the catalytic amination of C-H bonds to C-N bonds. Another recent example to establish nitrogen functionalised polyolefins is the post-polymerisation functionalisation via catalytic nitrene addition by Pérez and co-workers via silver-based catalysts [21]. Another major advantage of post-polymerisation functionalisation is that a wide variety of starting materials can be used. [22]. Most common techniques use radicals or plasmas to introduce polar functionalities into the polymer backbone. Unfortunately, these reactions induce high degrees of uncontrollable crosslinking, drastically altering polymer architectures [17], [18]. In general, post-polymerisation functionalisation strategies are currently limited to a very narrow range of substituents, often involve expensive reagents, and are accompanied by crosslinking and scission of the polymer chains involved. Furthermore, high temperatures and non-polar solvents are required to dissolve conventional polyolefins, and these conditions are incompatible with most developed functionalisation methods. In addition, the reaction can be challenging due to chain conformations and the difficulty of product purification. Another major drawback is that post-polymerisation functionalisation of polyolefins requires harsh conditions due to their chemical inertness. Currently, catalytic techniques are being developed to overcome these problems, but these methods are still far from ideal [18].

Alternatively, direct copolymerisation of polar and non-polar vinyl monomers can be employed to obtain random functionalised polyolefins. Although it is the most logical approach, this method faces many challenges [18]. This copolymerisation is generally carried out via free-radical polymerisation, for instance, the free-radical copolymerisation of ethene and methyl methacrylate [23]. The major flaw of this method is that only branched polymers can be obtained, and ratios of incorporated polar comonomers are hardly controllable [17]. Furthermore, this method requires harsh conditions (high temperatures and pressures), and this branching translates to lower mechanical strength, stiffness, melting point, and barrier properties [18]. Alternatively, copolymerisation catalysed by transition-metal complexes could be used to synthesise more linear functional polyolefins, for instance, zirconium (Zr) catalysed copolymerisation of ethylene with amino-olefins [24]. However, early transition-metal catalysts, such as Zr, suffer from poisoning by polar comonomers, resulting in the incorporation of only small amounts of polar monomers. One approach to address this poisoning is to shield the functional group with an appropriate protecting group prior to the polymerisation process [22]. However, this requires an additional post-polymerisation step to deprotect the functional group. Furthermore, efforts have been made to modify catalysts to increase functional-group tolerance, but these modifications have compromised stereoregularity. On the other hand, late-transition-metal catalysts, such as nickel and palladium, exhibit inherently high tolerance for

polar groups. Therefore, these catalysts can copolymerize non-polar and polar vinyl monomers, such as methyl methacrylate, as demonstrated by Haiyang Gao and co-workers [25], as well as other monomers, including vinyl acetate, acrylic esters, and vinyl esters. However, catalysts with palladium or nickel as the metal centre also yield branched polyolefins via β -hydride elimination and polymer chain walking [26]. In general, catalyst activities are markedly lower for copolymerisation with polar comonomers than for homopolymers, thereby making direct copolymerisation inefficient.

A third established method to produce randomly functionalised polyolefins is ring-opening metathesis polymerisation (ROMP) with functionalised cyclic alkenes. This ring-opening metathesis polymerisation is a chain-growth polymerisation in which cyclic alkenes are converted into linear polymers via a metal-catalysed olefin metathesis reaction, followed by hydrogenation of the resulting polyunsaturated polymer. This reaction is driven by the release of ring strain of the cyclic olefin monomers. The big advantage of this method is that it can produce remarkably linear polyolefins, with precise control over the incorporation of functional groups through design of the cyclic olefin monomers [26]. This, while having high functional group tolerance and requiring mild reaction conditions. Fan and co-workers greatly demonstrated the advantages of ROMP by synthesising 3 distinct functional cyclopentenones, which they then polymerised into different ester-functionalised polyolefins via the ROMP reaction pathway [27]. However, ROMP also has some major drawbacks. It requires very specific monomers and occurs in a multi-step fashion [18]. Furthermore, it requires a stoichiometric amount of ruthenium initiator with respect to the polymer chains formed, which corresponds to a high and expensive catalyst loading [28]. Lastly, it is extremely challenging to remove these toxic metal contaminants from the synthesised polymers, making the process unattractive for industrial and biomedical applications [28].

Acyclic diene metathesis polycondensation (ADMET) is another possible route for the synthesis of random-functionalised polyolefins. ADMET is a step-growth polycondensation reaction of special symmetrically functionalised α,ω -diene monomers. The reaction releases ethylene as a byproduct, from which the elution is typically used as the thermodynamic driving force of the reaction [29]. ADMET reactions typically yield unsaturated, almost perfectly linear polymers that can be hydrogenated in a subsequent step. The reaction course of ADMET is based on the same elemental reaction steps as ROMP and consequently has the same drawbacks [18]. In 2000, Wagener et al. showed already the applicability of this method to produce functional polyolefins when they used ethylene-co-acrylate, -co-styrene, and -co-vinyl chloride monomers to manufacture functionalised polyethylenes [30].

Next to these randomly functionalised polyolefins, as discussed so far, there are chain-end-functionalised copolymers, block copolymers, and graft copolymers. These chain-end functionalised copolymers can serve as a valuable starting point for manufacturing complex macromolecular architectures from otherwise unreactive polyolefin chains. However, only the end groups are functionalised, so this has little effect on bulk properties [18]. Furthermore, block and graft copolymers perform well as compatibilisers, thereby promoting the use of polymer blends, which complicates recycling streams, as discussed earlier. Moreover, their synthesis can be very challenging. Often, multi-step approaches with distinct polymerisation techniques are required. Although the grafting of maleic anhydride onto polyolefins is extensively used in industry to fulfil commercial requirements for food packaging [22], these

block and graft copolymers are less interesting from an industrial point of view than the earlier discussed random functionalised polyolefins, because these block and graft copolymers are generally more difficult and expensive to synthesise, as well as having a narrower application range.

To conclude, polar-functionalised polyolefins show great potential to resolve current compatibility and designability challenges faced by conventional polyolefins. Due to the combination of the inherent good polyolefin properties with improved properties such as dyeability, printability, adhesion, compatibility, and rheology, these functionalised polyolefins can bypass the need for polymer blends, additives, or multilayer materials, restoring the inherent recyclability of polyolefins [10]. However, currently developed functionalisation methods exhibit major limitations, such as requiring harsh conditions, specific chemicals, and low control over the incorporation of polar groups. The latter is especially true for nitrogen-functionalised polyolefins. Therefore, the development of alternative methods that allow precise control over both the incorporation of polar groups and the polymer architecture under mild conditions would be broadly applicable.

2.4 Nitrile butadiene rubber as starting materials for functionalised polyolefins

Nitrile butadiene rubber (NBR) and hydrogenated nitrile butadiene rubber (HNBR) are widely available synthetic elastomers that can serve as ideal starting materials for the production of functionalised polyolefins. The nitrile functionality present along their polymer backbone can be readily modified into a variety of functional groups.

2.4.1 Nitrile butadiene rubber (NBR)

Poly(acrylonitrile-co-butadiene) or nitrile butadiene rubber, often abbreviated as NBR, is a random copolymer of acrylonitrile and butadiene. This rubber is mass-produced with a total trade volume of 1.5 million Mt in 2022 at an average price of \$2.6/kg, with Western Europe being the largest importer [31]. The nitrile butadiene rubber market was valued at USD 1.9 billion and is forecast to grow to USD 3.8 billion by 2032, representing a CAGR of 5.2%. This growth can mainly be attributed to increasing demand from the automotive, construction, and medical industries.

NBR is typically produced via emulsion polymerisation. Water, emulsifiers, monomers (acrylonitrile and butadiene), radical initiators, and other ingredients, such as buffers, chain transfer agents, and stabilisers, are charged into the reactor vessel. The reaction mixture is then stirred and maintained at temperatures between 5°C and 15°C, allowing the initiator to generate radicals that initiate copolymerisation of acrylonitrile and butadiene within the emulsion droplets. Eventually, the polymerisation yields a latex, which is coagulated to form crumb rubber. This crumb rubber can then be milled and pressed into sheets or blocks for storage or further processing. Alternatively, the crumb rubber can be directly compounded. Vulcanised NBR, which is produced by heating NBR with sulphur or peroxides, can be moulded or extruded into a wide range of finished products [32].

The combination of the two monomers acrylonitrile and butadiene provides unique properties. On the one hand, the nitrile units provide chemical resistance, thermal stability, and good barrier properties, while on the other hand, the butadiene units provide elasticity, toughness, and impact resistance. That's why NBR-based products exhibit excellent resistance to fuels, oils, greases, and chemicals. Therefore, it's no surprise that NBR finds its main use in gaskets, seals, and O-rings in fuel systems, fuel hoses, or even gloves in laboratory settings [33]. Furthermore, this polymer is rather hydrophobic and insoluble in water or other polar solvents, but the nitrile groups (-CN) are polar and reactive, which makes this polymer ideal for post-polymerisation functionalisation.

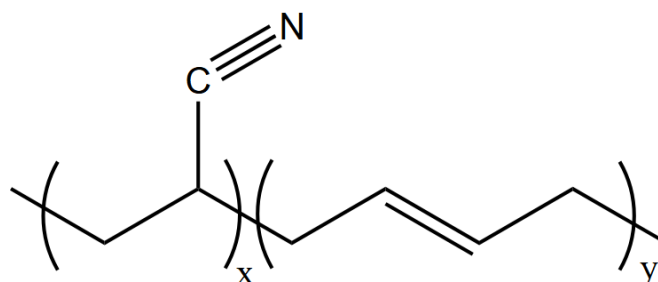


Figure 3: Structure of poly(acrylonitrile-co-butadiene) or nitrile butadiene rubber [34].

2.4.2 Hydrogenated nitrile butadiene rubber (HNBR)

However, NBR became widely used in industry owing to its high strength, excellent elasticity, and good resistance to oils and fuels. Nevertheless, the presence of olefinic bonds in its polymer backbone limits thermal stability, chemical resistance, and long-term mechanical performance. In particular, NBR exhibits poor ageing and weather resistance, making it susceptible to oxidative and ozonolytic degradation [35]. This makes it unsuitable for demanding environments such as oil drilling or the automotive industry. These deficiencies have driven the development of hydrogenated nitrile butadiene rubber (HNBR). HNBR is a high-performance elastomer obtained by selective catalytic hydrogenation of NBR, in which the double bonds in the butadiene units are saturated.

The HNBR market in 2024 was estimated at USD 600 million and is forecast to grow to USD 1.2 billion by 2035. So, the market will grow with a CAGR of 6.5%. This market growth is driven by rising demand for industrial, gas, oil, and automotive products. The average price at which HNBR is currently sold in Europe is around \$27.8/kg [36], [37].

On an industrial scale, HNBR is predominantly produced via the Bayer process, which employs Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$). However, due to economic and environmental concerns, alternative production processes are undergoing rapid development. A major drawback of the currently used homogeneous processes is their reliance on rhodium-based catalysts, which are both scarce and costly. In addition, this noble catalyst is difficult to recover from the reaction mixture, resulting in limited recyclability and reduced process sustainability [35].

The selective hydrogenation of the olefinic bonds in butadiene units improves mechanical, chemical, and thermal properties. Most importantly, HNBR shows excellent resistance to thermal oxidation, along with improved strength, elongation, hardness, and abrasion resistance compared to NBR, while maintaining excellent resistance to chemicals and oils [35]. HNBR finds numerous applications in the automotive industry, for instance, in air-conditioning hoses, fuel and engine-system seals, timing belts, and even components in the battery

systems of electric cars. Furthermore, HNBR is used more frequently in the oil and gas industries for long-lasting, chemical-resistant seals and gaskets [35], [36].

To summarise, the transition from NBR to HNBR represents a key advancement in elastomer technology, enabling reliable performance under conditions of prolonged exposure to heat, oil, aggressive chemicals, or mechanical stresses. However, widespread production remains hindered by reliance on costly metal catalysts.

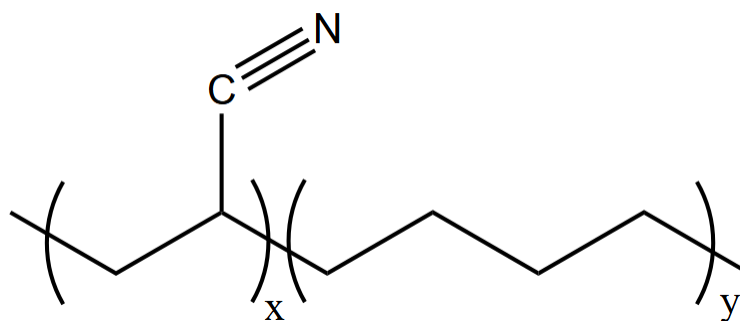


Figure 4: Structure of hydrogenated nitrile butadiene rubber.

2.4.3 Hydrogenation of NBR to HNBR

HNBR has become the most significant hydrogenated elastomer and the workhorse for high-performance elastomer applications because HNBR exhibits excellent thermal stability and resistance to oil and chemicals [38]. The rapid development of selective hydrogenation techniques is driven by the increasing demand for high-performance, oil-resistant elastomers. However, the main challenge faced in the production of HNBR is the selective hydrogenation of the C=C double bonds in NBR while leaving the nitrile groups unaffected [35].

In the 1970s, the chemical company Bayer established the first successful industrial process that selectively hydrogenated NBR to HNBR. This process uses Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$), supplemented with a large excess of the PPh_3 ligand to stabilise the rhodium species [39]. In this solution hydrogenation process, the substrate polymer, NBR, is dissolved in a suitable organic solvent, such as monochlorobenzene (MCB) or Methyl Ethyl Ketone (MEK). Then, an inert gas is used to purge out all oxygen from the reactor. Then the reactor is heated to the desired temperature, between 130°C and 150°C, before hydrogen gas is introduced. Depending on the specific conditions, the Rh-catalyst and PPh_3 co-catalyst are either added to the reaction mixture before or after the setup temperature and pressure are reached. Then Wilkinson's catalyst activates molecular hydrogen and subsequently transfers it to the carbon-carbon double bonds of the butadiene units in NBR, ultimately yielding HNBR. Following hydrogenation, the solvent and catalyst are separated, recovered, and recycled, while the hydrogenated polymer is precipitated, dried, and baled [35]. Although less expensive homogeneous ruthenium- and osmium-based catalysts have been developed as alternatives to the extremely scarce and expensive rhodium catalysts, rhodium remains the most widely used metal for industrial NBR hydrogenation because it produces HNBR with a lower intrinsic viscosity, whereas ruthenium- or osmium-based catalysts are prone to undesirable crosslinking reactions [39]. Furthermore, rhodium complexes, such as Wilkinson's catalyst, are well recognised for their stability and very high selectivity for olefinic bonds, even in the presence of functional groups such as nitriles. Wilkinson's catalyst also effectively suppresses

crosslinking, readily achieves high conversions, and exhibits excellent air stability in solid form [35].

A second major drawback of the conventional hydrogenation process is its high consumption of organic solvents, such as MCB, which increases production costs and raises environmental concerns. Consequently, alternative approaches, such as latex hydrogenation or heterogeneous catalytic hydrogenation, are being actively developed.

The advantage of latex hydrogenation is that it eliminates the need for polymer coagulation prior to hydrogenation, reduces solvent consumption, and improves the process's overall energy efficiency. In latex hydrogenation, the NBR latex obtained after polymerisation is used directly without prior coagulation. A rhodium-based catalyst and PPh_3 are added to the latex. Then, air is purged out with N_2 gas. Subsequently, hydrogenation is initiated by introducing hydrogen gas into the reactor. In this process, PPh_3 serves not only as a ligand but also as a phase-transfer agent, transporting $\text{RhCl(PPh}_3)_3$ from the aqueous phase to the polymer. Because PPh_3 is compatible with both NBR and HNBR, it enhances catalyst-polymer interactions and dispersion throughout the polymer matrix [35]. Despite being a greener, almost solvent-free process, latex hydrogenation has not achieved widespread industrial adoption because challenges such as gel formation, mass-transfer limitations, and reduced catalyst efficiency continue to favour solution hydrogenation.

In addition to homogeneous catalysis, heterogeneous catalysis could also be employed to hydrogenate NBR. In literature, several rhodium (Rh), ruthenium (Ru), Nickel (Ni), and palladium (Pd) complexes have been reported to achieve successful selective heterogeneous hydrogenation of NBR without overreduction of the nitrile groups [40], [41], [42]. Currently, Pd catalysts dispersed on activated carbon or on silica are the main commercially used catalysts for heterogeneous hydrogenation of NBR, as for the manufacturing of Zetpol® from the company ZEON in Japan [43]. The typical process sequence of a heterogeneous hydrogenation is to first dissolve the polymer into a suitable solvent and then contact it with the heterogeneous catalyst under a hydrogen atmosphere [35]. Heterogeneous reactions are highly appraised for their much easier catalyst recoveries. A simple filtration or centrifugation operation of the reaction mixture is, in most cases, sufficient to recover the catalyst. This can be a major advantage when expensive or scarce catalysts, such as Rh, are used. However, in heterogeneous catalysis, contact between the polymer and the catalyst is limited due to higher viscosities and steric hindrance from the polymer chains, resulting in lower-grade HNBR compared to homogeneous catalysis. Because the main market for HNBR is high-performance elastomeric applications, homogeneous catalysis remains the predominant industrial method for its production.

2.5 From (Hydrogenated) Nitrile Butadiene Rubber to Nitrogen-functionalised polyolefins

The methodology proposed in this thesis for the synthesis of nitrogen-functionalised polyolefins starting from nitrile butadiene rubber consists of three sequential steps: retro-hydrocyanation, hydrogenation, and functionalisation. Although each of these steps has been investigated previously in the literature, they have generally been studied on different substrates and for different purposes. The following sections review the current state of the art for each of these three consecutive reaction steps and highlight their relevance to the proposed synthetic strategy.

2.5.1 Retro- hydrocyanation of small nitriles

This section reviews the current literature on the concept, mechanism, and available catalytic systems for (retro-)transfer hydrocyanations, with a focus on their potential use in polymer (de)functionalisation.

2.5.1.1 Shuttle catalysis

Traditionally, hydrocyanation has been a valuable organic synthesis method allowing alkenes to be converted into nitriles under the addition of the hazardous hydrogen cyanide gas (HCN). This reaction plays an important role in the preparation of natural products, pesticides, pharmaceuticals, and cosmetics [44]. However, HCN is highly volatile, flammable, and extremely toxic, making its handling associated with significant health and safety risks, even on a laboratory scale. Nevertheless, the chemical company DuPont has successfully implemented an industrial hydrocyanation process based on HCN, producing approximately one million tonnes of adiponitrile annually, a key precursor of nylon-6,6 production [45]. Hydrocyanation processes, such as the DuPont process, typically employ transition metal catalysts, such as nickel-phosphite or nickel-phosphine complexes, which are prone to deactivation by HCN gas through the formation of inactive catalytic species [44]. The synthetically valuable retro-hydrocyanation, which would allow the conversion from nitriles into alkenes, is thermodynamically unfavourable and has therefore been challenging to achieve.

Recent advancements by Morandi and co-workers have addressed these challenges by developing a catalytic reversible alkene-nitrile interconversion mechanism [44]. This enables a transfer hydrocyanation and retro-hydrocyanation reaction in which a HCN moiety is directly transferred from a nitrile-containing molecule (i.e., an HCN donor) to an alkene (i.e., an HCN acceptor) without ever being released as HCN gas, a concept known as shuttle catalysis.

In shuttle catalysis, a chemical group or compound, often referred to as the shuttled group, is transferred between a donor and an acceptor molecule. The concept is illustrated in Figure 5. In the forward reaction, a simple, inexpensive sacrificial donor molecule functionalises the acceptor, often an alkene. In contrast to the reverse or defunctionalisation process, wherein a common sacrificial acceptor molecule is employed to remove a functional group from the donor molecule through a bond-breaking process [46]. Reactions in shuttle catalysis are considered isodesmic, meaning that all chemical bonds broken on the reactant side are the same as those formed on the product side. Therefore, these reactions are, in theory, reversible [46].

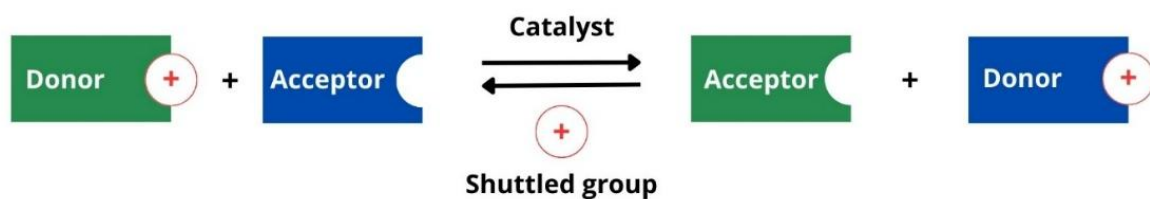


Figure 5: Visual representation of the shuttle catalysis principle [46].

The successful realisation of the shuttling of a functional group between donor and acceptor depends on several factors: the nature of the interchanged functional group, the nature of the acceptor molecule, and the thermodynamic and kinetic stability of the resulting products [47].

A major challenge in shuttle catalysis is controlling the thermodynamic equilibrium to favour either the forward or reverse reaction. The equilibrium can be shifted in the desired direction, making use of simple thermodynamic driving forces, including the generation and off-gassing of gaseous products, the precipitation of insoluble products, the formation of conjugated systems, or the release of ring strain [46]. Moreover, identifying a catalytic system capable of overcoming all kinetic barriers and performing this shuttle transfer of the desired group under mild conditions remains a significant challenge.

The shuttle catalysis concept is inspired by the H₂-free transfer hydrogenation reactions [44], which has had a profound impact on organic synthesis [48]. Through this approach, controllable hydrogenation and dehydrogenation can be achieved under similar conditions. Building on the success of transfer hydrogenation, the shuttle catalysis concept has been extended to reversible transfer functionalisation involving groups other than hydrogen. Shuttle catalysis is particularly attractive when the transferred group is highly toxic, reactive or unstable, as in the case for HCN, HF, nitrenes or carbenes [46].

Transfer hydrocyanation, which can be viewed as an HCN shuttle reaction, has emerged as an effective and attractive strategy for the selective hydrocyanation of alkenes. In addition, this shuttle catalysis approach enables the valuable retro-hydrocyanation, providing a valuable route for defunctionalisation of nitrile-containing substrates [44]. In the transfer hydrocyanation, simple aliphatic nitriles are used as hydrocyanating agents, while the reaction equilibrium is thermodynamically controlled through evaporation or conversion of the resulting small alkenes [49]. In contrast, in the retro-hydrocyanation, chemical substances such as norbornadiene (NBD) and norbornene (NBE) have been evaluated as effective trapping reagents due to their substantial amount of ring strain that is (partially) released through this HCN transfer, which thermodynamically drives the retro-hydrocyanation towards product formation [44].

2.5.1.2 Mechanism of retro-hydrocyanation

In 2016, Morandi and co-workers reported a dual Ni(DPEphos)/AlMe₂Cl-catalysed transfer hydrocyanation protocol [44]. Nickel was initially chosen as the transition metal catalyst because Ni(0) complexes show very high activity in oxidative addition of polar bonds, such as C-CN bonds, and they are very active and extensively used in traditional hydrocyanation processes, such as the DuPont adiponitrile process [45]. The Lewis acidic AlMe₂Cl co-catalyst was used to facilitate the nickel-mediated oxidative addition and reductive elimination of C-CN by coordinating to the nitrile functional group. Furthermore, they demonstrate the feasibility of using AlCl₃ as the Lewis acidic co-catalyst as a safer alternative to the highly flammable AlMe₂Cl [44].

The plausible reaction mechanism proposed in the literature for a catalytic system consisting of $\text{Ni(cod)}_2/\text{DPEphos}/\text{AlMe}_2\text{Cl}$ will be further outlined, with isovaleronitrile as HCN donor and α -methyl styrene as HCN acceptor (Figure 6). The proposed reaction mechanism is primarily based on the mechanism proposed by Morandi and co-workers [44] and Li Dang and co-workers [50]. The mechanism begins with π -coordinated bond formation between Ni(0) and the CN group of the HCN donor, thereby activating the nitrile. Then, the C-CN bond is broken, and both the CN-group and the remaining alkyl fragment are added to the Ni(0) -centre, oxidising it to a Ni(II) -complex. This step is known as the oxidative addition [50]. In the next step, β -hydride elimination occurs; the β -hydrogen atom is abstracted from the remaining alkyl group and attaches to the empty coordination site of the Ni(II) complex. This sequence of steps results in the molecular shuttle H-Ni(II)-CN . In this case, the Ni(II) -catalyst is coordinatively saturated. To continue the catalytic cycle, the previous step is followed by ligand exchange, in which the weakly bound alkene produced in β -hydride elimination leaves the Nickel catalyst and is replaced by a new alkene, the HCN acceptor.

The next step of the catalytic cycle is the migratory insertion of the alkene into the Ni-H bond, transferring the hydride to the alkene substrate. The last step of the catalytic cycle is reductive elimination, yielding a new nitrile product. In this last step, the CN ligand and the alkyl ligand bound to the metal centre form a σ -bond, thereby reducing the Nickel catalyst to Ni(0) . This step involves the formation of a π -oriented bond between Ni(0) and the newly formed nitrile substrate. This newly formed nitrile dissociates from the Ni catalyst, allowing the next catalytic cycle to begin.

The catalytic cycle diverges into two pathways after ligand exchange, as displayed in Figure 6. The outermost pathway will lead to the formation of linear nitriles, whereas the innermost pathway will lead to the formation of branched nitriles. The presence of a suitable co-catalyst, such as the Lewis acidic AlMe_2Cl , can favour the outermost pathway leading to a mixture of products with linear nitriles present as the most dominant isomer [51]. The Lewis acid facilitates both the nickel-mediated C-CN oxidative addition and the C-CN reductive elimination, thereby making the formation of linear and branched nitriles accessible. Linear nitriles are thermodynamically more stable and less reactive and will therefore be formed predominantly. This is often referred to as anti-Markovnikov selectivity [51]. Oxidative addition and reductive elimination are the rate-determining steps of the catalytic cycle, which the Lewis acid facilitates by lowering their activation energies. When the catalytic cycle is executed in the absence of a Lewis acid, the innermost catalytic pathway is favoured, and only branched nitriles are observed with high Markovnikov selectivity. The key to this selectivity is the lower activation energy of the oxidative addition and reductive elimination at the benzylic position for the formation of branched nitriles.

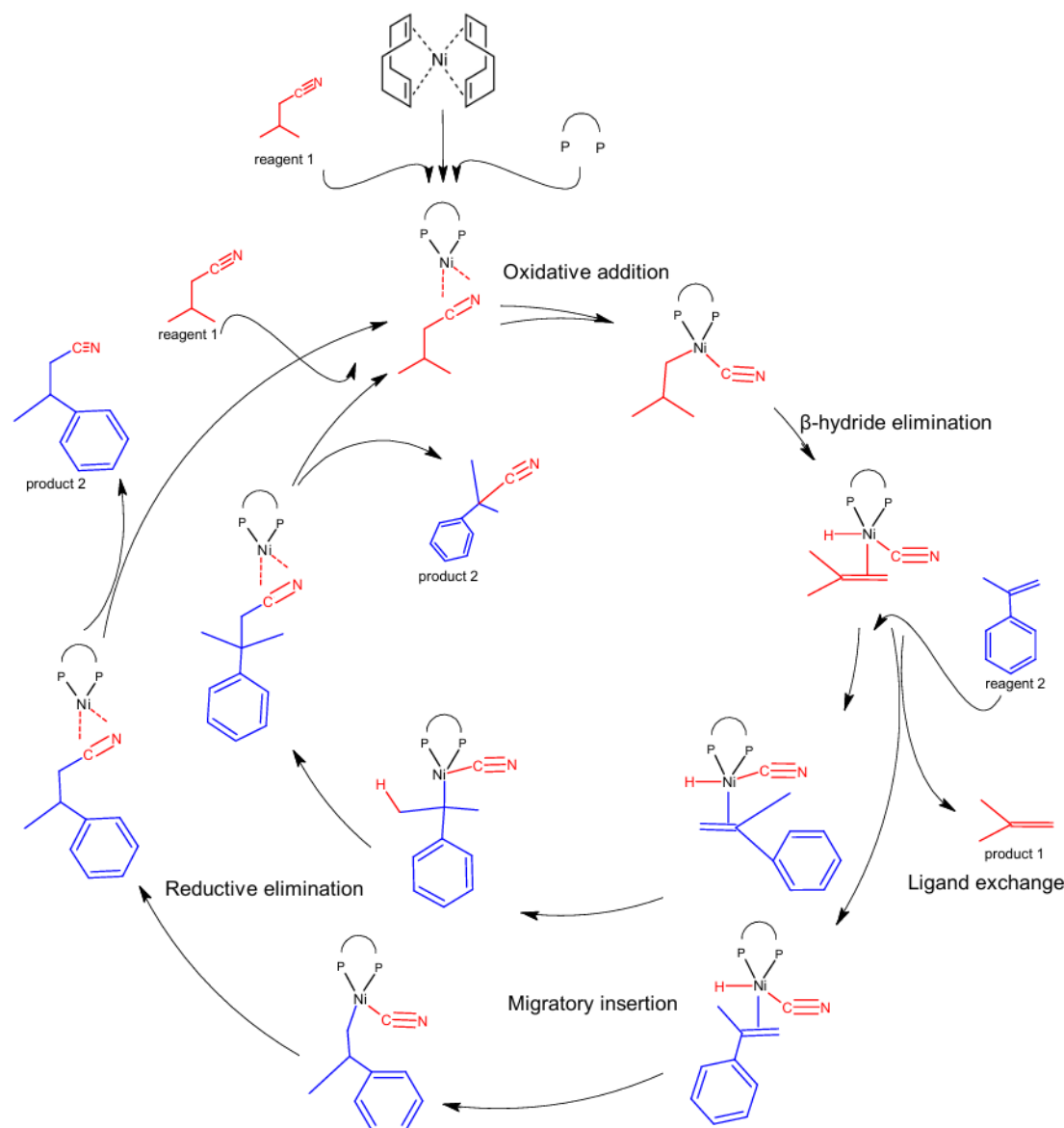


Figure 6: Proposed catalytic reaction mechanism for the transfer hydrocyanation based on the mechanistic study of Dang *et al.*[50].

2.5.1.3 Other relevant catalytic systems for retro-hydrocyanations

Alternatively, Studer *et al.* 2018 investigated a cooperative palladium/Lewis acid-catalysed transfer hydrocyanation system using a very specific HCN-donor (1-methylcyclohexa-2,5-diene-1-carbonitrile) [47]. This study uncovers the potential of employing aromatisation as a thermodynamic driving force for the transfer hydrocyanation. Aromatisation can be used since the formation of the aromatic product from 1-methylcyclohexa-2,5-diene-1-carbonitrile is thermodynamically favourable. The most effective catalytic system consisted of $\text{Pd}(\text{PPh}_3)_4$ / DPEphos in combination with the Lewis acid BPh_3 as a co-catalyst. Other biphosphine ligands, including dppe, dppp, and BINAP, resulted in lower yields owing to their smaller bite angles, which are less effective at promoting the rate-determining reductive elimination [52]. Similarly, other Lewis acids, such as BF_3 , AlMe_2Cl , AlMe_3 , and AlCl_3 , afforded lower yields. Moreover,

Studer and co-workers proposed a catalytic reaction mechanism for palladium that closely resembles the mechanism proposed by Morandi and co-workers for nickel. Most importantly, by employing norbornene as an HCN acceptor and exploiting ring-strain release as a thermodynamic driving force, they demonstrated that Palladium complexes can also catalyse retro-hydrocyanation reactions.

In a different study published in 2020, Studer *et al.* looked deeper into nickel-catalysed transfer hydrocyanation, but in the absence of Lewis acidic co-catalysts [53]. They reported the synthesis of nitriles with very high Markovnikov selectivity in reactions carried out in the absence of a Lewis acid. This contradicts the result reported by Morandi, who obtained yields with a high linear-to-branched ratio or anti-Markovnikov selectivity in the presence of a Lewis acid. These results led to extensive mechanistic studies of the role of the Lewis acid on the thermodynamic selectivity during the transfer hydrocyanation reaction, as studied by Li Dang and co-workers [50] and the work of Zhao *et al.* [54]. Furthermore, Studer used a very specific HCN source, namely 1-isopropylcyclohexa-2,5-diene-1-carbonitrile, and employed Ni(cod)₂ as the TM catalyst with Xantphos as the ideal ligand. However, using DPEphos provided similar results [44][54].

The research group of Morandi further elaborated on these findings, showing that transfer hydrocyanation reactions conducted in the absence of a Lewis acid exhibit high selectivities towards the thermodynamically less favourable branched nitriles. This was done because one fundamental drawback of shuttle catalysis is that it operates under thermodynamic control, due to its reversibility. This leads to a mixture of products, as was the case for their first reported catalytic system. The ratios of the products being formed reflect their thermodynamic stability. In a paper addressing the selectivity issues of transfer hydrocyanations published in 2020, they used a catalytic system consisting of Ni(cod)₂ and Xantphos to exploit the lower barrier for C-CN oxidative addition and reductive elimination in the absence of a Lewis acid towards branched nitriles [51]. Most importantly for the retro-hydrocyanation, this paper showed that norbornadiene, which is typically a potent sacrificial HCN acceptor, does not react in the absence of a Lewis acid. This underscores the vital role of the Lewis acid in enabling retro-hydrocyanations [51].

At the beginning of 2022, the research group of Morandi tried to address the major challenges faced by their original method to make their process scalable and operationally simple [55]. The originally proposed method used the air- and thermally sensitive catalyst Ni(cod)₂, which required specialised equipment for reaction and storage, thereby limiting the scalability and widespread use of the process. Nevertheless, they successfully replaced this catalyst with the air-stable and inexpensive NiCl₂ (pre)catalyst. In the latter, a Lewis acid, such as AlMeCl₂, is expected to reduce the Ni(II) to the active Ni(0) hydrocyanation catalyst. Importantly, this catalytic system successfully performed retro-hydrocyanation of aliphatic nitriles with norbornene as the HCN acceptor molecule [55]. Their last improvement was replacing the sacrificial HCN donor, isovaleronitrile, with the cheaper butyronitrile. All these advancements make the HCN-free transfer- and retro-hydrocyanations simpler, more robust, and scalable.

Around the same period, Yosikai *et al.* reported a study on cobalt-catalysed transfer hydrocyanation of alkynes. They reported a catalytic system consisting of a low-valent cobalt-diphosphine catalyst and Zn(OTf)₂ as Lewis acidic co-catalyst [56]. This catalytic system uses easy-to-handle (pre)catalysts, in contrast to the established nickel-based catalytic systems used initially by the Morandi group. Furthermore, they reported similar findings on the effective transfer hydrocyanation of alkynes using the inexpensive butyronitrile as a sacrificial HCN

donor. Yosikai and co-workers were the first to report a catalytic system based on a low-valent cobalt catalyst to successfully perform hydrocyanation and carbocyanation [56]. This study greatly complements the previous improvements of the Morandi group, but for a catalytic cobalt system. Unfortunately, the ability of this catalytic system to carry out the valuable retro-hydrocyanation is not addressed.

More recently, the research group of Dirk De Vos made significant improvements in the field of shuttle catalysis for transfer hydrocyanation reactions by employing zeolites as equilibrium-shifting agents [49]. The reversibility of these isodesmic transfer hydrocyanation reactions limits the applicability to specific donor and acceptor molecules and leads to challenges regarding atom economy and practicality [49]. However, by exploiting the shape-selective and catalytic properties of zeolites, the equilibrium can be driven to near completion, and yields can be increased to 80%. The zeolites act as molecular traps that selectively capture and irreversibly convert the alkene byproduct, thereby shifting the reversible hydrocyanation equilibrium towards product formation. Due to steric constraints imposed by the zeolite pore architecture, the substrate and nitrile product are excluded from the pores to prevent unwanted reactions. Lastly, these zeolites enable the diversification of HCN donors into readily available, inexpensive, safer, and easier-to-handle ones, such as the industrially relevant propionitrile.

To summarise, retro-hydrocyanation has emerged as a valuable method with several available catalytic systems that enable the conversion of nitriles towards alkenes along the backbone of a substrate. This transformation shows great potential for a controllable (partial) defunctionalisation of polymers, such as NBR or HNBR, and can be a useful strategy to finetune functional-group content of nitrile-functionalised polymeric materials.

2.5.2 Hydrogenation

This section reviews the state of the art in selective hydrogenation of nitriles to primary amines and discusses the reaction mechanisms and catalytic systems that enable this transformation.

2.5.2.1 Hydrogenation of nitriles to primary amines

Hydrogenation of nitriles is one of the most direct and atom-efficient synthesis routes for the production of primary amines in a sustainable way [57]. These amines are extremely valuable and widely used in chemical manufacturing because they are fundamental organic compounds or key intermediates in the synthesis of pharmaceuticals, dyes, plastics, surfactants, and agrochemicals, such as herbicides and pesticides [57].

On a laboratory scale, nitriles can be easily and effectively transformed to primary amines with a reduction carried out with lithium aluminium hydride (LiAlH_4), followed by aqueous work-up [58]. The hydride nucleophile reacts with the electrophilic carbon in the nitrile to form an imine anion. This anion will be stabilised by Lewis acid-base complexation. Consequently, the imine salt can accept a second hydride to form a dianion, which can be converted to an amine by the addition of water. Due to cost and safety reasons, this method is not scalable. Therefore, on an industrial scale, heterogeneous catalysts such as Raney® nickel or cobalt are typically employed to selectively hydrogenate nitriles to primary amines using hydrogen gas. This is, for instance, employed in the DuPont nylon-6,6 production for the reduction of adiponitrile towards hexamethylenediamine [59]. However, the selectivity of the reaction is strongly affected by inevitable side reactions to secondary and tertiary amines, driven by the high reactivity of the imine intermediate. The industrial separation of primary amines from the reaction mixture is very challenging due to small differences in boiling point. Therefore, more selective methods towards primary amines are highly desirable [60]. Some attempts have been made to increase selectivity by the addition of ammonia or some appropriate bases, such as NaOH or LiOH [61]. But even these methods are limited by incomplete conversion and difficult purification.

Alternatively, homogeneous catalysis can be considered as a more selective approach. In contrast to heterogeneous catalysts, homogeneous catalysts are more difficult to recover and handle, making them less industrially attractive. However, they exhibit other major advantages, such as having a higher selectivity and reactivity towards primary amines. Furthermore, homogeneous catalysis offers catalytic mobility and therefore circumvents the problem of orienting the long chain on the immobile active side of the catalyst, as is the case for heterogeneous catalysts, which therefore suffer from severe mass transfer limitations [35]. Meanwhile, in homogeneous catalysis, the catalyst and polymer are in the same phase, and the catalyst molecules are mobile. This mobility allows the catalyst to move freely and interact with the reactive sites along the polymer chain without requiring the chain to orient itself towards a fixed surface. Furthermore, heterogeneous systems often require higher catalyst loadings, longer reaction times, and higher temperatures and pressures, which can lead to polymer degradation or gelation.

Over the years, several homogeneous catalysts based on the transition metals Ru, Co, Fe, and Mn have proven successful in catalysing the hydrogenation of nitriles. Among these transition-metal catalysts, Ru complexes have been investigated most intensively in the literature. In 2008, Beller's research group developed a highly selective hydrogenation method for primary amines, using a practical in situ catalyst consisting of $\text{Ru}(\text{cod})(\text{methylallyl})_2$ and triphenylphosphine (PPh_3) as the ligand, dissolved in toluene. The addition of a suitable base,

such as potassium tert-butoxide (KOtBu), increased the yields of primary amines to as high as 98% for certain aromatic nitriles [62].

2.5.2.2 Mechanism

$\text{Ru}(\text{cod})(\text{methylallyl})_2$ serves as a precatalyst from which the cyclooctadiene (cod) and/or methylallyl ligands are displaced by triphenylphosphine, forming a stable ruthenium-phosphine complex, as depicted in Figure 7. Remarkably, the active catalyst lacks a well-defined composition. Upon reaction with hydrogen, molecular hydrogen undergoes H–H bond cleavage, generating a ruthenium hydride species that can generally be represented as $\text{RuH}(\text{PPh}_3)_2\text{L}_2$ [63]. In the subsequent step, ruthenium hydride species will transfer hydrides to the substrate, ultimately yielding the hydrogenated product. Furthermore, the coordinated PPh_3 plays a crucial role in tuning the catalytic properties of the ruthenium complex. It modifies the ligand sphere by increasing electron density at the ruthenium centre, thereby facilitating hydrogen activation and hydride formation, both of which are essential for effective nitrile hydrogenation. Consequently, the presence of the phosphine ligands enhances the catalytic activity and improves selectivity towards primary amines while suppressing the formation of secondary amine byproducts [64].

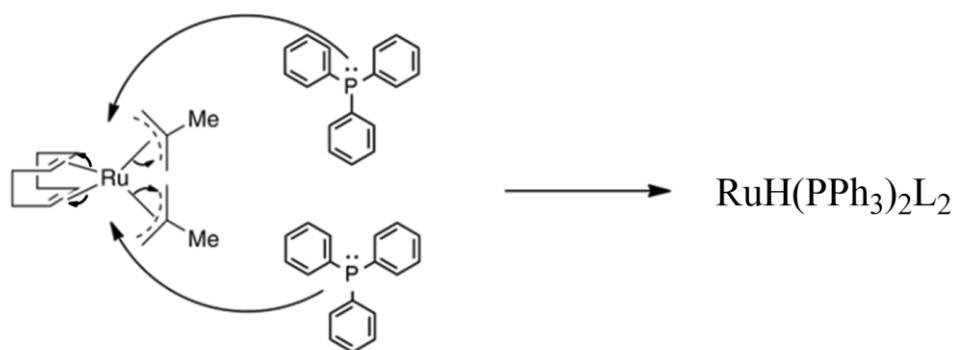


Figure 7: Activation of the ruthenium centre by triphenylphosphine ligands.

Mechanistically, KOtBu also plays a crucial role in catalyst activation by promoting the formation of the catalytically active ruthenium hydride species, thereby enabling efficient catalytic cycles towards primary amines under relatively mild conditions. More specifically, the strong base facilitates heterolytic cleavage of molecular H_2 , in which the base accepts a proton (H^+) while a hydride (H^-) ligand is transferred to the ruthenium centre. The resulting ruthenium hydride (Ru-H) species is essential for the hydrogenation of nitriles to amines. This heterolytic cleavage of H_2 , promoted by KOtBu and the ruthenium hydride formation are schematically illustrated in Figure 8 [65].

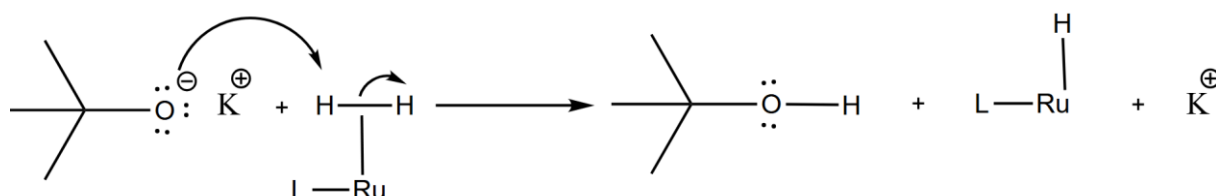


Figure 8: Role of KOtBu in the formation of ruthenium hydride required for effective nitrile hydrogenation.

After formation of the ruthenium hydride species, the nitrile substrate coordinates to the ruthenium centre through the nitrogen lone pair. Subsequently, hydride transfer from the ruthenium to the nitrile carbon generates a metal-bound imide-like intermediate, in which the nitrogen atom carries a negative charge. Consequently, proton transfer from the solution to the nitrogen, followed by reductive elimination, yields the imine intermediate. The active Ru-H is regenerated for the next catalytic cycle by activating another H₂ molecule. This proposed mechanism is consistent with the typical inner-sphere mechanism proposed in the literature for ruthenium–phosphine catalysts [66], [67].

In the hydrogenation of nitriles to primary amines, this sequence effectively occurs twice, as nitriles are first reduced to an imine intermediate and subsequently to the corresponding primary amine, as illustrated in Figure 9. However, the formation of secondary and tertiary amines may occur as undesirable side reactions. These by-products arise from the condensation of a primary amine with an imine intermediate, followed by further hydrogenation of the resulting condensation product [68].

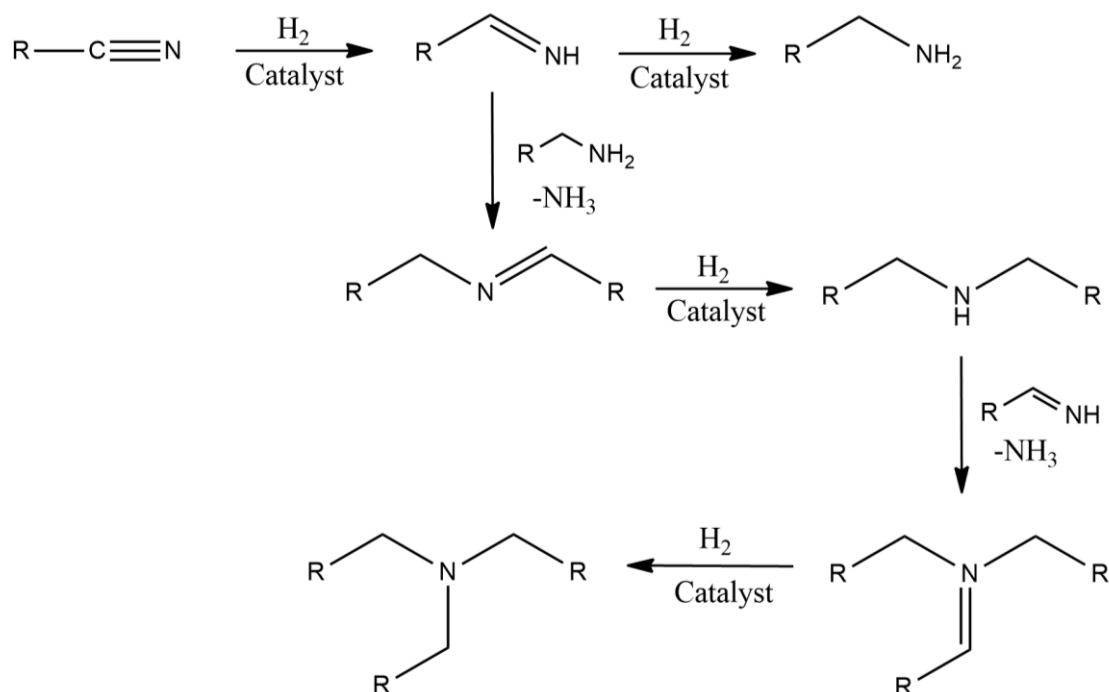


Figure 9: Hydrogenation of nitriles to primary amines and undesired side reaction leading to secondary and tertiary amines [68].

2.5.2.3 Other catalytic systems for selective hydrogenation

In 2008, Beller reported two additional promising ruthenium-based catalytic systems for the hydrogenation of aromatic, heteroaromatic, and aliphatic nitriles, achieving high product yields. These systems employed $RuCl_2(PPh_3)_3$ and $(RuCl_2(C_6H_6))_2$ in combination with PPh_3 , both in the presence of $KOtBu$ [59], [69]. Among the catalytic systems considered in this study, $RuCl_2(PPh_3)_3$ with $KOtBu$ in dioxane appears to be the most practical choice. The catalyst already contains the desired phosphine ligands, eliminating the need for an initial ligand-exchange step, and has been reported to deliver excellent yields and high catalytic activity [69]. Furthermore, the chloride ligand enables easy and controlled catalyst activation.

An alternative reported system by the Beller group consists of $Ru(cod)methylallyl_2$ in combination with PPh_3 and $KOtBu$. This system affords primary amine yields comparable to

those obtained with $\text{RuCl}_2(\text{PPh}_3)_3$. The main difference between the two systems is that $\text{Ru}(\text{cod})\text{methylallyl}_2$ is a precatalyst and requires ligand exchange before the active catalytic species is generated. Therefore, the $\text{Ru}(\text{cod})\text{methylallyl}_2$ has improved stability during handling and storage due to its lower sensitivity to air and moisture [63]. The same study by the Beller group evaluates several other phosphorus-based ligands in combination with $\text{Ru}(\text{cod})\text{methylallyl}_2$ and KOtBu . Ligands such as PCy_3 and $(p\text{-F-C}_6\text{H}_4)_3\text{P}$ afforded primary amine yields comparable to those obtained with PPh_3 [69]. However, PPh_3 is relatively cheap, widely available, and well established in industrial applications. Therefore, PPh_3 is recommended as the ligand of choice [62].

Alternatively, in 2011, Leitner and co-workers developed a new catalytic system consisting of ruthenium hydride complexes bearing PNP pincer ligands, achieving near quantitative yields for the conversion of aliphatic and aromatic nitriles into primary amines [70]. Although the method is highly effective, the high air- and moisture-sensitivity of many pincer complexes makes them less convenient to work with and often requires inert-atmosphere handling. In 2020, Gröger and co-workers evaluated the performance of various homogeneous and heterogeneous ruthenium catalysts for the selective hydrogenation of nitriles to primary amines [71]. Using a heterogeneous Ru/C catalyst, conversions up to 99% are achieved, but the selectivity towards primary amines remains rather low, with a maximum of 60%. The study further demonstrates the excellent performance of some ruthenium-based pincer complexes, such as Ru-MACHO-BH and Ru-Gusev , which afforded conversions of 98-99% in isopropanol with >99% selectivity towards primary amines. However, these catalysts have proven to be air sensitive.

The Beller research group has reported numerous additional catalytic systems for selective nitrile-to-primary-amine hydrogenations. [65]. In 2014, the research group introduced an iron-based catalyst bearing a PNP pincer ligand that exhibited good functional-group tolerance. This represented the first non-noble-metal catalytic system that successfully performed selective hydrogenation with a high yield of up to 99% [72], [73]. Alternatively, a catalytic route was established via the non-noble metal $\text{Co}(\text{acac})_3$ in combination with a specific phosphine ligand ($\text{tris}(2\text{-(dicyclohexylphosphanyl)ethyl})$). This base metal catalyst can achieve high yields for the selective hydrogenation of a wide range of aromatic and aliphatic nitriles to the corresponding amines [74].

In 2016, the Beller group published the first manganese PNP pincer-based complex, which kick-started the explosive growth within the field of catalytic hydrogenation over manganese [75]. In 2019, Garcia and co-workers made another breakthrough in the field by establishing non-pincer manganese-based catalysts, which catalysed the hydrogenation of a range of aliphatic and aromatic nitriles with yields up to 97% under mild conditions [76]. The catalytic system consisted of a bidentate Mn complex, a KOtBu base, and 2-butanol as solvent. These catalysts are also more stable and much easier to handle than the previously reported pincer complexes. In 2020, Gröger and co-workers reported two homogeneous manganese-phosphine complexes, in addition to the ruthenium-based pincer catalysts, both of which gave excellent conversion and yield of primary amines, with selectivity and conversion higher than 99%. These catalysts give the best results when at least 1 mol% catalyst loading, 10 mol% KOtBu , and 50 Bar H_2 are used at 100 °C, in Toluene or 2-Me-THF [71]. The ongoing pursuit of greener, more sustainable catalysis drives the development of earth-abundant first-row metal catalysts, such as manganese, to replace currently used noble-metal catalysts [77]. Consequently, these catalysts may offer a more cost-effective and sustainable alternative for large-scale industrial processes.

2.5.3 Overview of other functionalisation strategies

Functional groups have a decisive influence on the properties of a polymer because they govern how polymer chains interact with one another and with their environment. As functional groups and intermolecular interactions are strongly intertwined, they affect the polymer's mechanical properties, such as stiffness, strength and toughness. Moreover, functional groups determine how a polymer responds to heat, light, oxygen, or solvent exposure, thereby defining its chemical behaviour. The following sections discuss well-established methodologies for the transformation of nitriles and amines into a range of functional groups.

2.5.3.1 Nitriles functionalisation

Nitrile derivatives can serve as precursors to many chemical intermediates and products, including aldehydes, ketones, carboxylic acids, alcohols, amines, amides, pyrazoles, and tetrazoles [45], [78]. As the goal of this Master's thesis is the synthesis of N-functionalised polyolefins, the focus will be on functionalisation reactions where the nitrogen atom is retained, especially amines (see 2.5.2) and amides.

The conversion of nitriles to amides has been extensively investigated, as amides are fundamental to life, acting as the primary linkage between amino acids in proteins, and are essential to major synthetic materials, such as Nylon and Kevlar [79]. Moreover, amide-containing molecules are of particular interest for the pharmaceutical sector due to their diverse biological activities, including anticancer, antiviral, and antibacterial effects. Both aliphatic and aromatic nitriles can be converted into their corresponding amides via a traditional Bronsted-acid-catalysed hydration. However, the reaction requires concentrated acids and high temperatures to achieve acceptable reaction rates. These harsh conditions often lead to over-hydrolysis to carboxylic acids, making it difficult to achieve high selectivity towards amides. A mixture of trifluoroacetic acid (TFA) and sulphuric acid enables the selective conversion of nitriles to amides in a single step via indirect acid-catalysed hydration [80]. Due to environmental concerns and the fact that TFA is a forever chemical (PFAS), this approach is not sustainable. Furthermore, this approach is only applicable to sterically unhindered nitriles. The other conventional approach is base-catalysed hydration of nitriles into amides. In practice, a strong base, such as NaOH or KOH, is often used to nucleophilically attack the nitrile carbon, which then undergoes tautomerization to form the final amide [81]. However, the base-catalysed approach also suffers from over-hydrolysis to carboxylic acids and unwanted product formation, leading to complex product separation and low amide yields. Another possible pathway is the Ritter reaction, which converts a nitrile and a carbocation ion precursor, such as a tertiary alcohol or substituted olefin, into an amide using a strong acid and water [82]. Firstly, the carbocation precursor reacts with a strong acid, forming a carbocation that is subsequently attacked by the nitrile, yielding a nitrilium ion. Subsequent water hydrolysis and a series of proton transfer steps then yield the final amide product. The main downside of the Ritter reaction is that it requires stoichiometric amounts of strong acids. The reaction applicability is therefore limited to compounds containing acid-stable functional groups. Furthermore, handling strong acids and nitriles poses health and safety risks, and the reaction generates significant amounts of salt waste during the neutralisation step. Due to the limitations associated with conventional nitrile-to-amide conversions, attention has shifted towards metal-catalysed approaches.

Metal-catalysed hydration of nitriles towards amide functionalities has emerged as a cost-effective and efficient approach [83]. The conversion of nitrile-functionalised polyolefins into amide-functionalised analogues is particularly attractive, as the direct incorporation of amide

functionalities into polyolefins remains challenging because amides can retard chain growth during copolymerisation [84]. The hydration of nitriles can be carried out using homogeneous catalysts based on metals such as Pt, Os, Rh, Mn, Ir, and Ru [83]. González-Fernández *et al.* have introduced specific Osmium complexes that, in combination with amino-phosphane ligands as $\text{PPh}_2(\text{NMe}_2)$, can achieve high yields without the addition of acids or bases [85]. More recently, Czégéni and co-workers reported the hydration of nitriles using Rh(I)-N-heterocyclic complexes in a water/isopropanol solvent mixture. In this approach, NaOH is added to facilitate nucleophilic attack. This approach reached a maximum amide yield of 98%. Furthermore, Singh and co-workers have recently developed ruthenium complexes with N-heterocyclic carbene ligands for the efficient hydration of a wide range of aromatic and heterocyclic nitriles towards their amide counterparts. These reactions gave yields up to 93% and exceptional catalyst recyclability. In heterogeneous catalytic routes for the hydration of nitriles to amides, transition-metal oxides play an important role. The oxygen-rich surface of these metals accelerates substrate coordination and facilitates nucleophilic attack by water [83]. The best-documented catalytic systems in the literature are MnO_2 , Ru/MnO_2 , and Ag/MnO_6 . Feng-Shou Xiao and co-workers achieved remarkably high conversions and selectivities of up to 99.5% using a nanorod- MnO_2 catalyst under mild conditions [86]. Furthermore, the catalyst showed great consistency and recyclability over five consecutive runs. The high catalytic activity of MnO_2 has been attributed to the presence of surface oxygen species, which promote the generation of hydroxyl species that facilitate the nucleophilic attack on the nitrile group [83]. Hussain and co-workers have developed a catalytic system utilising manganese oxide as support for a ruthenium catalyst (Ru/MnO_2). This heterogeneous catalyst demonstrates outstanding activity for a wide range of aliphatic and benzylic nitriles in water at 60°C. For the model molecule octanenitrile, conversions of 95% and selectivities >95% are achieved using this catalyst at 60°C for 20 hours under atmospheric conditions [87]. At first glance, this method requires relatively high catalyst loadings, but the recyclability and ease of workup compensate for it.

The addition of sodium azide to nitriles catalysed by zinc readily affords tetrazoles. Tetrazoles have attracted considerable academic attention over the years because they are important in medicinal and coordination chemistry. Today, tetrazole-containing compounds are widely used and have found their main industrial applications in pharmaceuticals and material chemistry. In 2001, Sharpless *et al.* pioneered a practical method for the synthesis of tetrazoles by refluxing nitriles with sodium azide (NaN_3) and a zinc salt catalyst, such as zinc bromide (ZnBr_2), in water [88]. This methodology provides high yields for a broad range of nitrile substrates. However, less reactive nitriles require high reflux temperatures of up to 170°C and reaction times of up to 24 h. Tetrazoles possess a high nitrogen content. Therefore, when tetrazoles decompose, they can rapidly form nitrogen gas, releasing significant amounts of energy. As a result, many tetrazoles are classified as explosives or energetic materials, and certain tetrazoles and their derivatives are sensitive to shock, friction, and heat. Consequently, their handling requires appropriate safety precautions.

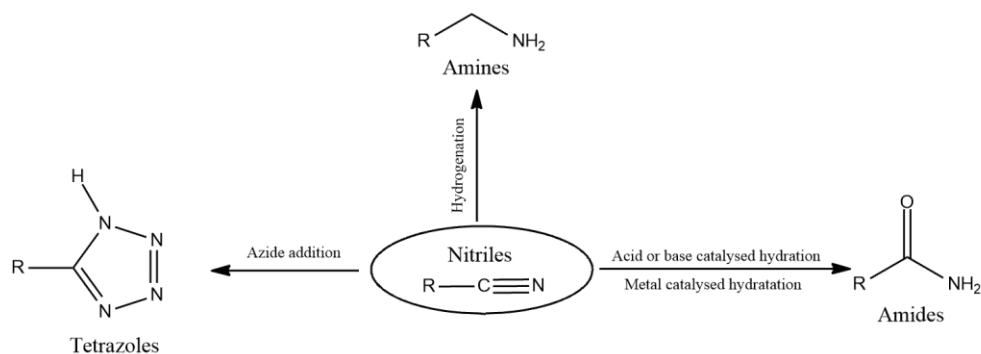


Figure 10: Possible nitrile functionalisation pathways that preserve the nitrogen atom.

2.5.3.2 Amine functionalisation

Amino groups are among the most valuable intermediates in organic synthesis because of their exceptional versatility and reactivity. The lone pair of electrons on nitrogen imparts both nucleophilic and basic character to amines, enabling them to undergo a wide range of transformations under mild and controllable conditions. As a result, primary amines serve as key precursors to amides, imines, carbamates, phthalimides, and higher-order amines. In this Master's thesis, the focus will be on the conversion into higher-order amines, amides, and phthalimides.

Alkylation of amines with alkyl halides via second-order nucleophilic substitution (S_N2) is the easiest and most straightforward pathway to synthesise higher-order amines from primary amines. The amine's nitrogen attacks the alkyl halide, displacing the halide and forming a new C-N bond. This reaction is typically carried out in the presence of a base, such as NaOH, to keep the amine deprotonated and neutralise acids generated during the reaction. The major drawback of this method is its very poor selectivity, often resulting in mixtures of primary, secondary, and tertiary amines. The separation of these various amines is often difficult [64]. Converting the pendant NH_2 groups of an amino-functionalised polyolefin into higher-order amines can improve the polymer's thermal and oxidative stability.

An alternative method that can be operated with much better control is reductive amination. This method plays a paramount role in pharmaceutical and medicinal chemistry [89]. Typically, an amine reacts with an appropriate carbonyl compound (a ketone or aldehyde) to form a hemiaminal, which then undergoes reduction. If the starting product is a secondary amine, an iminium cation is generated from the hemiaminal, which is then reduced to yield a tertiary amine. Alternatively, direct hydrogenation of the hemiaminal yields the same tertiary amine. If the starting amine is a primary amine, then an imine is formed from the hemiaminal by water elimination and is then further reduced to a secondary amine [89]. Reductive amination generally proceeds under mild conditions, and a variety of reducing agents are available. The most commonly used reducing agents are the borohydride complexes such as $NaBH_3CN$ and $NaBH_4$.

Acylation of amines is a fundamental transformation in organic synthesis, leading to the formation of amides via a nucleophilic acyl substitution [64]. This reaction is often referred to as the Schotten-Baumann reaction. In this reaction, amines act as nitrogen nucleophiles that attack the carbonyl carbon of an acyl halide or anhydride, as illustrated in Figure 11. In general, acid chlorides are the preferred acylating agents because of their high reactivity, which arises from the strong electron-withdrawing nature of chloride and its excellent leaving-group ability.

The reaction typically proceeds rapidly at room temperature in aprotic solvents such as DCM, THF, or ethyl acetate. In addition, a suitable base, such as a tertiary amine or pyridine, is added to neutralise the HCl generated during the reaction, thereby shifting the thermodynamic equilibrium towards product formation. More critically, in the absence of a HCl-scavenging base, the liberated HCl protonates the remaining unreacted amine, converting it into the corresponding ammonium salt. The ammonium salt is unreactive towards acylation because the nitrogen lone pair is no longer available for nucleophilic attack, and this is further disfavoured by charge repulsion between the positively charged ammonium salt and the partially positively charged carbonyl carbon [90]. Consequently, a stoichiometric amount of base is required to deprotonate the ammonium salt and regenerate the free amine for continued acylation.

The Schotten-Baumann method is particularly useful for the synthesis of amides from sterically hindered amines and amines sensitive to acidic conditions [91]. The reaction is widely adopted because of its simplicity, broad substrate scope, functional-group tolerance, and typically high yields. Consequently, a wide variety of amides can be synthesised by reacting a diverse range of amines with acyl chlorides or anhydrides. Industrially, the Schotten-Baumann method is widely used for peptide and pharmaceutical synthesis, the production of agrochemicals such as herbicides, pesticides, and fungicides, and the manufacture of dyes and colourants.

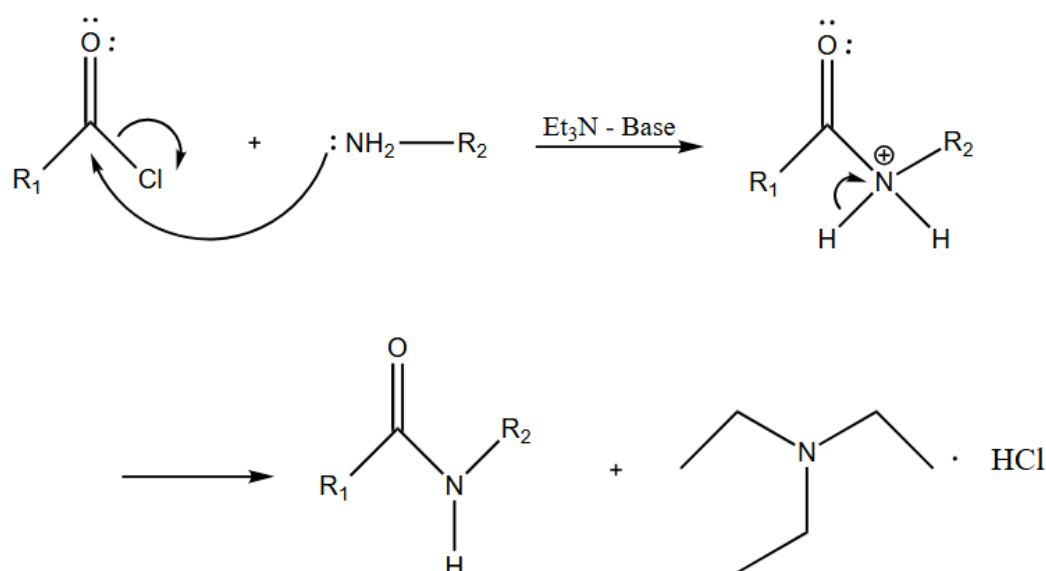


Figure 11: Schotten-Baumann reaction mechanism for the conversion of a primary amine to an amide using an acyl halide and Et₃N as HCl scavenger.

Carbamates can be synthesised by carbamoylation of amines with chloroformates (ROC(O)Cl). Carbamates, also referred to as urethanes, are widespread functional groups in organic chemistry and constitute the characteristic linkage in polyurethane materials. Consequently, they are of considerable industrial importance. In addition, carbamates are frequently employed as amino-protecting groups and play an important role in drug design [92]. In this reaction, the amine attacks the carbonyl carbon of the chloroformate, forming a tetrahedral intermediate that subsequently collapses upon expulsion of chloride, yielding a carbamate. Alternative methods for carbamate synthesis often involve the extremely hazardous reagent phosgene. More recently, efforts have been made to employ carbon dioxide (CO₂) as a sustainable feedstock for carbamate synthesis. Carbon dioxide readily reacts with amines in the presence of a suitable catalyst and base to form carbamates [93].

Furthermore, amines can be functionalised to yield pyrazoles. Pyrazoles are important heterocyclic compounds primarily used in pharmaceuticals and crop protection chemicals. Traditionally, pyrazoles are synthesised by reacting hydrazines with 1,3-dicarbonyl compounds, as in the Knorr pyrazole synthesis. In 2021, Szafer and co-workers reported a direct preparation method for N-substituted pyrazoles from primary aliphatic and aromatic amines under mild reaction conditions, offering a rare alternative to conventional synthetic routes [94].

Lastly, phthalimides can be synthesised from primary amines by dehydrative condensation with phthalic anhydride. Phthalimides are cyclic imides characterised by a benzene ring fused to an imide moiety containing two electron-withdrawing carbonyl groups. They are widely recognised as versatile scaffolds in medicinal chemistry, pharmacology, and organic synthesis due to their high structural stability and ease of modification [95]. Moreover, they exhibit a wide range of significant biological activities, including anticancer, anti-inflammatory, antimalarial, antibacterial, and anti-HIV [96], [97]. Therefore, it is not surprising that phthalimides are primarily used in pharmaceutical applications. However, they are also widely utilised in the production of dyes, polymers, and pesticides. Various synthetic approaches have been documented for the preparation of phthalimides, including both metal-catalysed and metal-free methodologies [96]. Although many of these methods rely on carbon monoxide as a carbonyl source, concerns regarding its toxicity, flammability, and handling have motivated the development of alternative synthetic routes. The catalytic preparation of phthalimide is typically carried out over transition-metal catalysts such as Ni, Pd, Rh, or Ru. However, metal-free synthetic methods offer a greener alternative, being more cost-effective, less toxic, and generally less sensitive to moisture and oxygen [96]. In 2004, Li and co-workers reported the synthesis of phthalimides via the amidation of phthalic anhydride with a primary amine in xylene at 100°C for 48 h. The products were obtained with excellent yields, with only trace amounts of acyclic products. Earlier studies had already demonstrated that phthalimides could be obtained in yields of up to 96% by refluxing phthalic anhydride with amino compounds in non-polar solvents while continuously removing the water formed during the reaction [98]. Remarkably, when the water was not separated, the yield decreased to 50%. The mechanism of phthalimide formation is depicted in Figure 12. First, the amine acts as a nitrogen nucleophile, opening the anhydride ring to form phthalamic acid. Subsequent cyclisation of phthalamic acid involves intramolecular dehydration, forming the corresponding phthalimide. Because cyclisation is generally only possible at temperatures above 100°C, chemical dehydration agents such as acetic anhydride or phosphorus halides are often added to facilitate ring-closure [99]. The incorporation of phthalimide functionalities into polyolefins has attracted considerable interest because of their ability to modify polymer properties. Hartwig and co-workers demonstrated that the incorporation of only 1.4 mol% phthalimidyl groups into a polyethylene backbone increased the strain to failure from 230% to 1170% [17]. In addition, phthalimide functionalities can influence the adhesion, thermal, and structural properties of polyolefins, highlighting their potential for polymer modification.

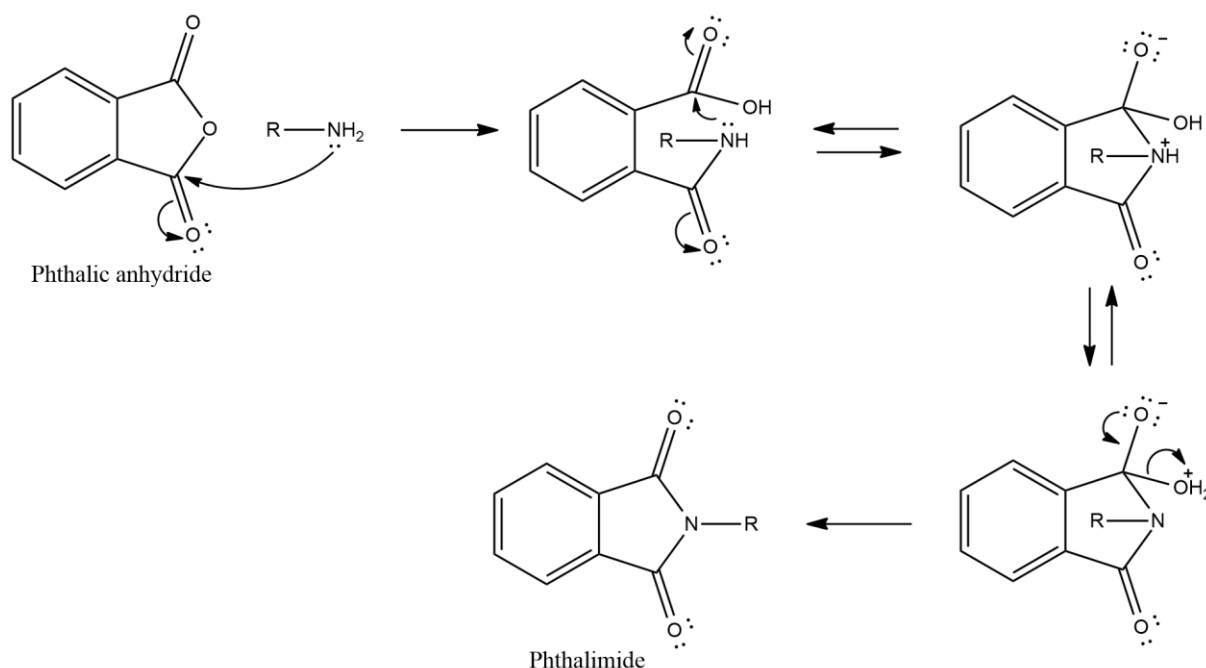


Figure 12: Proposed mechanism of the phthalimide formation with phthalic anhydride [97].

Figure 13 presents an overview of nitrogen-functionalisation strategies accessible from primary amines. The remainder of this thesis focuses primarily on the acylation of primary amines to form amides and on the synthesis of phthalimides. These two transformations are selected because they are well-established synthetic methods and enable the preparation of nitrogen-functionalised polymers with promising material properties.

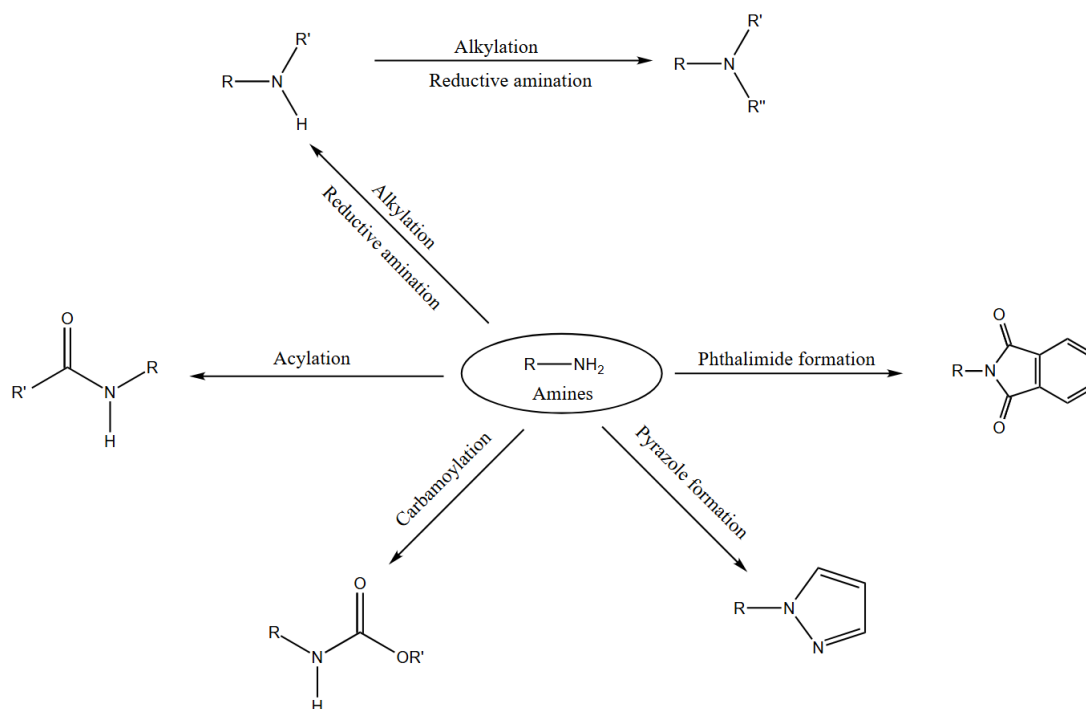


Figure 13: Possible transformations of primary amines into different nitrogen-containing functional groups.

3 OBJECTIVE OF EXPERIMENTS

This thesis aims to establish a new way of synthesising N-functionalised polyolefins. The newly synthesised polymers will be characterised by NMR and FTIR spectroscopy.

Poly(acrylonitrile-co-butadiene) (NBR) was selected as the initial substrate because it is industrially available, relatively inexpensive, and contains pendant nitrile groups that can be transformed into a wide range of functional groups. In the first step of the proposed methodology, a portion of the nitrile functionalities present on the polymer backbone is converted into carbon-carbon double bonds via retro-hydrocyanation. The objective of this catalytic retro-hydrocyanation is to selectively remove 75-95% of the initial nitrile groups present on the substrate by dosing 0.75-0.95 equivalents of a highly strained sacrificial acceptor, such as norbornene, norbornadiene or vinyl norbornene (Figure 14).

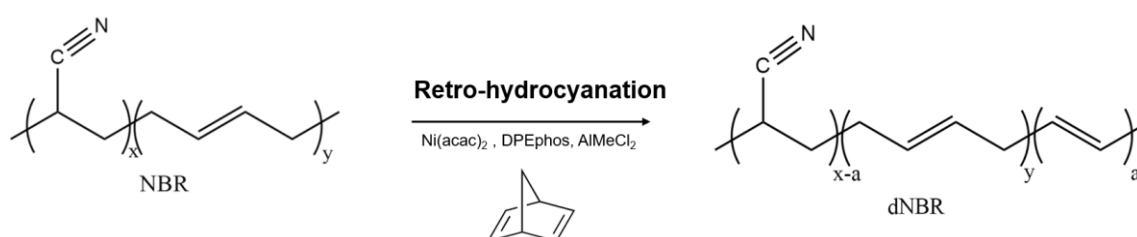


Figure 14: Partial defunctionalisation of NBR via catalytic retro-hydrocyanation with sacrificial acceptor molecule norbornadiene.

In the subsequent hydrogenation step, the partially defunctionalised nitrile butadiene rubber (dNBR) can be selectively hydrogenated to yield dHNBR. In this case, a chemoselective catalyst is required to hydrogenate only the olefinic bonds in the backbone. Alternatively, dNBR can be fully hydrogenated to produce a methylamine-functionalised polyethylene. This material consists of a polyethylene-like backbone bearing pendant aminomethyl groups. The resulting methylamine-functionalised polyethylene will subsequently be characterised and further functionalised.

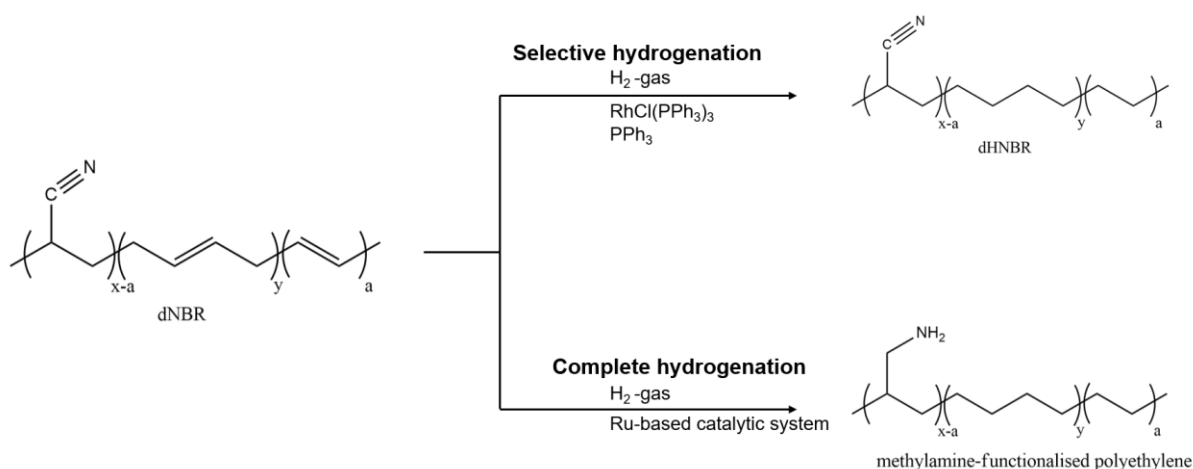


Figure 15: Selective hydrogenation of partially of defunctionalised NBR with the Wilkinson catalyst ($\text{RhCl(PPh}_3)_3$) and triphenylphosphine or complete hydrogenation with a Ru-based catalytic system.

Both products obtained from the hydrogenation step are suitable for further functionalisation. However, in this thesis, the focus will be on the conversion of the pendant aminomethyl groups of methylamine-functionalised polyethylene into amide and phthalimide groups, although numerous other functionalisation strategies are also possible. The resulting amide- and phthalimide-functionalised polyethylenes will subsequently be characterised.

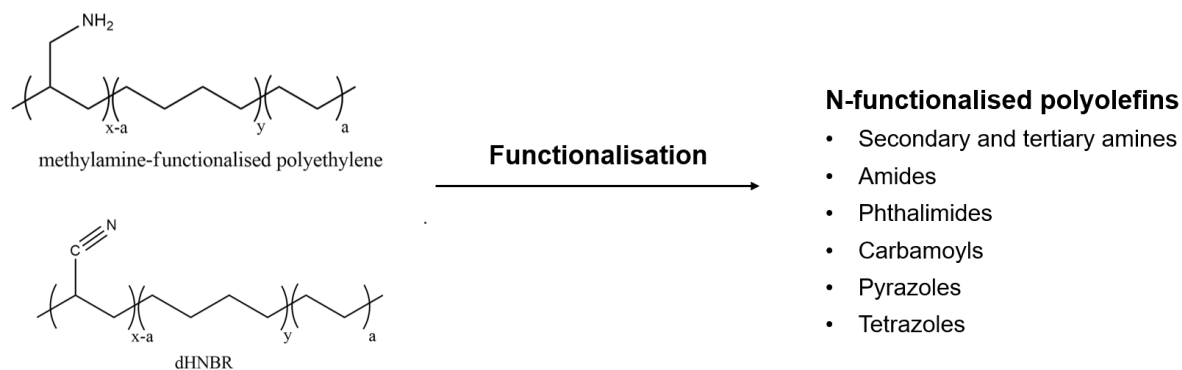


Figure 16: Overview of possible N-functionalisation pathways for amine- and nitrile-functionalised polyolefins.

4 METHODS AND MATERIALS

This chapter presents experimental methods, materials, and analytical techniques used throughout this work. It includes catalytic and non-catalytic reactions, as well as the analysis of reaction mixtures and polymers.

4.1 Materials

The materials used in this work, including solvents, transition metal catalysts, catalyst precursors, ligands, and substrates, were commercially available. An overview of all chemicals used, along with their respective suppliers and purities, is provided in Appendix 1. The chemical structures of the ruthenium catalyst precursors and phosphine ligands used throughout this work to catalyse hydrogenations are shown in Appendix 2.

4.2 Retro-hydrocyanation

The application of the transfer hydrocyanation reaction to HNBR substrates was previously optimised by PhD student Jarne Leinders at cMACS and will be utilised in this work to control the nitrile group content of nitrile butadiene rubbers for further functionalisation.

4.3 Hydrogenation

All catalytic hydrogenation reactions were performed under homogeneous liquid-phase conditions using various ruthenium-based catalysts. Reagents and catalytic components were first dissolved in solution before hydrogen gas was introduced into the headspace of the small stainless-steel high-pressure reactor. Consequently, dissolved hydrogen interacts with the homogeneous ruthenium complex in solution, generating the catalytically active ruthenium hydride species, which transfers the hydride to the substrate, yielding the hydrogenated product. The reactor pressure and heating-block temperature were continuously monitored throughout all experiments. A list of the materials used in these hydrogenation experiments is provided below.

Substrates

- Hexanenitrile
- Trans-4-octene
- Nitrile butadiene rubber (NBR, 38wt% acrylonitrile)
- Hydrogenated nitrile butadiene rubber (HNBR, 37.2wt% acrylonitrile)
- Defunctionalised hydrogenated nitrile butadiene rubber (dHNBR, 6.6wt% acrylonitrile)

Catalyst

- $\text{RuCl}_2(\text{PPh}_3)_3$
- $(\text{RuCl}_2(\text{C}_6\text{H}_6))_2$
- $\text{Ru}(\text{cod})\text{methylallyl}_2$
- $\text{RuHClCO}(\text{PPh}_3)_3$

Ligands

- Triphenylphosphine (PPh_3)
- 1,1'-Bis(diphenylphosphino)ferrocene (dppf)
- Tricyclohexylphosphine (PCy_3)
- 2,2'-bis(diphenylphosphino)-1,1'-binaftyl (BINAP)
- 1,4-Bis(diphenylphosphino)butane (dppb)
- Tris(4-methoxyphenyl) phosphine ($\text{P}(\text{4-MeO-Ph})_3$)
- Tris(4-fluorophenyl) phosphine ($\text{P}(\text{4-F-Ph})_3$)

Solvents

- Toluene
- Tetrahydrofuran (THF)
- Dioxane
- Cyclopentyl methyl ether (CPME)
- 2-Methyltetrahydrofuran (2-MeTHF)
- Chlorobenzene (PhCl)

Bases

- Potassium tert-butoxide (KOtBu)
- Sodium tert-butoxide (NaOtBu)
- Triethylamine (Et_3N)
- Cesium carbonate (Cs_2CO_3)

Gasses

- Argon (Ar)
- Nitrogen (N_2)
- Hydrogen (H_2)

Internal standard

- n-Decane

4.3.1 Hydrogenation of hexanenitrile as a model substrate

Hexanenitrile was selected as a model substrate to optimise the catalytic system and reaction conditions, as it closely resembles the nitrile functionalities present in the NBR substrate. These experiments aimed to achieve the complete conversion of hexanenitrile to hexylamine while suppressing the formation of higher-order amines, such as dihexylamine and trihexylamine. In particular, the effects of the catalyst precursor, ligand, base, hydrogen pressure, temperature, reaction time, and solvent were systematically evaluated.

In a typical experiment, unless stated otherwise, 49.5 μl hexanenitrile (0.4 mmol) and 19.5 μl n-decane (0.1 mmol, internal standard) were dissolved in 1 ml toluene under an argon atmosphere in a crimp-cap vial. In a separate crimp-cap vial, 1 mol% Ru-catalyst precursor (0.004 mmol) and 2 mol% monophosphine ligand (0.008 mmol), or 1 mol% diphosphine ligand (0.004 mmol), were dissolved in 1 ml of toluene under an argon atmosphere. The catalyst solution was stirred at 50°C in a preheated aluminium block until completely dissolved. Subsequently, a magnetic stirring bar and 4.5 mg of KOtBu base (0.04 mmol, 10 mol%) are added to the reactor vial. The substrate and catalyst solution were then combined in the reactor vial, after which the reactor was sealed. The reactor was flushed three times with nitrogen gas and once with hydrogen, after which 50 bar of hydrogen gas was introduced into the headspace of the stainless-steel high-pressure reactor. The sealed reactor was placed in a preheated aluminium block at 120°C for 4 hours. After completion of the reaction, the reaction was quenched by cooling the reactor in an ice bath to room temperature. The reaction mixture was subsequently transferred to a 2 ml GC vial and analysed by gas chromatography.

4.3.2 Hydrogenation of a second model substrate: trans-4-octene

Trans-4-octene was selected as a model substrate to evaluate the performance of the catalytic system and the influence of reaction parameters on the hydrogenation of olefinic bonds, since such functionalities are also present in the NBR substrate.

In a typical experiment, unless otherwise stated, 64.75 μl of trans-4-octene (0.4 mmol) and 19.5 μl of n-decane (0.1 mmol internal standard) were dissolved in 1 ml of toluene under argon. In a separate crimp-cap vial, 1 mol% Ru(cod)methylallyl₂ (1.28 mg) and 2 mol% monophosphine ligand (0.008 mmol) or 1 mol% di-phosphine ligand (0.004 mmol) were dissolved in 1 ml of toluene. Subsequently, a magnetic stirring bar and 10 mol% KOtBu (4.5 mg, 0.040 mmol) were added to the reactor vial. The substrate and catalyst solution were then transferred to the reactor vial, after which the reactor was sealed. The reactor was flushed three times with nitrogen and once with hydrogen before being pressurised to 50 bars with hydrogen. Subsequently, the reactor was placed in a preheated aluminium block at 120 °C for 4 hours. After completion of the reaction, the reactor was cooled to room temperature using an ice bath. The reaction mixture was then transferred to a 2 ml GC vial and analysed by gas chromatography.

4.3.3 Hydrogenation of the polymers of interest: NBR and HNBR

Hydrogenations of nitrile-butadiene rubber (NBR) or hydrogenated nitrile-butadiene (HNBR) were initially conducted under conditions analogous to those employed for the model compounds hexanenitrile and trans-4-octene. Because these standard conditions resulted in incomplete hydrogenation of the polymeric substrate, several modifications were introduced, primarily to the choice of solvent, substrate concentration, catalyst loading, and reaction time.

In a typical experiment, unless stated otherwise, 34.9 mg NBR (0.25 mmol nitriles) or 35.7 mg HNBR (0.25 mmol nitriles), 5.6 mg KOtBu (20 mol%), and a magnetic stirring bar were added directly to the reactor vial. For the hydrogenation of HNBR, 2 mol% Ru(cod)methylallyl₂ (1.6 mg) and 4 mol% PPh₃ ligand (2.62 mg) were weighed and dissolved in a crimp-cap vial under an inert atmosphere, then dissolved in 2 ml of THF. After dissolution, the content of the vial is transferred into the reactor. For the hydrogenation of NBR, 3 mol% Ru(cod)methylallyl₂ (2.4 mg) and 6 mol% PPh₃ (3.93 mg) were weighed and dissolved in a crimp-cap vial under an inert atmosphere, then dissolved in 2 ml of THF. The reactor was then sealed and flushed 3 times with nitrogen gas and once with hydrogen, after which 50 bar of hydrogen gas was introduced as a hydrogenating agent. Subsequently, the reactor was placed in a preheated aluminium block at 120 °C and stirred for 18 hours. After completion of the reaction, the reactor is cooled in an ice bath to room temperature. The reaction mixture was subsequently analysed by proton nuclear magnetic resonance spectroscopy (¹H NMR) as such (200 µL reaction mixture and 300 µL deuterated solvent). Alternatively, the polymer was precipitated in 5 ml of methanol and dried under vacuum for Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis.

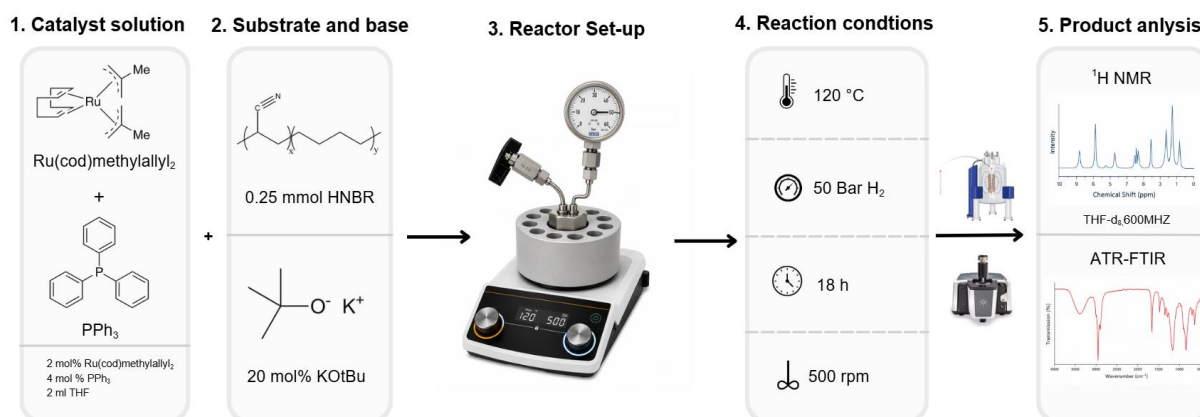


Figure 17: Schematic representation of the catalytic hydrogenation of the HNBR using the Ru(cod)methylallyl₂/PPh₃/KOtBu catalytic system in 2 ml THF in a high-pressure reactor at 50 bar H₂, 125 °C, and 500 rpm for 18 h. The products are characterised by ¹H NMR analysis and ATR-FTIR.

4.4 Acylation

All acylation reactions were performed under homogeneous, non-catalytic conditions. Benzoyl chloride was selected as the acylating agent due to its high reactivity, ease of handling, and ability to form stable products. Triethylamine was added as a base to neutralise the hydrochloric acid byproducts generated during the reaction. All reactions were conducted under ambient atmospheric conditions.

Substrates

- Hexylamine
- Methylamine-functionalised polyethylene

Solvents

- Tetrahydrofuran (THF)
- Dichloromethane (DCM)
- Toluene
- Chlorobenzene (PhCl)
- Acetonitrile (MeCN)
- Dioxane
- Dichlorobenzene (DCB)
- Benzonitrile (PhCN)
- Ethyl acetate (EtOAc)
- Tetrachloroethane (TCE)
- Cyclopentyl methyl ether (CPME)

Internal Standard

- 1,3-dimethoxybenzene

4.4.1 Acylation of model substrate hexylamine

Hexylamine was selected as a model substrate to investigate the acylation of amines using benzoyl chloride.

In a typical acylation reaction performed in this research, 1 ml of solvent was added to a 2 ml GC vial, followed by the addition of 52 μ l triethylamine (0.375 mmol). Subsequently, 33 μ l hexylamine (0.25 mmol) and 29 μ l benzoyl chloride (0.25 mmol) were added, along with a stirring bar. The order of addition was important to minimise the release of HCl gas. The reaction mixtures were stirred in preheated aluminium blocks at 30 °C for 2 hours. The reactions were quenched by adding two droplets of water. For analysis, NMR tubes were filled with 50 μ l of the reaction mixture and 450 μ l of CDCl₃ and subsequently analysed using a Bruker Avance II+ 600 or a Bruker Avance III HD 400 spectrometer.

The same procedure was employed using phthalic or succinic anhydride (0.25 mmol) as the acylating agent. In these reactions, no HCl is generated as a byproduct, eliminating the need for an acid-scavenging base.

4.4.2 Acylation of the polymer of interest

After withdrawal of the NMR samples, the reaction mixture containing the hydrogenated polymer (methylamine-functionalised polyethylene) was transferred from the high-pressure reactor to a crimp-cap vial, allowing visual monitoring of the subsequent acylation reaction. Subsequently, 52 μ l triethylamine (0.375 mmol) was added to the reaction mixture. In a separate vial, 29 μ l benzoyl chloride (0.25 mmol) was dissolved in 1 ml THF, after which the solution was added dropwise to the reaction mixture under continuous stirring. The reaction mixture was then placed in a preheated aluminium heating block at 30°C for 2h and stirred at 600 rpm. Upon completion of the reaction, the resulting polymer was precipitated in 5 ml of methanol. The precipitated polymer was then washed with 5 ml of water to remove any residual Et₃N · HCl salt, followed by two additional washing steps with methanol. The polymer was subsequently dried under vacuum at 50°C until completely dry, using a Schlenk line. ATR-FTIR spectra were recorded of the dried polymers before redissolution in 500 μ l of tetrachloroethane-d₂ for NMR analysis. The same procedure was employed using phthalic or succinic anhydride as the acylating agent. In these reactions, no HCl is generated as a byproduct, eliminating the need for an acid-scavenging base and a water wash step.

4.5 Phthalimide formation

Phthalimide formation was carried out to introduce phthalimide functionalities onto the target substrate. All reactions were performed under homogeneous, non-catalytic conditions using phthalic anhydride as the phthaloylating reagent. Phthalic anhydride was selected due to its high reactivity towards nucleophilic amines and its common use in the formation of phthalimide derivatives. All reactions were performed under ambient atmospheric conditions.

Substrates

- Hexylamine
- Methylamine-functionalised polyethylene

Solvents

- Xylene
- Chlorobenzene (PhCl)
- N-Butyl-2-pyrrolidone (NBP)
- Dimethylformamide (DMF)
- N-butyl acetate (BuOAc)
- Tetrahydrofuran (THF)
- Toluene
- Dioxane
- 1,2-Dichlorobenzene (DCB)

Internal Standard

- 1,3-dimethoxybenzene

4.5.1 Phthalimide formation with hexylamine

Hexylamine was selected as a model compound to investigate the phthalimide formation of amines using phthalic anhydride. In a typical phthalimide formation carried out in this work, 37.0 mg of phthalic anhydride (0.25 mmol) and 33 μ l of hexylamine (0.25 mmol) were added to a 2 ml GC vial and dissolved in 1 ml of solvent. The vial was then placed in a preheated aluminium block for 24 h and stirred with a magnetic stirring rod at 600 rpm at the desired temperature. Upon completion of the reaction, the mixture was cooled in an ice bath to room temperature. For analysis, NMR samples were prepared by mixing 50 μ l of the reaction mixture with 450 μ l of CDCl_3 . The spectra were recorded on a Bruker Avance II+ 600 or a Bruker Avance III HD 400 spectrometer.

4.5.2 Phthalimide formation with the polymer

After withdrawal of the NMR samples, the reaction mixture containing methylamine-functionalised polyethylene in THF was retained in the high-pressure reactor. Subsequently, 37.0 mg of phthalic anhydride (0.25 mmol) is dissolved in 1 ml of THF and added, under continuous stirring, at room temperature to the high-pressure reactor. Afterwards, the reactor is sealed under atmospheric conditions and placed in a preheated aluminium block at 150°C, and stirred at 600 rpm for 24h. Upon completion of the reaction, the reactor is cooled to room temperature in an ice bath. The resulting polymer was precipitated in methanol and washed three times with a fresh portion of methanol. The polymer was then dried under vacuum at 50°C until completely dry. ATR-FTIR spectra are recorded before redissolving part of the polymer in 500 μ l tetrachloroethane- d_2 for NMR analysis.

4.6 Gas chromatography (GC)

GC-data were obtained using a Shimadzu (GC-2010) equipped with a flame ionisation detector (FID) and an Agilent CP-SIL 8 column. The resulting chromatograms were analysed using the GC-solution V2.44 software provided by Shimadzu Corporation. n-Decane was used as an internal standard, and appropriate methods were developed based on the composition of the reaction mixture. As an initial step, GC-chromatograms of commercially available reagents and products were recorded to determine their retention times and to calculate effective carbon numbers (See section 4.6.1).

Figure 18 shows a representative gas chromatogram of the hydrogenation of hexanenitrile to hexylamine, performed as described in section 4.3.1 but at 100°C to ensure detection of both reagents and products. The CP-SIL 8 column is highly apolar, and with a temperature program starting at 60°C and increasing at 20°C/min to 250°C, separation occurred predominantly based on volatility. So, the solvent toluene (boiling point 110°C) eluted first. Then the product hexylamine (boiling point 131.5 °C) eluted at approximately 5.13 min, followed by the unreacted hexanenitrile (boiling point 164 °C) at approximately 5.47 min. The internal standard, 0.10 mmol of n-decane (boiling point of 174°C), eluted after approximately 6.73 min. Typical byproducts of nitrile hydrogenation, such as dihexylamine and trihexylamine, were not observed in the chromatograms. The small peak at around 6 min is most likely due to column bleed.

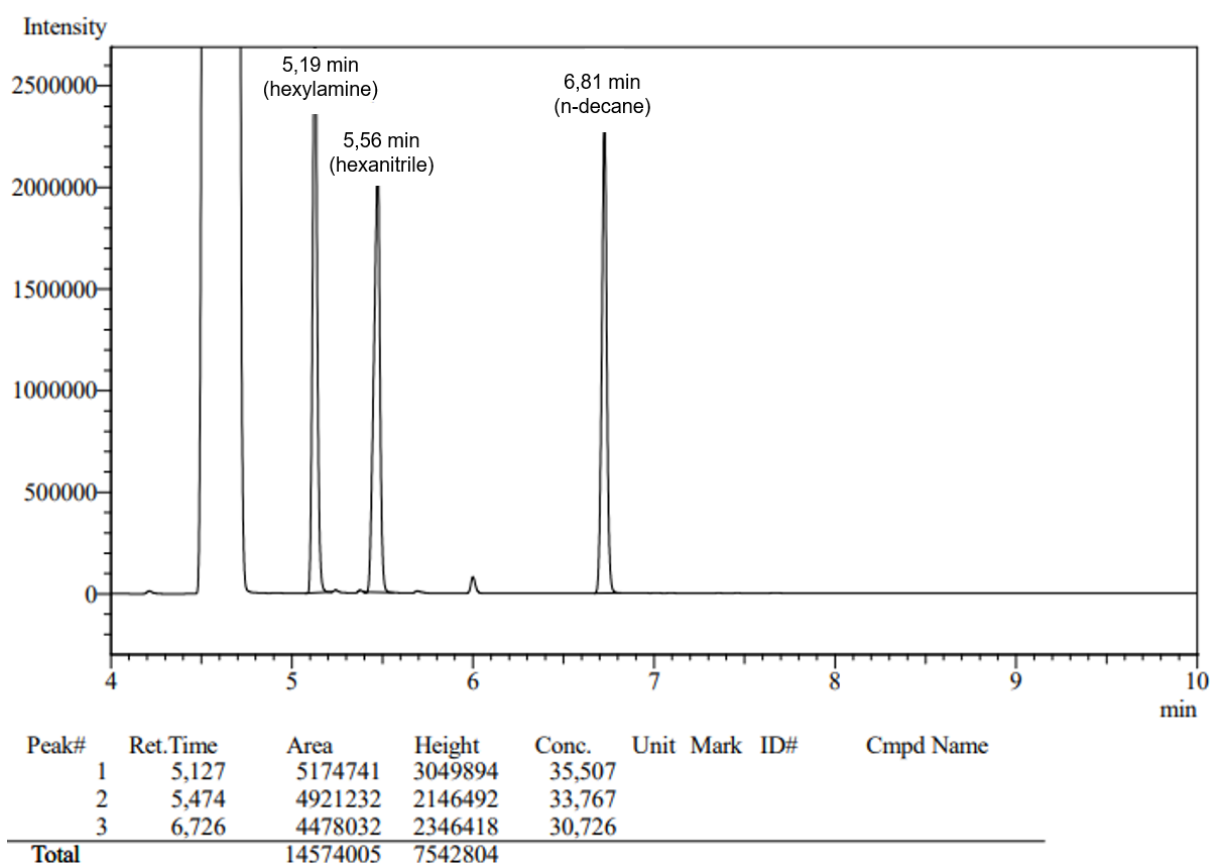


Figure 18: Representative Gas Chromatogram Illustrating peak distribution of the hydrogenation of hexanenitrile. The hexylamine product peak eluted at 5.13 min, residual hexanenitrile at 5.47 min, and n-decane at 6.73 min.

4.6.1 Effective Carbon Number (ECN)

Throughout this work, the concept of effective carbon number, as published by Scanlon and Willis, was used to quantify the peaks observed in gas chromatograms [100]. The effective carbon number is a quantitative parameter used in gas chromatography to describe the relative detector response of a compound when using a flame ionisation detector. It represents the number of carbon atoms in a molecule that effectively contribute to the detector signal. The ECN accounts for the fact that different functional groups influence the FID response differently. In this approach, the ECN-value of an aliphatic or aromatic carbon equals 1. Other functional groups have deviating ECN-values. In theory, nitrile groups have an ECN of 0.3, and primary amines have an ECN of -0.5. Because the effective carbon number is specific for each Flame ionisation detector, the effective carbon number of each reagent and product is determined experimentally. The effective carbon number of n-decane is set to 10, and the ECN values of the other components are calculated relative to this standard. Using the relative weight response factor $F(R - wt)$, as defined in Equations 1 and 2, the ECN of a compound can be calculated according to Equation 3.

$$F(R - wt) = \frac{area\ counts_{ref} \times wt_{comp}}{area\ counts_{comp} \times wt_{ref}} \quad (1)$$

$$F(R - wt) = \frac{MW_{comp} \times ECN_{ref}}{MW_{ref} \times ECN_{comp}} \quad (2)$$

$$ECN_{comp} = \frac{MW_{comp} \times ECN_{ref}}{MW_{ref} \times F(R - wt)} \quad (3)$$

The experimentally determined effective carbon numbers for hexanenitrile (5.54), hexylamine (5.36), dihexylamine, octane (8), and trans-4-octene (7.9) were used throughout this work to quantify the corresponding peaks in the gas chromatograms.

Figure 19 shows the chromatogram used to determine the effective carbon numbers (ECNs). Hexylamine, dihexylamine, and hexanenitrile were dissolved in 1.5 ml of toluene at a concentration of 0.25 mmol, together with 0.10 mmol of n-decane as the internal standard.

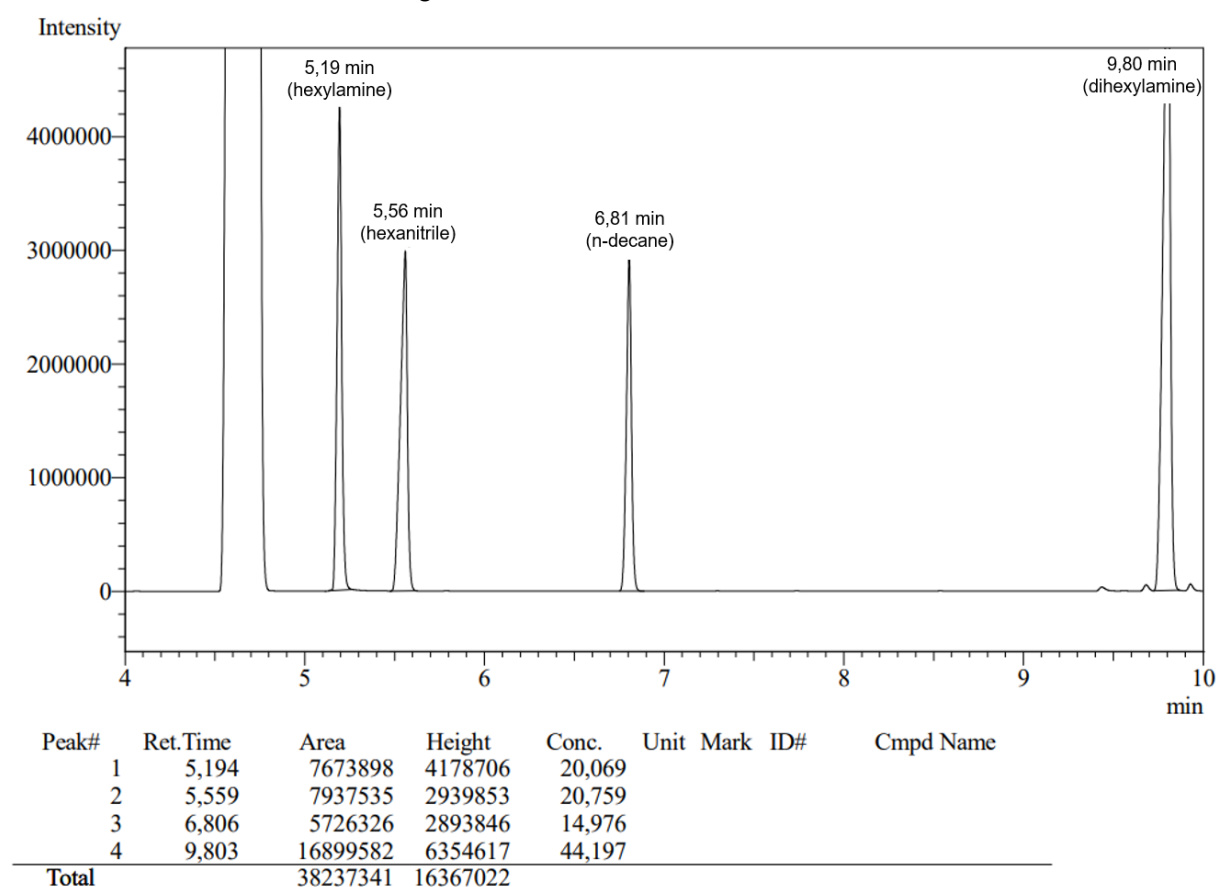


Figure 19: Chromatogram for the determination of the effective carbon numbers of reagents and products in the nitrile hydrogenation.

The concept and calculation of the effective carbon number are shown for the product hexylamine, which eluted after 5.194 min. The ECN-values of other reagents or products were determined analogously.

The internal standard, n-decane, eluted at a retention time of 6.806 min and was used as the reference compound, with an assigned ECN value of 10 ($ECN_{ref} = 10$). The corresponding peak area amounted to 5 726 326 ($area\ counts_{ref} = 5\ 726\ 326$). The chromatographic peak areas are presented in Figure 19.

Since the amounts of both the internal standard, n-decane, and the product, hexylamine, are known, F(R-wt) could be calculated according to Equation 1 as follows:

$$F(R - wt) = \frac{5\,726\,326 \times 25.3 \text{ mg}}{7\,673\,898 \times 14.2 \text{ mg}} = 1.33$$

The resulting relative weight response factor was then substituted into Equation 3, yielding an ECN value of 5.36 for hexylamine.

$$ECN_{comp} = \frac{101.19 \frac{g}{mol} \times 10}{142.29 \frac{g}{mol} \times 1.33} = 5.36$$

The calculated ECN of 5.36 enables straightforward quantification of the hexylamine formed in each obtained chromatogram. Since the ECN values of both hexylamine and n-decane are known and the amount of the internal standard, n-decane, was standard 0.10 mmol, Equation 4 can be applied directly to determine the amount of hexylamine formed.

$$n_{comp} = n_{ref} * \frac{A_{comp}}{A_{ref}} * \frac{ECN_{ref}}{ECN_{comp}} \quad (4)$$

$$n_{comp} = 0.10 \text{ mmol} * \frac{5\,174\,741}{4\,478\,032} * \frac{10}{5.36} = 0.22 \text{ mmol}$$

Based on the initial amount of hexanenitrile (0.40 mmol), the reaction yield was calculated as follows:

$$Yield (\%) = \frac{n_{hexylamine, \text{ formed}}}{n_{hexanenitrile, \text{ initial}}} * 100\% = \frac{0.22 \text{ mmol}}{0.40 \text{ mmol}} * 100\% = 55\% \quad (5)$$

4.7 Fourier-Transform-infrared spectroscopy (FTIR)

To obtain qualitative data on the functional groups present in the polymers, FTIR spectra were recorded using an Agilent Cary 630 FTIR spectrometer with attenuated total reflectance (ATR). For each polymer synthesis, FTIR spectra were recorded for the substrate, intermediate, and product polymers. These spectra were used to confirm the disappearance of nitrile functionalities and olefinic bonds originally present in the substrate and to monitor the appearance of new vibrational bands associated with the desired functional groups. Peak assignments were based on absorption frequencies reported in the literature [101].

4.8 Nuclear magnetic resonance (NMR)

The ¹H- and ¹³C-NMR spectra were recorded using either a Bruker Avance III HD 400 spectrometer or a Bruker Avance II+ 600 spectrometer. NMR samples were typically prepared by diluting 50 µl of the reaction mixture with 450 µl deuterated chloroform (CDCl₃). The acquired data were processed and analysed using Bruker TopSpin software (Version 5.0.0). All chemical shifts are reported relative to tetramethylsilane (TMS).

4.8.1 Calculation method for the yield of the hydrogenation reaction

Because polymers cannot be analysed by gas chromatography, an alternative approach was required to determine the hydrogenation yield. This section establishes the calculation procedure used throughout this work. According to the supplier specifications, the NBR substrate consists of 38 wt% acrylonitrile and 62 wt% butadiene, corresponding to 38.5 mol% acrylonitrile and 61.5 mol% butadiene. Because the integral of an NMR signal is directly proportional to the number of contributing protons, signal integrals can be used to quantify the extent of hydrogenation and thereby determine the reaction yield. The protons contributing to the reference CH₂ signal are highlighted in blue in Figure 20. Taking the relative abundances of both monomers into account, these correspond to a total of 14.8 protons per repeat unit, as calculated in Equation 6. Upon complete hydrogenation, the protons highlighted in green of the resulting aminomethyl functionality correspond to two per repeat unit. Consequently, the integral of the newly formed CH₂ (amine peak, green), relative to the theoretical integral for complete conversion (equivalent to 2), can be used as a measure of amine yield.

$$CH_{2,ACN} + \frac{61.5 \text{ mol}\%}{38.5 \text{ mol}\%} * CH_{2,butadiene} = 2 + \frac{61.5 \text{ mol}\%}{38.5 \text{ mol}\%} * 8 = 14.8 \quad (6)$$

$$Yield_{hydrogenation} (\%) = \frac{CH_{2,observed}}{CH_{2,theoretical}} * 100\% = \frac{1.99}{2.00} * 100\% = 99.5\%$$

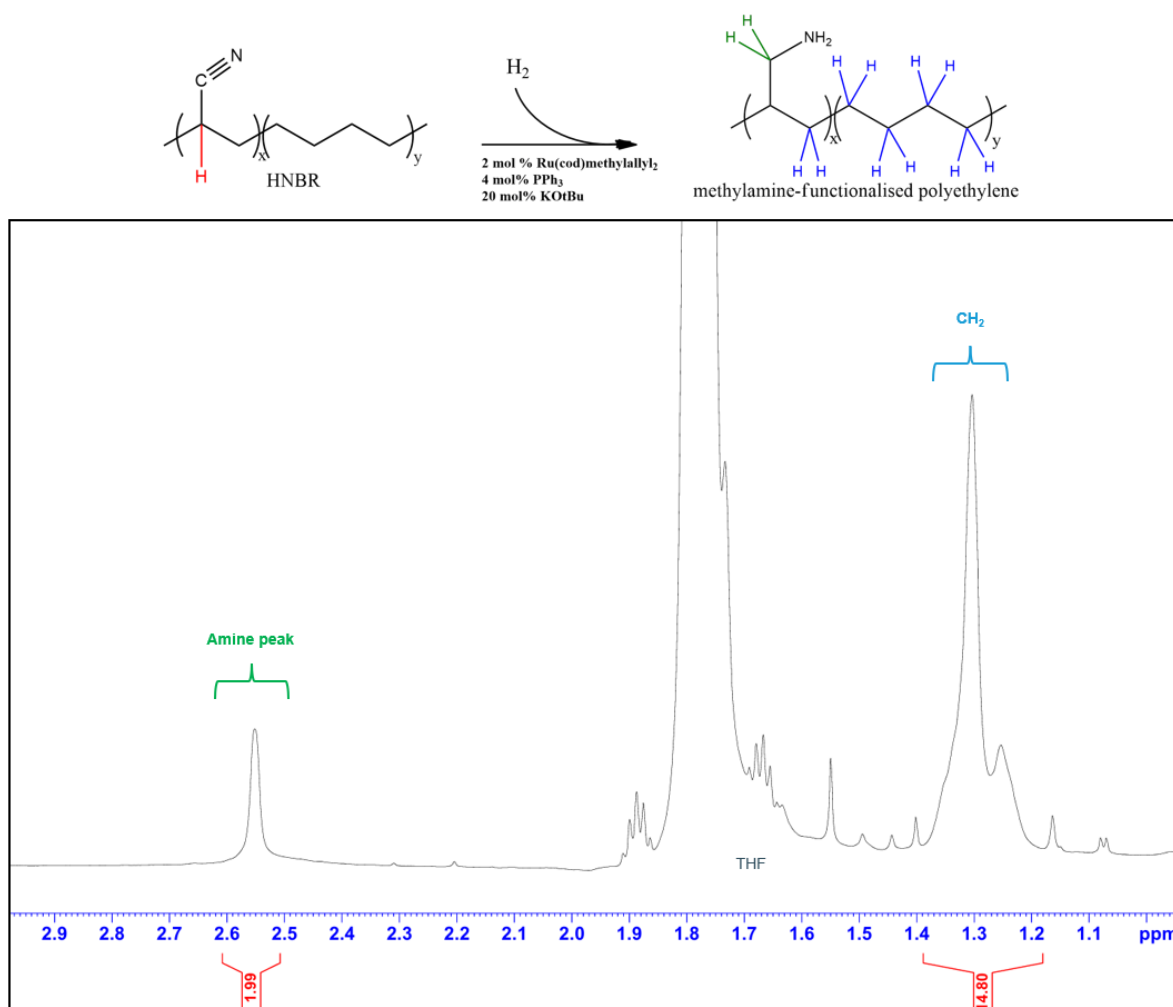


Figure 20: Illustrative ¹H NMR of methylamine-functionalised polyethylene for yield calculation based on the CH₂ and amine signal integration values.

5 RESULTS AND DISCUSSION

The results and discussion chapter presents and interprets the relevant outcomes and key findings of this research. Section 5.1 focuses on the hydrogenation reaction and the optimisation of the reaction conditions. Section 5.2 discusses the acylation reaction as a potential post-hydrogenation functionalisation strategy. Section 5.3 describes the phthalimide formation as an alternative functionalisation route following the hydrogenation reaction.

5.1 Synthesis of Methylamine-functionalised polyolefins by hydrogenation

The first objective of this thesis was the successful hydrogenation of the substrate (H)NBR and partially defunctionalised (H)NBR to yield methylamine-functionalised polyethylene with varying degrees of aminomethyl functionalisation. To achieve this, a bottom-up approach was adopted in which the catalytic system was first developed and optimised on model compounds. The influence of various reaction parameters was then systematically investigated before the acquired knowledge was applied to the polymeric substrates.

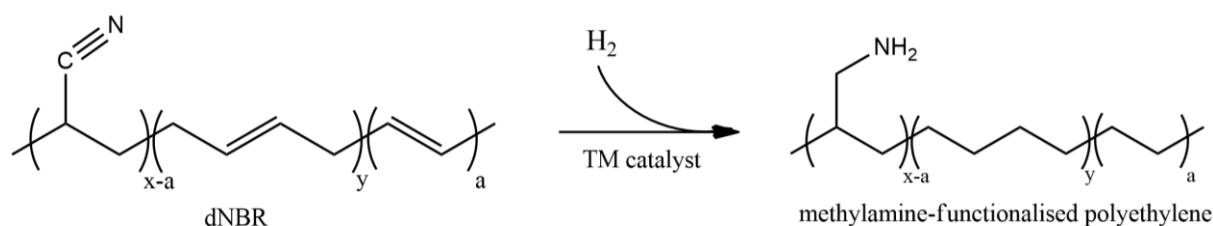


Figure 21: Schematic representation of the complete hydrogenation.

5.1.1 Hydrogenation of model compounds

The NBR substrate contains both nitrile functionalities and olefinic bonds. For simplicity and practicality, it would be highly desirable to hydrogenate both functionalities using a single transition-metal catalyst. Therefore, hexanenitrile was selected as a model compound to evaluate the performance of a catalytic system for the hydrogenation of nitriles to primary amines. In parallel, trans-4-octene was selected as a model compound to assess the ability of the catalytic system to hydrogenate olefinic bonds.

5.1.1.1 The catalytic system

The catalytic hydrogenation of hexanenitrile yields hexylamine as the primary product by reducing the nitrile group to a primary amine, a reaction that requires 2 equivalents of H₂ Gas.

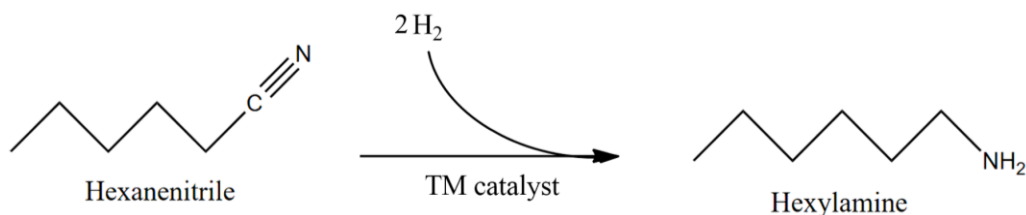


Figure 22: Model reaction used for catalyst screening: hydrogenation of hexanenitrile to hexylamine using a transition-metal catalyst and H₂.

Numerous catalytic systems capable of selectively converting nitriles into primary amines have been reported in the scientific literature. Ruthenium-based catalysts are particularly attractive because of their exceptional versatility and their proven ability to hydrogenate both nitriles and olefinic double bonds [102], [103]. Therefore, an extensive catalyst screening was conducted using commercially available ruthenium catalyst precursors in combination with various phosphine ligands. Phosphine ligands play a crucial role in ruthenium-catalysed hydrogenations because they stabilise the metal centre and tune its steric and electronic properties to achieve high activity and selectivity. Lastly, they facilitate the formation of active ruthenium-hydride species, which are the active intermediates responsible for delivering hydrides to the unsaturated substrate. The catalyst screening is conducted using 1 mol% Ru catalyst precursors with either 1 mol% diphosphine or 2 mol% monophosphine ligands.

The results of the catalyst screening are depicted below in Figure 23.

The four ruthenium pre-catalysts screened:

- 1 = RuCl₂(PPh₃)₃
- 2 = Ru(cod)methylallyl₂
- 3 = (RuCl₂(C₆H₆))₂
- 4 = RuHClO(PPh₃)₃

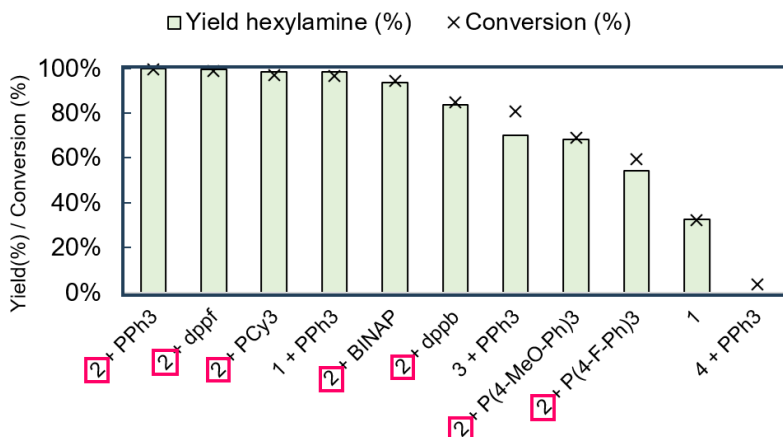


Figure 23: Catalyst screening of ruthenium catalyst precursors and phosphine ligands for nitrile-to-primary-amine hydrogenation, highlighting the superior performance of Ru(cod)methylallyl₂. Reaction conditions: 0.4 mmol hexanenitrile, 2 ml toluene, H₂ (50 Bar), 120°C, 4h.

The results of the trans-4-octene to octane hydrogenation, presented in Figure 25, demonstrate the superiority of PPh₃, PCy₃, and dppb ligands for olefinic bond hydrogenation. Among these ligands, PPh₃ performed exceptionally well in both nitrile and olefin hydrogenation and was therefore selected as the ligand of choice for subsequent experiments. Compared to many other phosphine ligands, PPh₃ is relatively inexpensive, air-stable, widely available, and already widely adopted in industry. These characteristics facilitate its use and enhance the industrial applicability of our proposed synthesis method.

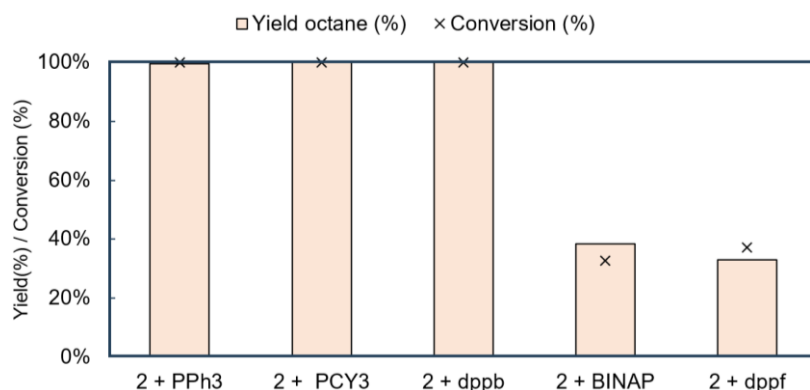


Figure 25: Catalyst screening of ruthenium catalyst precursors and phosphine ligands for hydrogenation of trans-4-octene to octane. Demonstrating that Ru(cod)methylallyl₂/PPh₃ also achieves complete hydrogenation of olefinic bonds. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml toluene, H₂ (50 Bar), 120°C, 4h.

According to literature, an effective catalytic system for the hydrogenation of nitriles to primary amines requires a transition-metal catalyst, a phosphine ligand, and a facilitating base. The necessity of each component is evaluated for both nitrile and olefinic bond hydrogenation by selectively omitting components from the reaction mixture. The results are presented in Figure 26.

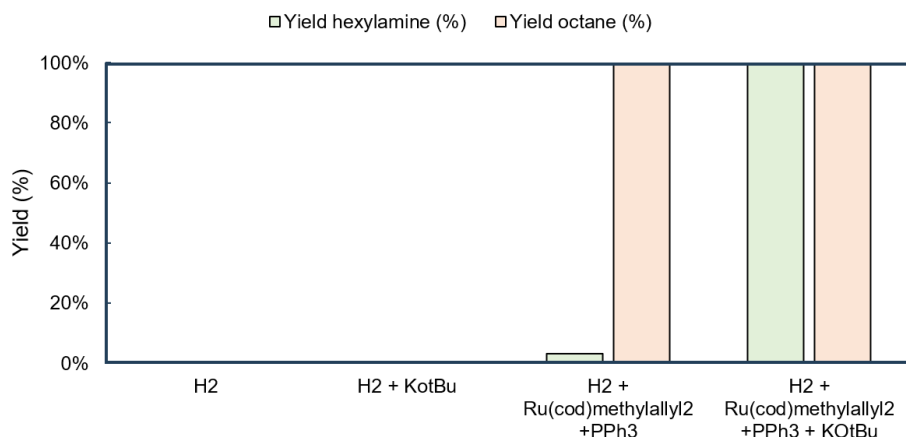


Figure 26: Effect of omitting the catalyst, ligand, and base on the yields of the hydrogenation reactions. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml toluene, H₂ (50 bar), 120°C, 4h.

The results of the component omission study of the catalytic system, shown in Figure 26, reveal clear differences between nitrile hydrogenation and olefinic bond hydrogenation. Efficient nitrile hydrogenation requires a ruthenium catalyst precursor, a phosphine ligand, and potassium tert-butoxide (KOtBu). The presence of KOtBu appears irrelevant to the hydrogenation of the olefinic bond. To understand the differences between these hydrogenations, it is necessary to

investigate how the substrate binds to the metal centre and how readily hydrogen is transferred to the substrate. An olefin binds moderately weakly to the metal centre. The π -bond is electron-rich and readily interacts with hydrogen activated on the metal catalyst. The mechanism is quite straightforward, so no base is needed to facilitate this. On the other hand, a nitrile group is strongly polarised and coordinates tightly to the metal catalyst with its nitrogen lone pair. Furthermore, nitriles are generally less electrophilic than olefinic bonds. Facilitating bases, such as KOtBu, weaken the nitrile-metal interaction and facilitate key proton-transfer steps towards the substrate, making catalytic cycles smoother. Therefore, facilitating bases such as KOtBu play a crucial role in the selective hydrogenation of nitriles to primary amines [106].

The downside of KOtBu is that it is extremely moisture sensitive. It can react violently with water or moisture in the air, producing KOH and tert-butanol. Consequently, it must be stored under inert conditions and preferably in a desiccator. In addition, KOtBu is generally more expensive than other strong bases, such as KOH. Therefore, a base screening of various bases which are commonly used in hydrogenation reactions was conducted to evaluate potential alternatives (Figure 27).

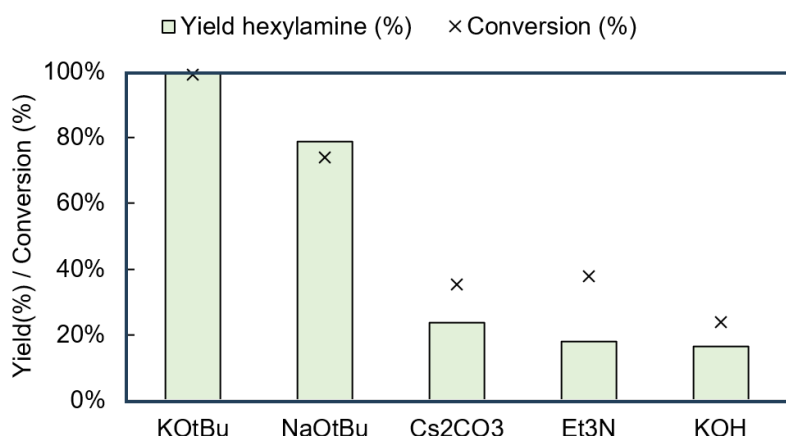


Figure 27: Base screening for nitrile-to-primary-amine hydrogenation, demonstrating the superior performance of KOtBu as a facilitating base. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml toluene, H₂ (50 bar), 120°C, 4h.

Unfortunately, none of the tested bases matched the performance of KOtBu. The slightly lower activity observed for NaOtBu can be attributed to stronger ion pairing between Na⁺ and OtBu⁻, which reduces the availability and reactivity of the base. Because K⁺ is a larger cation than Na⁺, it binds less tightly, leaving the OtBu⁻ more exposed and reactive. Therefore, KOtBu is considered a stronger base than NaOtBu [107]. The inferior performance of Cs₂CO₃ and Et₃N is most likely due to their lower basicity, which limits their ability to efficiently promote key proton-transfer steps in the catalytic cycle. Lastly, the poor performance of KOH is likely due to its low solubility in toluene.

In conclusion, the catalytic system consisting of Ru(cod)methylallyl₂, PPh₃, and KOtBu emerged as the most effective for the hydrogenation of nitriles and olefinic bonds. Consequently, this system is selected as the catalytic system of choice for all subsequent hydrogenation reactions investigated in this work.

5.1.1.2 Time screening

To gain a deeper understanding of the hydrogenation progress of both nitriles and olefinic bonds, a time-dependent study is conducted (Figure 28 and Figure 29). This investigation focuses on the two catalytic systems that showed the highest performance during the initial nitrile hydrogenation screenings: Ru(cod)methylallyl₂/PPh₃ and Ru(cod)methylallyl₂/dppf. The time-dependent experiments are designed to compare catalytic activity and conversion profiles of both systems, providing insight into reaction kinetics and overall reaction progress under the applied conditions.

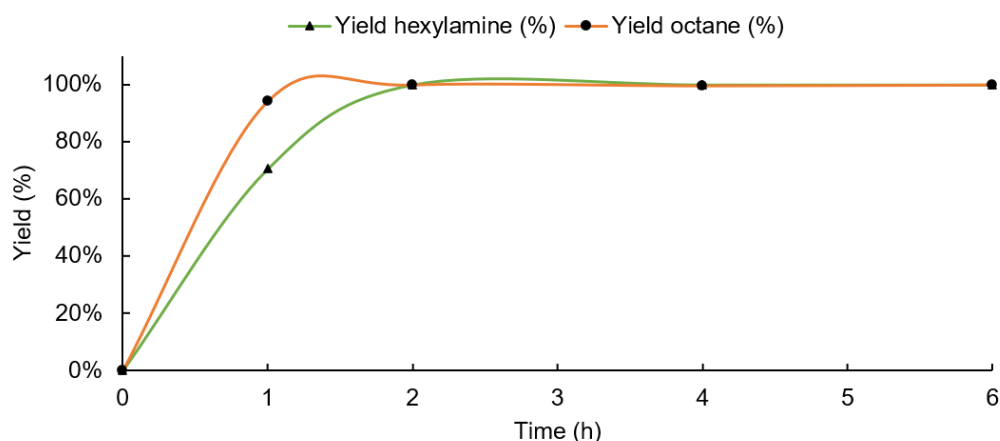


Figure 28: Time screening of hydrogenation of nitriles and olefinic bonds catalysed by Ru(cod)methylallyl₂/PPh₃/KOtBu. Near-quantitative conversion was achieved within 2 h for both model substrates, after which the reaction reached a plateau. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml toluene toluene, H₂ (50 bar), 120°C.

The catalytic system consisting of Ru(cod)methylallyl₂ and PPh₃ shows very high activity towards both nitriles and olefinic bonds. The hydrogenation of the olefinic bond to octane achieves near-complete conversion, slightly faster than the hydrogenation of the nitrile from hexanenitrile. Both reactions appear to be essentially complete by 2 hours, and the yield plateaus, indicating stability of the formed products.

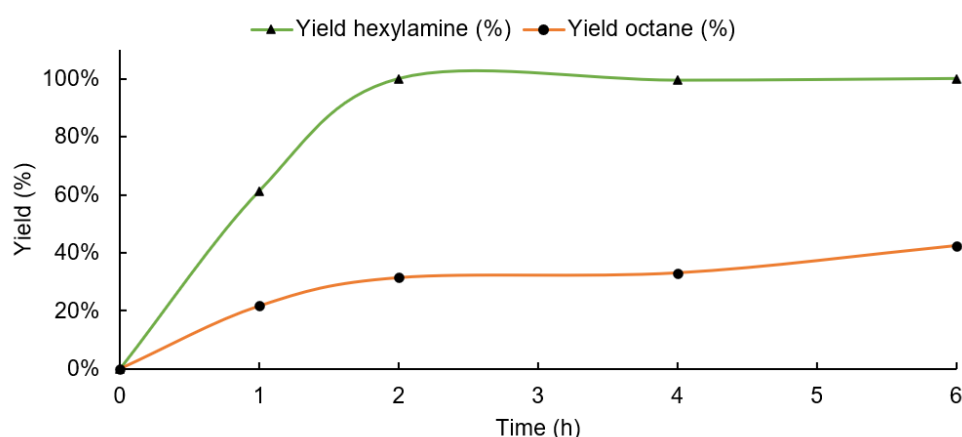


Figure 29: Time screening of hydrogenation of nitriles and olefinic bonds catalysed by Ru(cod)methylallyl₂/dppf/KOtBu. Near-complete hydrogenation of nitriles was achieved, whereas hydrogenation of olefinic bonds remained incomplete. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml toluene toluene, H₂ (50 bar), 120°C.

The catalytic system consisting of Ru(cod)methylallyl₂ and dppf shows markedly different activities toward nitriles and olefinic bonds. The nitrile hydrogenation shows a conversion profile very similar to that of the catalytic system with PPh₃. However, it could not fully hydrogenate trans-4-octene within the given timeframe. The inferior performance is most likely attributable to the steric and electronic properties of dppf. The ligand is very bulky and electron-rich, creating a very crowded metal centre to which weakly coordinating substrates, such as olefins, cannot bind effectively [108]. Conversely, nitrile groups are strongly coordinating functionalities that can bind effectively to the metal centre, with the lone pair on the nitrogen. Therefore, the catalytic system with dppf can successfully hydrogenate nitriles but performs rather poorly in the hydrogenation of olefinic bonds. On the other hand, PPh₃ is a monodentate ligand that associates with and dissociates from the metal centre more readily. PPh₃ is only moderately bulky and can adjust orientation around the metal. Moreover, it has a more balanced electronic environment. All of this makes PPh₃ a more versatile ligand compared to dppf. These findings further support the use of PPh₃ as a standard ligand for further reactions [108].

5.1.2 Reaction conditions

Following the identification of an effective catalytic system, a systematic investigation of key reaction parameters is undertaken to further optimise the hydrogenation process. The effects of temperature, pressure, catalyst loading, and solvent on the product yield are investigated. By varying each factor individually, insight into their impact on product yield is obtained. This study aims to establish optimal reaction conditions and to provide a deeper understanding of the factors that affect the performance of the Ru(cod)methylallyl₂/PPh₃/KOTBu catalytic system. The standard conditions employed, which served as the starting point for these experiments, are 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOTBu, at 50 Bar H₂ and 120°C for 4 h using 0.40 mmol of substrate.

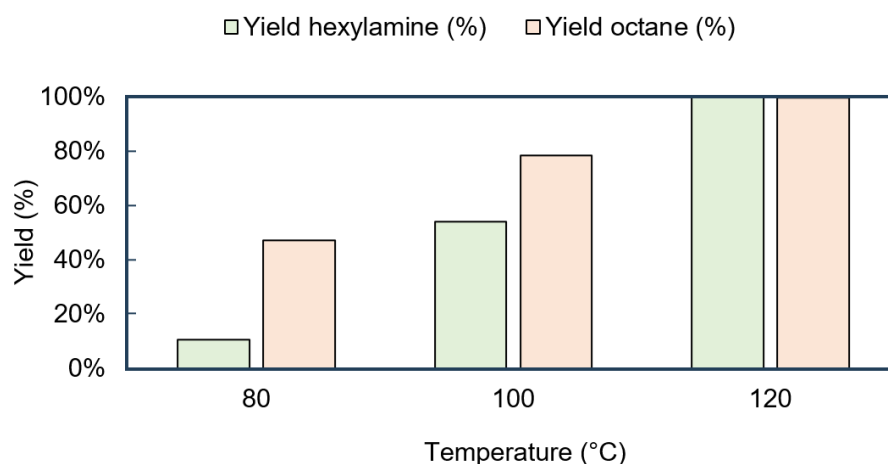


Figure 30: Influence of reaction temperature on the hydrogenation of nitriles and olefinic bonds catalysed by the Ru(cod)methylallyl₂/PPh₃/KOTBu catalytic system. The results indicate a strong temperature dependence, with 120°C as the minimum temperature required for quantitative yields in the hydrogenation reaction. Reaction conditions: 0.40 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOTBu, 2 ml toluene, H₂ (50 bar), 4h.

The results of the temperature screening indicate that product yield increases accordingly with an increase in temperature (Figure 30). Under the reaction conditions applied, a temperature of 120 °C was required to achieve near-complete hydrogenation of the model compounds within 4 h. Although hydrogenation reactions are exothermic and thus thermodynamically favourable at lower temperatures, increasing the temperature is necessary to overcome the activation energy barrier and achieve a sufficient reaction rate. Consequently, determining the optimal reaction temperature involves balancing kinetic and thermodynamic considerations.

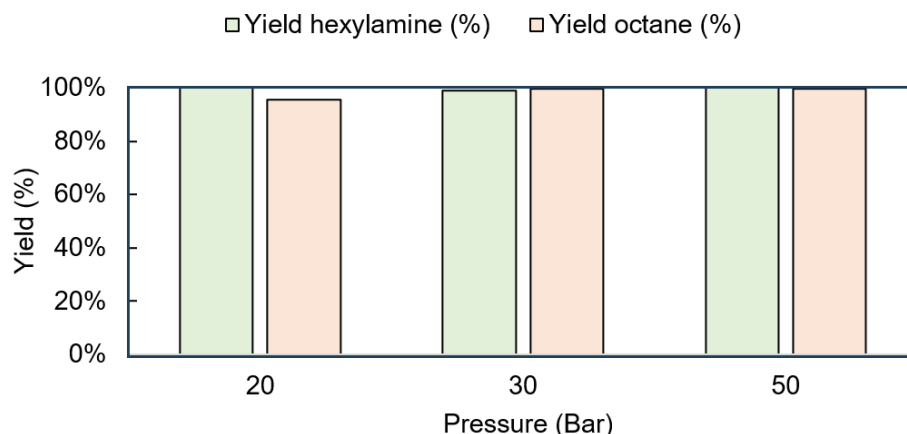


Figure 31: Influence hydrogen pressure on the hydrogenation of nitriles and olefinic bonds using a Ru(cod)methylallyl₂/ PPh₃/KOTBu catalytic system. The selected hydrogen pressure does not significantly affect the product yield within the range of 20 to 50 bar. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOTBu, 2 ml toluene, 120°C, 4h.

The influence of hydrogen pressure on the reaction outcome shows to be very minor within the investigated range. Hydrogen pressures as low as 20 Bar are already sufficient to achieve near-complete hydrogenation of nitriles and olefinic bonds. Nevertheless, hydrogen pressures are typically kept high during hydrogenation experiments to maximise the amount of dissolved hydrogen. Therefore, the hydrogen pressure was maintained at 50 bar for subsequent experiments to ensure that hydrogen was not a limiting factor in polymer hydrogenation.

The different catalyst loadings presented in Figure 32 are denoted in the format 1:2:10. In this notation, the first value (1) corresponds to the mol% of Ru(cod)methylallyl₂, the second value (2) represents the mol% of PPh₃, and the third value (10) indicates the mol% of KOTBu.

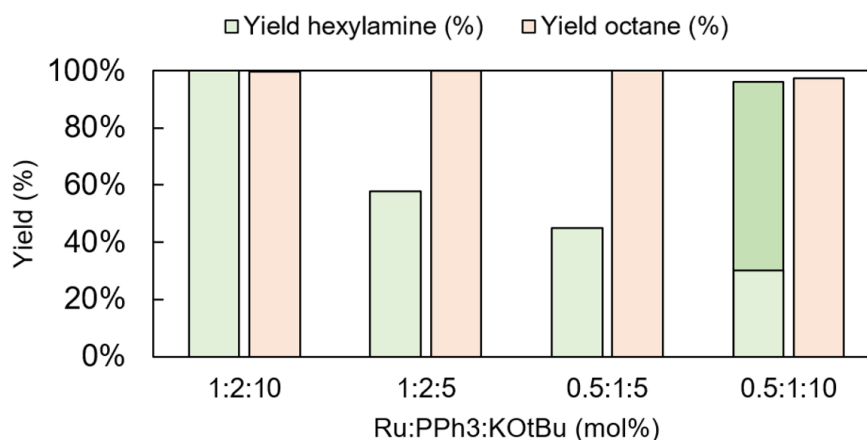


Figure 32: Effect of catalyst loading on the hydrogenation of nitriles and olefinic bonds using a Ru(cod)methylallyl₂/ PPh₃/KOTBu catalytic system. Nitrile hydrogenation is strongly influenced by catalyst loadings. Reaction conditions: 0.4 mmol substrate, 2 ml toluene, 120°C, H₂ (50 bar), 4h/18h.

The effect of catalyst loading, shown in Figure 32, reveals a clear difference between the hydrogenation of nitriles and of olefinic bonds. For nitrile hydrogenation, a minimum catalyst loading of 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, and 10 mol% KOtBu is required to achieve complete conversion in 4 hours. However, because the catalyst is not consumed during the reaction, lower catalyst loadings are expected to result in longer reaction times rather than incomplete final conversions, provided that catalyst degradation remains limited. This hypothesis was confirmed by the hydrogenation of hexanenitrile using a reduced catalyst loading of 0.5 mol% Ru(cod)methylallyl₂, 1 mol% PPh₃, and 10 mol% KOtBu, which afforded 96% yield after 18 hours (dark green bar, Figure 32). In contrast, olefinic bonds require substantially lower catalyst loadings than nitriles, while still achieving full conversion at half the catalyst loading.

The last reaction parameter varied is the solvent (Figure 33). All solvents tested are extra dry and contain molecular sieves. Because KOtBu can violently react with water, producing KOH and tert-butanol, which can compromise reaction yields.

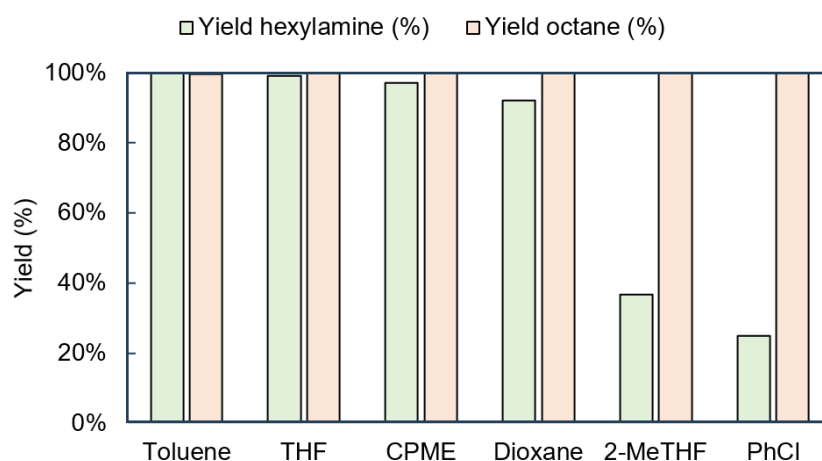


Figure 33: Solvent screening for hydrogenation of nitriles and olefinic bonds using a Ru(cod)methylallyl₂/ PPh₃/KOtBu catalytic system. Complete hydrogenation of olefinic bonds is achieved in all solvents, whereas efficient hydrogenation of nitriles is observed only in toluene, THF, CPME, and dioxane. Reaction conditions: 0.4 mmol substrate, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 2 ml solvent, H₂ (50 bar), 4h.

Finally, a solvent screening is performed. The olefinic bonds reach complete hydrogenation in every solvent tested. In contrast, nitrile hydrogenation only achieves near-complete conversion in toluene, THF, CPME, and dioxane. These results further demonstrate that nitrile hydrogenation is considerably more sensitive to the reaction environment than olefin hydrogenation. The lower nitrile hydrogenation yield observed in chlorobenzene (PhCl) may be attributed to interactions between the solvent and the ruthenium catalyst. Chlorobenzene is suspected of undergoing oxidative addition to the Ruthenium centre, blocking the necessary vacant sites required for H₂ activation and therefore poisoning the catalyst [109].

Throughout these hydrogenation screenings, a clear trend emerges. Olefinic bonds are hydrogenated more readily than nitriles. In general, higher yields and faster conversion profiles are observed for substrates containing olefinic bonds. This difference in reactivity can be attributed to the structural and electronic differences between a nitrile ($\text{-C}\equiv\text{N}$) and an olefinic bond ($\text{-C}=\text{C-}$). First, hydrogenation requires bond dissociation. The dissociation energy of a $\text{C}=\text{C}$ bond is around 614 kJ/mol, and for a nitrile bond, the $\text{C}\equiv\text{N}$ dissociation energy is around 891 kJ/mol, and the $\text{C}=\text{N}$ dissociation energy is around 615 kJ/mol [110]. So, the higher dissociation energies of nitriles make them more difficult to hydrogenate. Second, the electrons

in a nitrile are withdrawn towards the electronegative nitrogen, reducing its reactivity towards hydrogenation. Moreover, nitriles can coordinate strongly to the metal centre via the nitrogen lone pair, which may inhibit catalytic activity by blocking active sites on the catalyst. Lastly, complete hydrogenation of nitriles to primary amines requires 2 equivalents of hydrogen, whereas hydrogenation of olefinic bonds requires only 1 equivalent of hydrogen. These structural and electronic differences explain why nitriles are generally more challenging to hydrogenate than olefinic bonds [106].

5.1.3 Hydrogenation of the (hydrogenated) nitrile butadiene rubber

Based on the model compound screenings, the standard hydrogenation conditions were established as follows, with catalyst loadings expressed relative to the initial nitrile content: 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 120°C, 50 Bar hydrogen, 4h reaction time. The FTIR spectra of the substrate HNBR (blue) and the resulting polymer (orange) are displayed in Figure 34. However, the solvent was changed from toluene to THF due to poor solubility of HNBR and NBR in toluene.

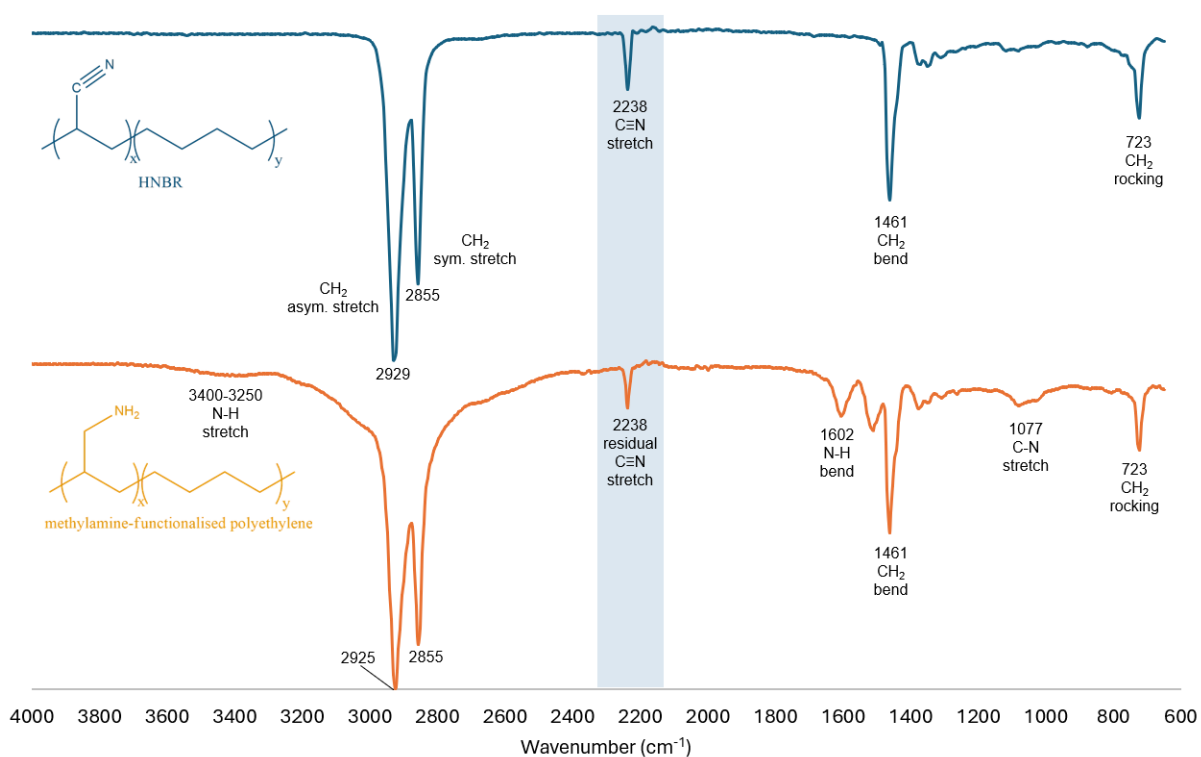


Figure 34: FTIR spectrum of hydrogenated nitrile butadiene rubber showing a pronounced residual nitrile (C≡N) absorption band, indicating only partial hydrogenation of the nitrile groups. Reaction conditions: 0.25 mmol HNBR, 2 ml solvent, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 4h, 50 bar H₂, and 120°C.

5.1.3.1 Optimisation of Reaction Conditions on the polymeric substrate HNBR

Unfortunately, the standard conditions established from model compound reactions are insufficient to achieve complete hydrogenation of the HNBR substrate. The FTIR spectrum, depicted in Figure 34, shows this by the fact that a rather large residual nitrile peak is observed (2238 cm^{-1}) [101]. The residual nitrile peak is highlighted by the blue box in Figure 34. Nevertheless, its intensity is noticeably lower than that of the starting HNBR substrate. Moreover, vibrational modes of formed amines appear in the product spectrum, including the N-H stretch ($3400\text{--}3250\text{ cm}^{-1}$), N-H bend ($1650\text{--}1580\text{ cm}^{-1}$), and C-N stretch ($1250\text{--}1020\text{ cm}^{-1}$). The appearance of these bands confirms that some of the nitrile groups have been successfully hydrogenated to primary amines. This conclusion is further supported by the ^1H NMR spectrum shown in Figure 35.

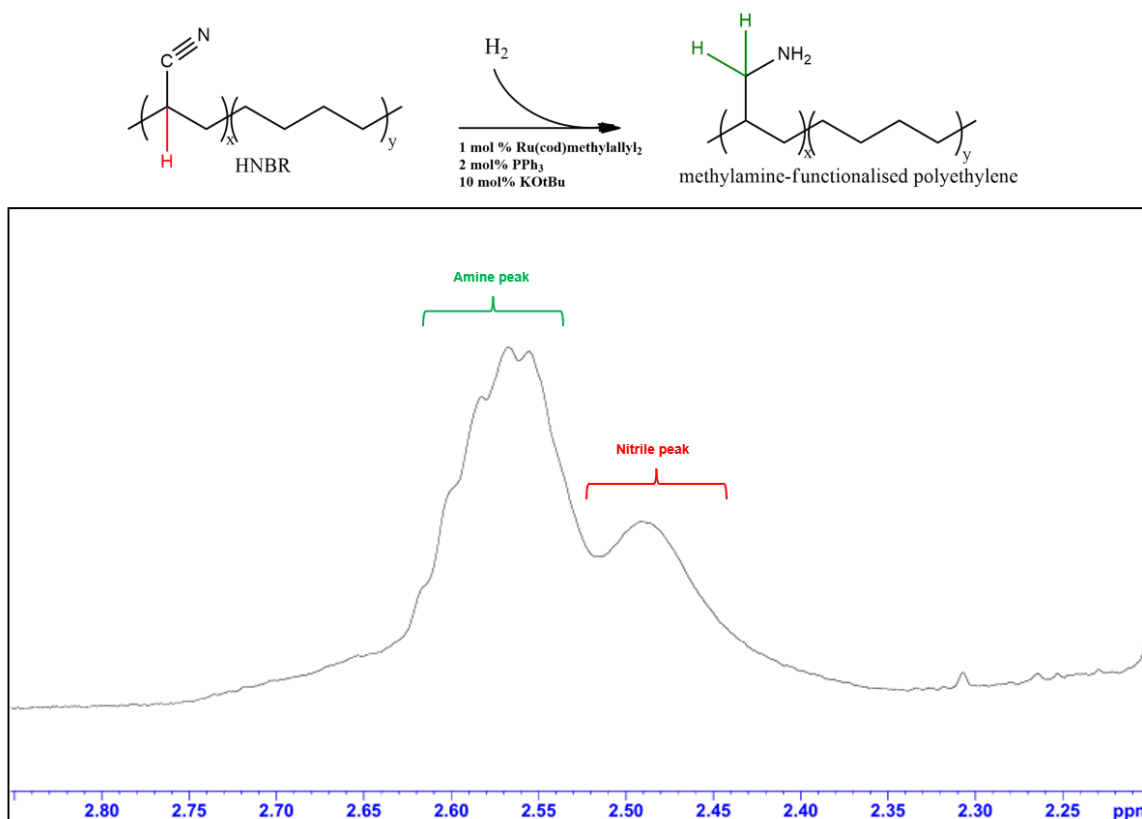


Figure 35: ^1H NMR spectrum displaying pronounced amine and residual nitrile signals, indicating partial hydrogenation of the nitrile functionalities under the applied conditions: 0.25 mmol HNBR, 2 ml THF, 1 mol% Ru(cod)methylallyl₂, 2 mol% PPh₃, 10 mol% KOtBu, 4h, 50 bar H₂, and 120°C.

The NMR spectrum displays signals corresponding to both aminomethyl and nitrile-containing functionalities, further confirming that the hydrogenation reaction proceeded only partially. The simultaneous presence of both signals indicates that a fraction of the nitrile groups remained unconverted under the applied reaction conditions.

These findings are consistent with the fact that hydrogenating polymers is significantly more challenging than small molecules. This is mainly because polymer reactions suffer from severe mass-transfer limitations, higher solution viscosities, and steric hindrance. Therefore, the long chains have limited ability to access the catalyst's active sites and react successfully. Furthermore, long polymer chains can get entangled, which further restricts mobility and blocks reaction sites. To compensate for these limitations, the reaction conditions were adjusted by increasing the reaction time from 4h to 18h and doubling the catalyst loading. The

implementation of these adjustments results in the complete conversion of the nitriles present in HNBR to primary amines, as confirmed by the FTIR and NMR spectra shown in Figures 36 and 37.

The FTIR spectra of the substrate, HNBR (blue), and methylamine-functionalised polyethylene (orange) are presented in Figure 36. Hydrogenation is performed under modified standard conditions for typical polymeric behaviour: 18 hours reaction time, 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, and 20 mol% KOtBu, at 50 Bar and 120 °C. The characteristic absorption bands are labelled in Figure 36 and discussed in the following section.

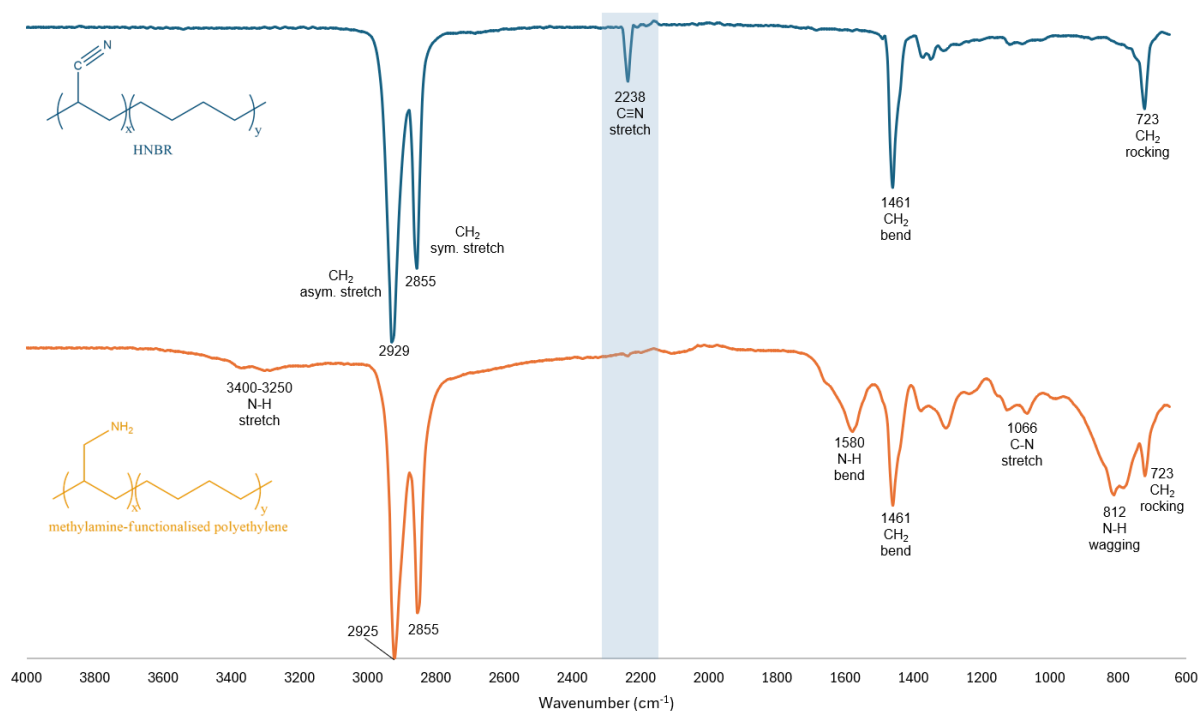


Figure 36: FTIR spectrum indicating near-complete hydrogenation of HNBR, evidenced by the complete disappearance of the nitrile absorption band at 2238 cm⁻¹(C≡N). Reaction conditions: 0.25 mmol HNBR, 2 ml THF, 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, 20 mol% KOtBu, 18h, 50 bar H₂, and 120°C.

The FTIR spectrum shown in Figure 36 indicates complete hydrogenation of the HNBR substrate, as no residual nitrile band is detected after reaction. The resulting polymer is identified as methylamine-functionalised polyethylene. Furthermore, all characteristic amine absorption bands, such as the N-H stretch (3400-3250 cm⁻¹), N-H bend (1650-1580 cm⁻¹) and C-N stretch (1250-1020 cm⁻¹), are present in the product spectrum. The appearance of these bands, combined with the complete disappearance of the nitrile absorption band, provides strong evidence for the successful synthesis of methylamine-functionalised polyethylene. Complete hydrogenation was achieved under modified reaction conditions, consisting of 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, and 20 mol% KOtBu at 50 bar H₂ and 120°C for 18 hours.

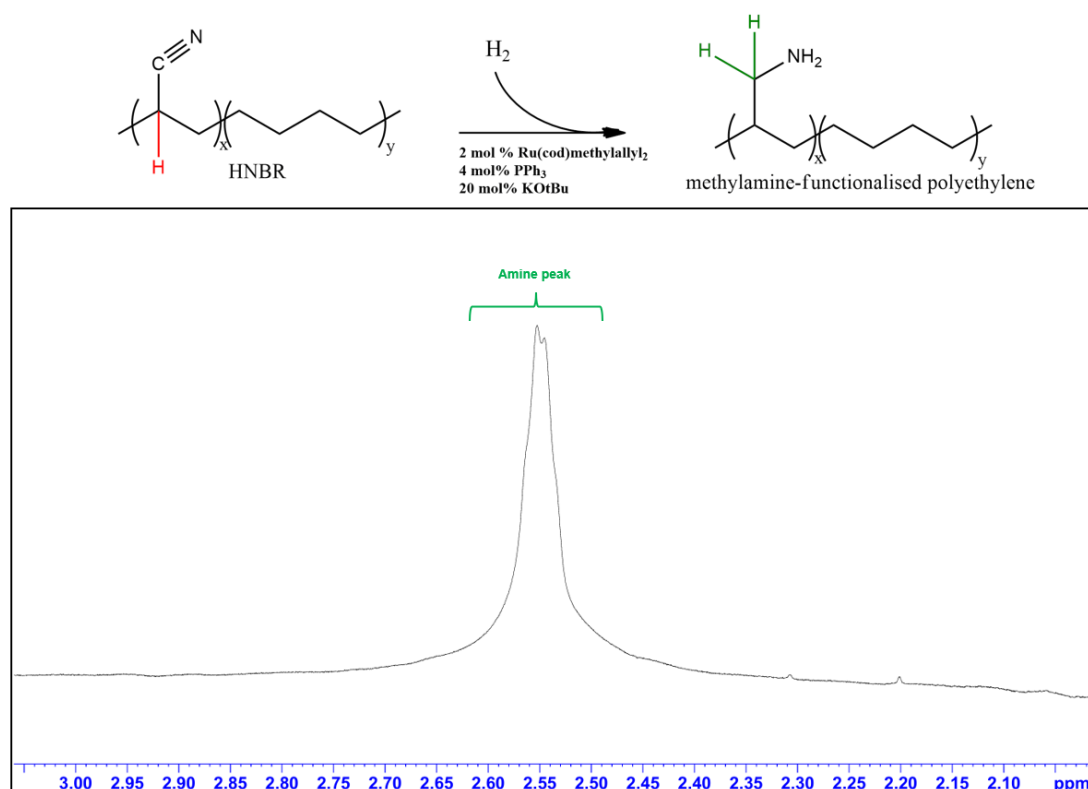


Figure 37: ^1H NMR spectrum showcasing the appearance of the amine product signal and the complete disappearance of the nitrile signal, confirming complete hydrogenation of the nitrile functionalities in HNBR. Reaction conditions: 0.25 mmol HNBR, 2 ml THF, 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, 20 mol% KOtBu, 18h, 50 bar H₂, and 120°C.

Lastly, completion of the hydrogenation reaction was further validated by ^1H NMR analysis, as shown in Figure 37. Comparison of this spectrum with the spectrum presented in Figure 35 reveals the disappearance of the nitrile signals and the exclusive presence of the aminomethyl signal. These observations are consistent with the complete conversion of the nitrile functionalities to primary amines. Therefore, the FTIR spectra shown in Figure 36 and the ^1H NMR spectrum presented in Figure 37 together provide strong evidence for near-quantitative hydrogenation of HNBR to methylamine-functionalised polyethylene. Consequently, the first thesis objective, namely demonstrating that an N-functionalised polyolefin can be synthesised from poly(acrylonitrile-co-butadiene), was successfully achieved under the modified reaction conditions.

5.1.3.2 Solvent screening HNBR hydrogenation

A solvent screening is performed to identify solvents that enable efficient hydrogenation of the polymeric substrate. The success of the hydrogenation is evaluated qualitatively using ATR-FTIR spectroscopy after the product polymers have been precipitated, washed, and dried, as explained in Section 4.3.3. In Figure 38, hydrogenation is considered successful when the nitrile band at 2238 cm^{-1} disappears, and absorption bands associated with primary amines become clearly visible, such as the N-H stretch ($3400\text{--}3250\text{ cm}^{-1}$), N-H bend ($1650\text{--}1500\text{ cm}^{-1}$), N-H wagging ($910\text{--}665\text{ cm}^{-1}$), and C-N stretch ($1250\text{--}1020\text{ cm}^{-1}$). The appearance of these bands indicates the successful formation of methylamines within the polymer structure [101].

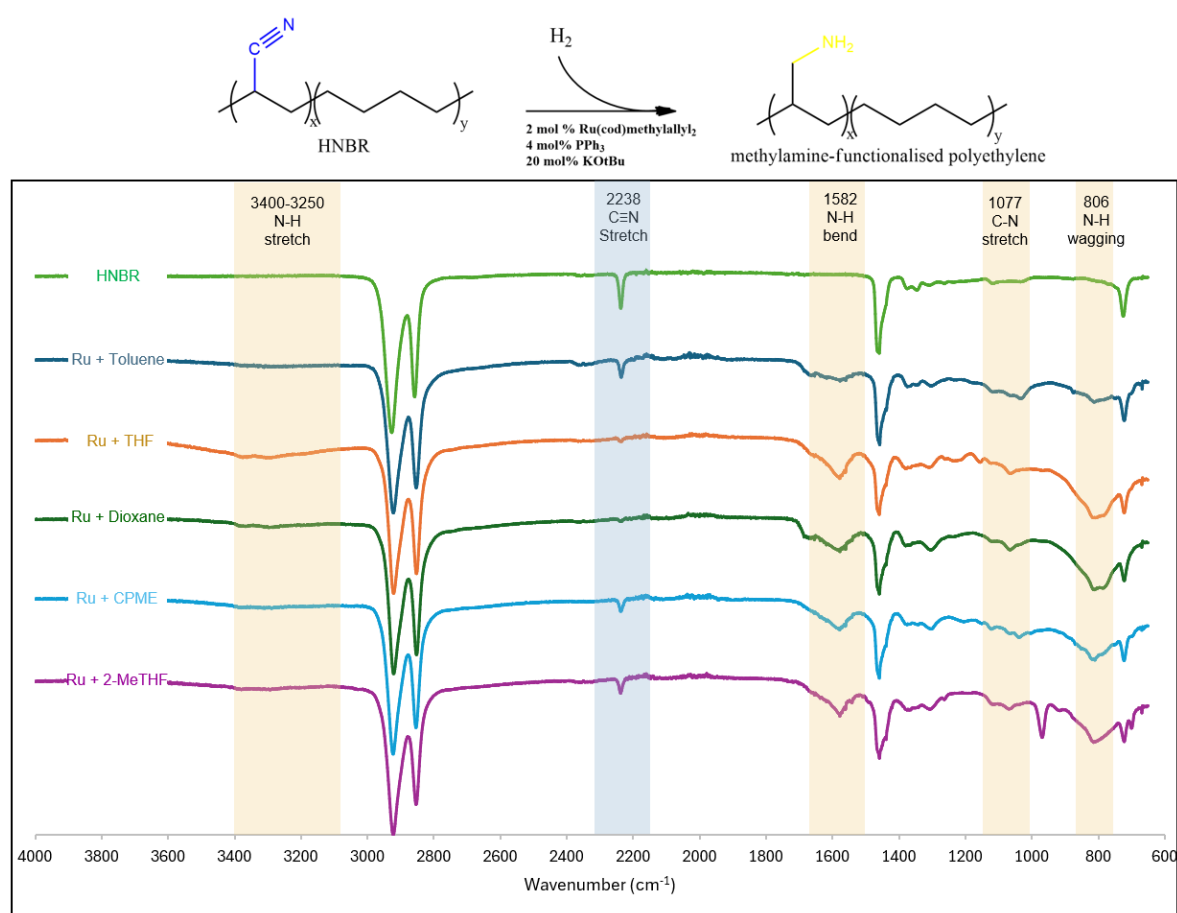


Figure 38: Overlay FTIR spectra of ruthenium-catalysed HNBR hydrogenations performed in different solvents (toluene, THF, dioxane, CPME, and 2-MeTHF), compared with the HNBR substrate. The nitrile absorption band is highlighted in blue, and the amine absorption peaks in yellow. The spectra indicate that THF and dioxane are the most effective solvents. Reaction conditions: 0.25 mmol HNBR, 2 ml solvent, 2 mol% Ru(cod)methylallyl $_2$, 4 mol% PPh_3 , 20 mol% KOtBu, 18h, 50 bar H_2 , and 120°C .

The solvent screening reveals that hydrogenation of HNBR proceeds efficiently and reaches near completion in both THF and dioxane. However, only the reaction in THF results in a homogeneous mixture after hydrogenation. Consequently, THF is selected as the solvent of choice for subsequent experiments because it facilitates both product analysis and further functionalisation of the polymer.

5.1.3.3 Time screening HNBR hydrogenation

To gain further insight into the reaction progress of HNBR hydrogenation, a time-screening study is performed. This investigation provides information on how reaction time influences the extent of nitrile conversion and amine incorporation within the polymer. By comparing FTIR spectra recorded at different reaction times (1, 2, 4, 6, and 18h), the gradual disappearance of the nitrile groups and the concurrent formation of amine-related functionalities can be monitored. These time screening reactions are performed using 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, and 20 mol% KOtBu under 50 Bar H₂ at 120°C.

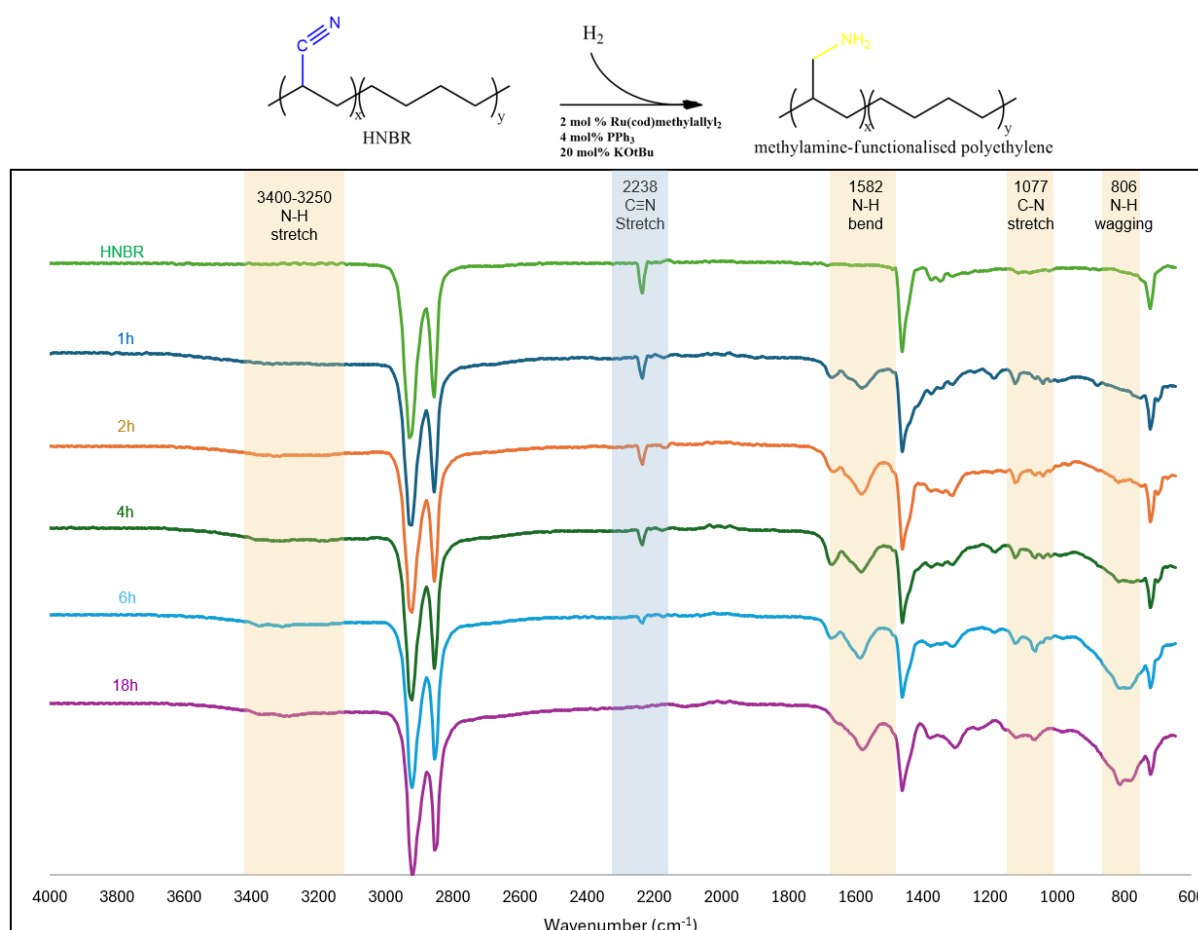


Figure 39: FTIR spectra monitoring the progress of catalytic hydrogenation of nitriles to amines in HNBR over a reaction time (1-18h). The disappearing nitrile peaks are labelled in blue, and the appearing amine peaks are labelled in yellow. Reaction conditions: 0.25 mmol HNBR, 2 ml THF, 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, 20 mol% KOtBu, 50 bar H₂, and 120°C.

The FTIR spectra of Figure 39 demonstrate the gradual disappearance of the characteristic nitrile absorption band at 2238 cm⁻¹ as reaction time increases. After 18 h under the applied reaction conditions, this band is no longer discernible, indicating complete conversion of the nitrile functionalities. Simultaneously, the characteristic amine absorption bands, including the N-H stretch (3400-3250 cm⁻¹), N-H bend (1650-1500 cm⁻¹), N-H wagging (910-665 cm⁻¹), and the C-N stretch (1250-1020 cm⁻¹), gradually appear and increase in intensity as the reaction proceeds [101]. The time-dependent FTIR analysis clearly visualises the progression of the hydrogenation reaction, showing the gradual disappearance of nitrile functionalities and the concurrent formation of aminomethyl groups.

5.1.3.4 Optimisation of Reaction Conditions on the polymeric substrate NBR

Ultimately, the target substrate, poly(acrylonitrile-co-butadiene) (NBR), is hydrogenated directly without prior hydrogenation of olefinic bonds. Unsurprisingly, complete hydrogenation of NBR is more challenging than that of HNBR, because in addition to the nitrile functionalities, the catalyst must also hydrogenate approximately 1.6 olefinic double bonds per nitrile group. To compensate for this increased substrate complexity, the catalyst loadings are further increased to 3 mol% Ru(cod)methylallyl₂, 6 mol% PPh₃, and 20 mol% KOtBu relative to the initial nitrile content of NBR.

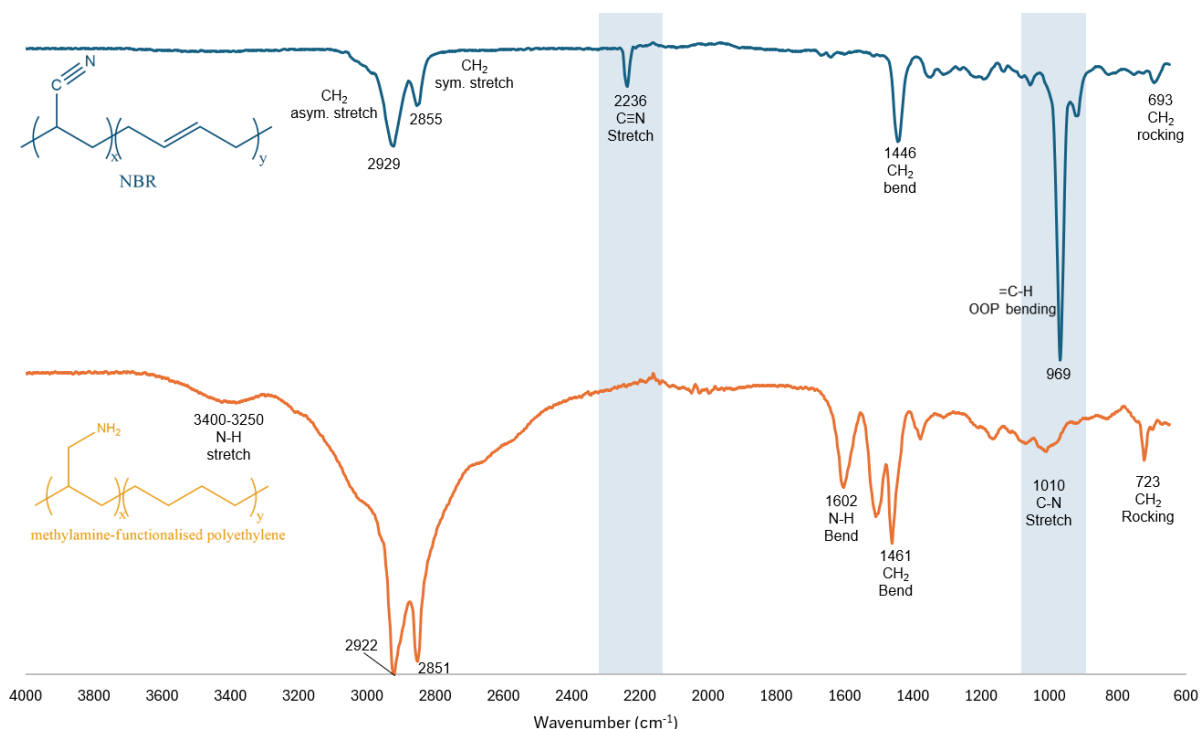


Figure 40: FTIR spectrum indicating near-complete hydrogenation of NBR, due to the disappearance of the nitrile stretch (C≡N) and =C-H out-of-plane bending. Both vibrations are highlighted in blue. Reaction conditions: 0.25 mmol NBR, 2 ml THF, 3 mol% Ru(cod)methylallyl₂, 6 mol% PPh₃, 20 mol% KOtBu, 18h, 50 bar H₂, and 120°C.

The FTIR data shown in Figure 40 indicate that the hydrogenation proceeded to near completion. Both the characteristic nitrile stretch (2236 cm⁻¹) and the out-of-plane =C-H bending (1000-650 cm⁻¹) vibration associated with olefinic double bonds are no longer observed in the spectrum of the resulting methylamine-functionalised polyethylene. This suggests that both the nitriles and olefinic bonds are effectively hydrogenated. Furthermore, the appearance of characteristic primary amine absorption bands, including the N-H stretch (3400-3250 cm⁻¹), N-H bend (1650-1500 cm⁻¹), and N-H wagging (910-665 cm⁻¹), and the C-N stretch (1250-1020 cm⁻¹), provides additional evidence for the successful conversion of NBR into methylamine-functionalised polyethylene using increased catalyst loadings of 3 mol% Ru(cod)methylallyl₂, 6 mol% PPh₃ and 20 mol% KOtBu.

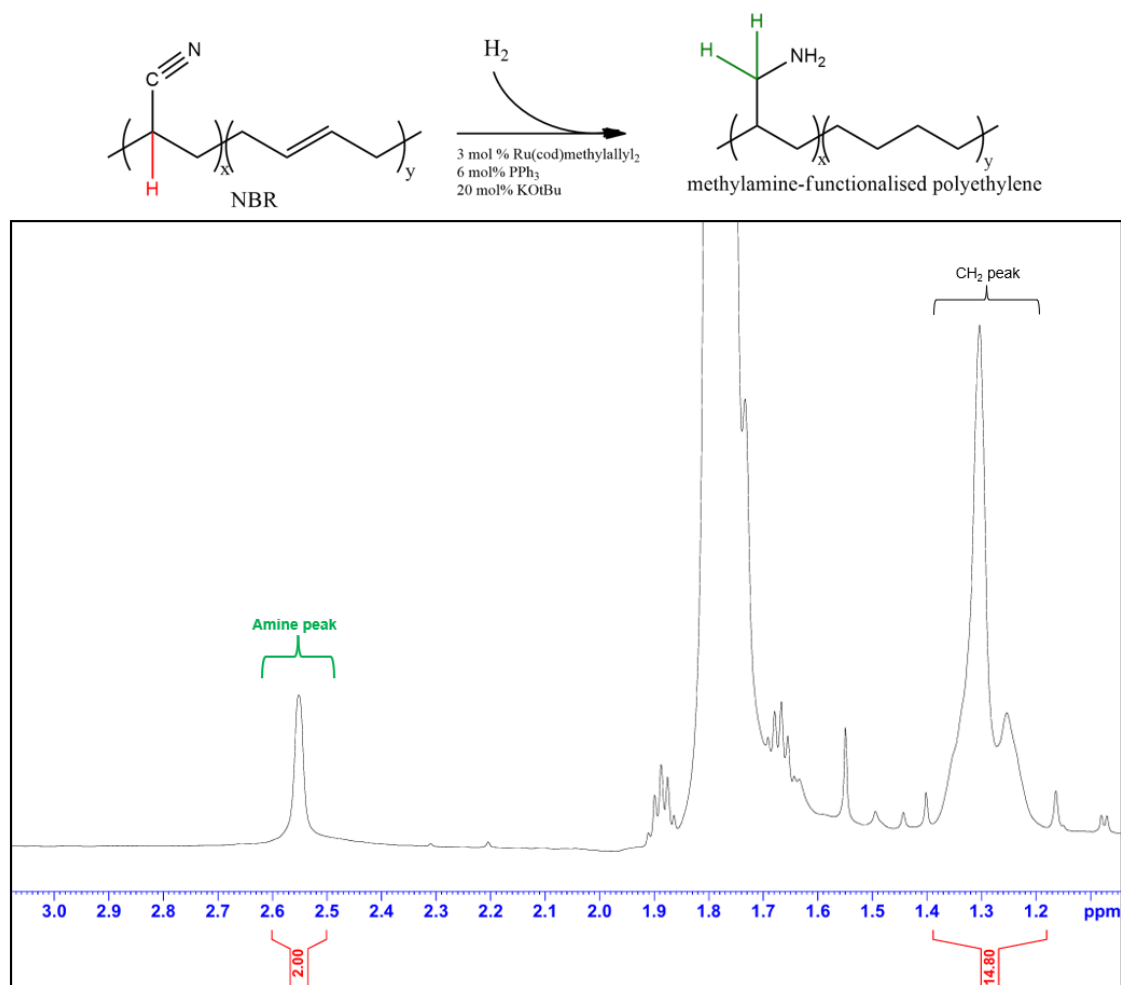


Figure 41: 1H NMR spectrum with signal integration showing the appearance of the amine product signal and the complete disappearance of the nitrile signal, confirming hydrogenation of NBR with a yield >99.9%. Reaction conditions: 0.25 mol NBR, 2 ml THF, 3 mol % $Ru(cod)methylallyl_2$, 6 mol % PPh_3 , 20 mol % $KOtBu$, 18h, 50 bar H_2 , and $120^\circ C$.

$$Yield_{hydrogenation} (\%) = \frac{CH_{2,observed}}{CH_{2,theoretical}} * 100\% = \frac{2.00}{2.00} * 100\% = > 99.9\%$$

The 1H NMR results further support the successful complete hydrogenation of the polymeric substrate. No residual nitrile signal is observed in the spectra, whereas the characteristic aminomethyl signal is present exclusively. In addition, the degree of hydrogenation can be quantified from the ratio of the aminomethyl CH_2 integral (amine peak) to the reference CH_2 integral, as described in Section 4.8.1. Based on this analysis, an aminomethyl incorporation exceeding 99.9% is achieved, confirming essentially quantitative hydrogenation.

The complete hydrogenation of both HNBR and NBR demonstrates the applicability of the ruthenium-based catalytic system for hydrogenating nitriles to primary amines and olefinic bonds to saturated C-C bonds in polymeric substrates. Both materials formed a suitable starting material to go to the desired methylamine-functionalised polyethylene, intermediate product polymer. Direct hydrogenation of NBR requires higher ruthenium catalyst loadings, whereas hydrogenation of HNBR requires an additional step with a $RhCl(PPh_3)_3$ catalyst. The results demonstrate that the first objective of this thesis, namely the synthesis of an N-functionalised polyolefin starting from poly(acrylonitrile-co-butadiene), was successfully achieved.

5.1.3.5 Transfer of Optimised Reaction Conditions to Partially Defunctionalised HNBR

Lastly, defunctionalised HNBR (dHNBR) was hydrogenated to demonstrate that the proposed methodology can also be applied to partially defunctionalised substrates. The FTIR spectra presented in Figure 42 show an overlay of 85% defunctionalised HNBR (blue), corresponding to a functionalisation degree of $\sim 3.5\%$ per C_2H_4 -unit (dHNBR_{3.5}), and the corresponding hydrogenated dHNBR_{3.5} (orange), which can likewise be identified as a methylamine-functionalised polyethylene.

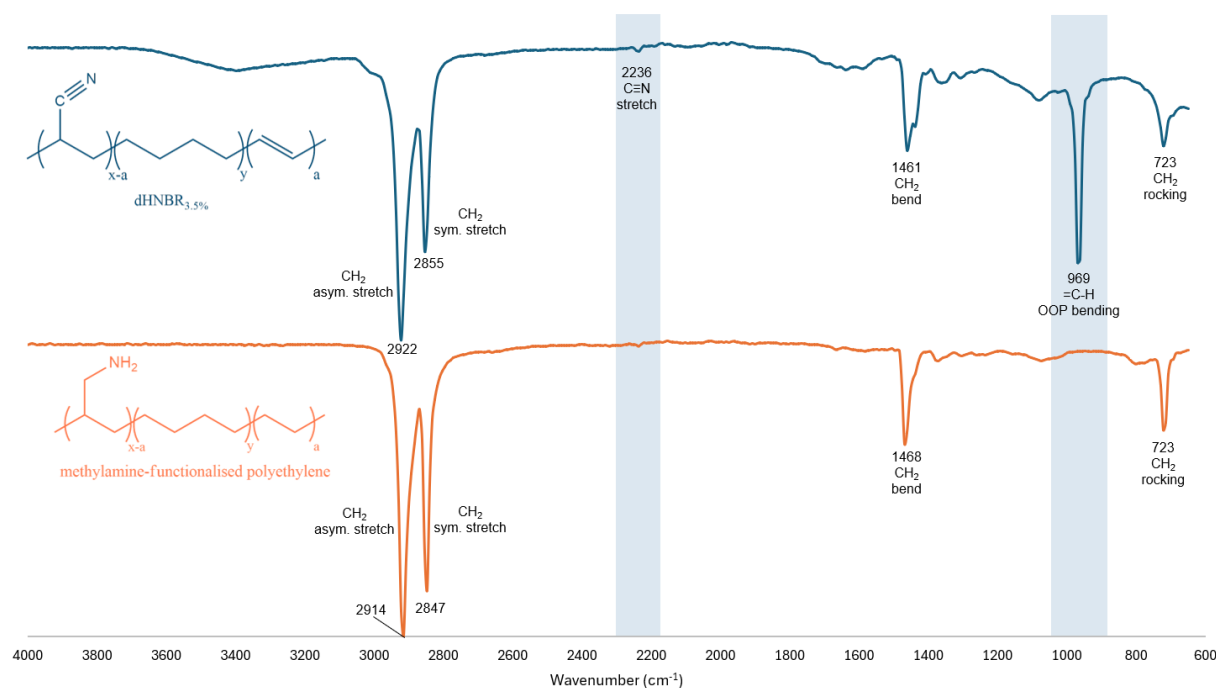


Figure 42: FTIR overlay of dHNBR 85% defunctionalised and the hydrogenated methylamine-functionalised polyethylene signifying complete hydrogenation. Reaction conditions: 2 mol% Ru(cod)methylallyl₂, 4 mol% PPh₃, 20 mol% KOtBu, 18h, 50 bar H₂ and 120°C.

The FTIR results presented in Figure 42 are less conclusive than those obtained for substrates with higher degrees of functionalisation. Because 85% of the nitrile functionalities are removed prior to hydrogenation, the disappearance of the nitrile peak is less pronounced than in previous reactions. Moreover, the low concentration of nitrile groups results in a correspondingly low concentration of amine functionalities after hydrogenation, making the characteristic amine absorption bands more difficult to observe. Nevertheless, the disappearance of the olefinic peak of the =C-H out-of-plane bending ($1000\text{--}650\text{ cm}^{-1}$) indicates successful hydrogenation of the double bonds. Although the conversion of the remaining nitrile functionalities cannot be directly verified by FTIR, it is assumed that the nitriles have been converted to primary amines. This assumption can be verified indirectly by subsequent functionalisation reactions, as nitriles are unreactive towards acylation or phthalimide formation, whereas primary amines will readily undergo these transformations. Consequently, the appearance of new absorption bands in the FTIR spectrum following amine functionalisation provides additional evidence that the preceding hydrogenation was successful.

5.2 Synthesis of Amide-Functionalised Polyolefins by Acylation

The hydrogenation reaction yields methylamine-functionalised polyethylene or a partially defunctionalised analogue, both of which contain pendant primary amine groups ideal for further functionalisation. In this work, these amine groups are acylated to introduce amide functionalities along the polymer backbone. This transformation is performed to modify the material's chemical and physical properties. The following section presents the spectroscopic evidence supporting successful acylation. The primary objective of this section is to demonstrate that the intermediate methylamine-functionalised polyethylene can be further functionalised into an amide-functionalised polymer.

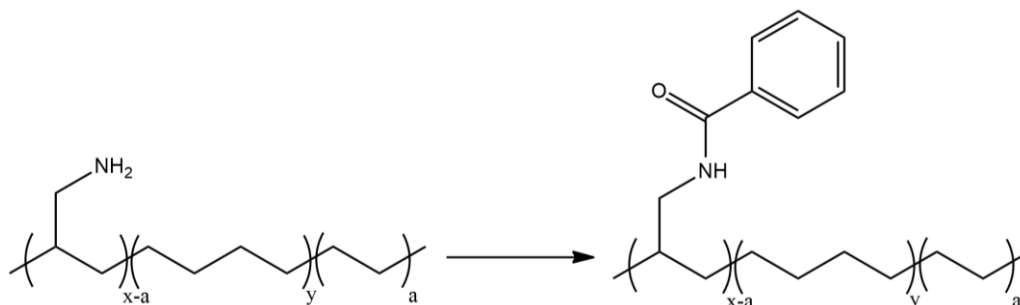


Figure 43: Schematic representation of the objective of the acylation reaction.

5.2.1 Acylation of hexylamine

Firstly, the acylation reaction is thoroughly investigated using hexylamine as a model compound, as it resembles the pendant amine groups present on methylamine-functionalised polyethylene. The acylation reactions are performed as described in Section 4.4.1 and analysed by NMR spectroscopy as outlined in Section 4.8. The first acylating reaction examined is the reaction of hexylamine with benzoyl chloride to yield N-hexylbenzamide, as shown in Figure 44. Benzoyl chloride is selected as the acylating reagent due to its widespread and high reactivity. This reactivity stems from its nature as an acyl halide, in which chloride acts as an excellent leaving group. In addition, Et_3N is added as an acid scavenger to neutralise the HCl formed as a byproduct.

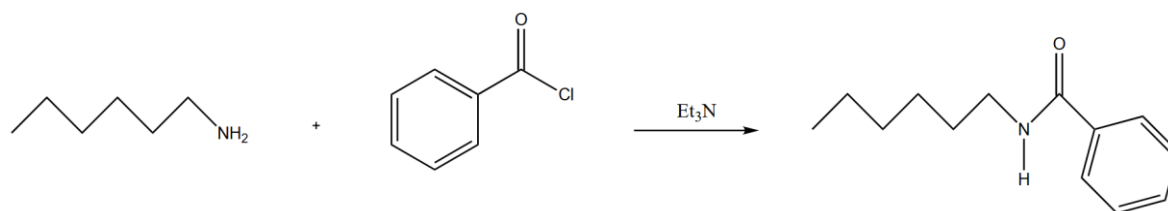


Figure 44: Model reaction for the investigation of the acylation reaction.

The NMR spectrum shown in Figure 45 indicates successful acylation, as all characteristic signals corresponding to the product, N-hexylbenzamide, can be clearly assigned. The remaining signals originate from the solvent THF, the residual CHCl_3 signal from the deuterated solvent, water used to quench the reaction, and the $\text{Et}_3\text{N} \cdot \text{HCl}$ salt formed upon neutralisation of the generated HCl gas. The absence of significant unidentified signals strongly suggests that the reaction proceeded with near-complete conversion. This conclusion is validated in Figure 46, where 1,3-dimethoxybenzene is used as an internal standard to quantitatively determine the reaction yield.

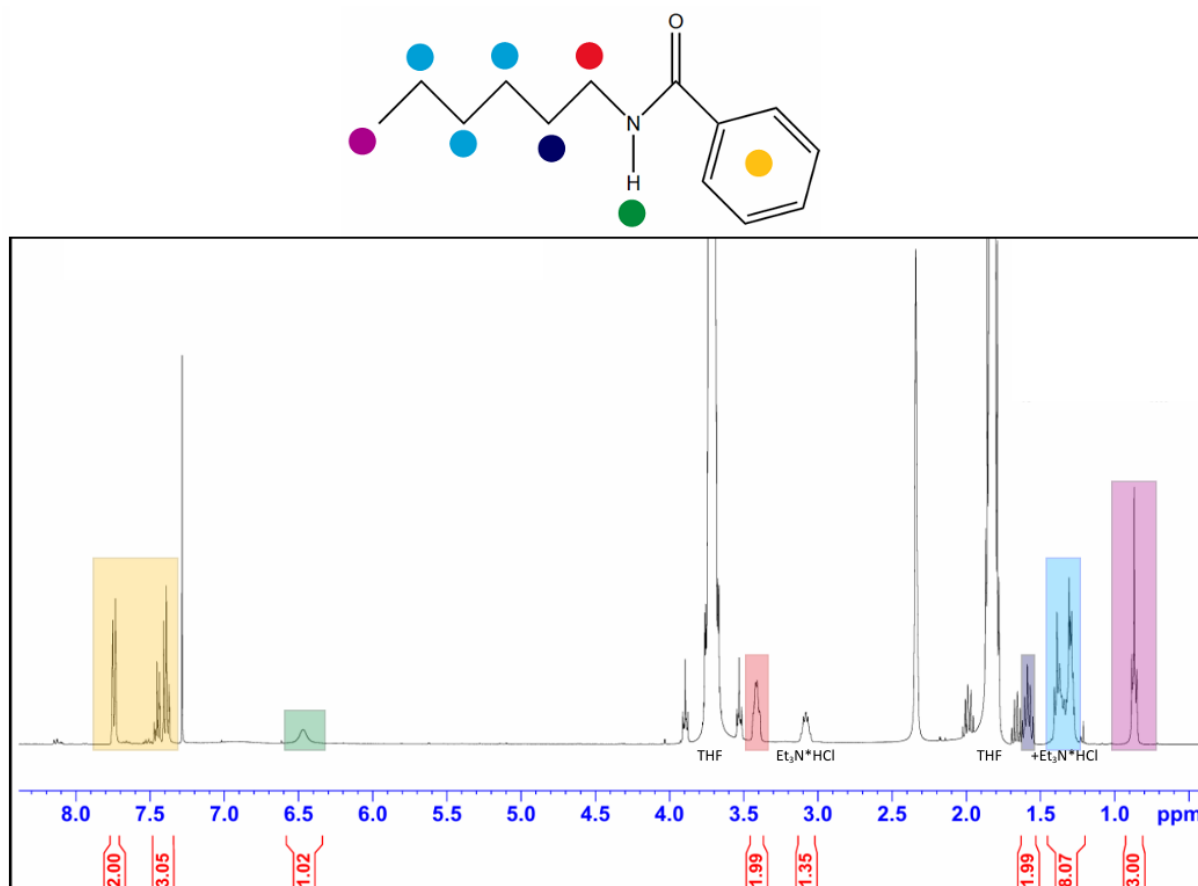


Figure 45: ^1H NMR spectrum of N-hexylbenzamide with peak assignment and signal integration confirming near complete acylation of hexylamine with benzoyl chloride. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 1 ml THF, 2h, 30°C , and 600 rpm.

A closer inspection of the ^1H NMR spectrum shown in Figure 45 reveals a signal at 3.08 ppm, assigned to the CH_2 groups of $\text{Et}_3\text{N}\cdot\text{HCl}$. The relatively low integration of this signal is likely due to the salt's poor solubility in THF. Furthermore, the combined integration of the overlapping $\text{Et}_3\text{N}\cdot\text{HCl}$ CH_3 and N-hexylbenzamide signals closely matches the experimentally observed value, supporting the proposed peak assignments.

5.2.1.1 Solvent screening

As a first step, a solvent screening was conducted to identify solvents in which the acylation reaction proceeds successfully. The reaction afforded near quantitative yields in all solvents tested, which are listed below. These are all aprotic solvents, whereas protic solvents such as water or alcohols can react with benzoyl chloride via solvolysis, forming benzoic acid. Therefore, anhydrous solvents are used whenever possible to minimise such side reactions.

- THF (dry)
- DCM (dry)
- Toluene (dry)
- PhCl (dry)
- Acetonitrile (dry)
- Dioxane (dry)
- Dichlorobenzene (dry)
- Benzonitrile
- Ethyl acetate

- Tetrachloroethane
- CPME (dry)

The *N*-hexylbenzamide yields were determined as illustrated with the ^1H NMR spectrum shown in Figure 46. In this spectrum, the signals used for quantitative analysis of the internal standard, 1,3-dimethoxybenzene, and the product, *N*-hexylbenzamide, are highlighted in the grey and red boxes, respectively. The integrals of the signal at 6.5 ppm, corresponding to the three aromatic protons ortho to the methoxy groups of the internal standard (grey), and of the signal at 3.4 ppm, corresponding to the $\alpha\text{-CH}_2$ protons of *N*-hexylbenzamide (red), were used in the calculations.

The relative molar amount of *N*-hexylbenzamide compared to 1,3-dimethoxybenzene (DMB) can be calculated as follows:

$$\frac{n_{N\text{-hexylbenzamide}}}{n_{DMB}} = \frac{\text{area}(3.4 \text{ ppm}) / 2 \text{ H}}{\text{area}(6.5 \text{ ppm}) / 3 \text{ H}} = \frac{0.99}{1.06} = 0.94$$

From the 1 ml reaction mixture containing 0.25 mmol hexylamine and benzoyl chloride, 950 μl was used for NMR analysis. The initial amount of both substrates is therefore $0.95 \times 0.25 \text{ mmol} = 0.2375 \text{ mmol}$. With 0.25 mmol of 1,3-dimethoxybenzene added, the absolute yield can be calculated as follows:

$$\text{Yield}_{N\text{-hexylbenzamide}}(\%) = \frac{n_{N\text{-hexylbenzamide}}}{n_{\text{substrates},0}} * 100\% = \frac{0.94 * n_{DMB}}{n_{\text{substrates},0}} * 100\% = 99\%$$

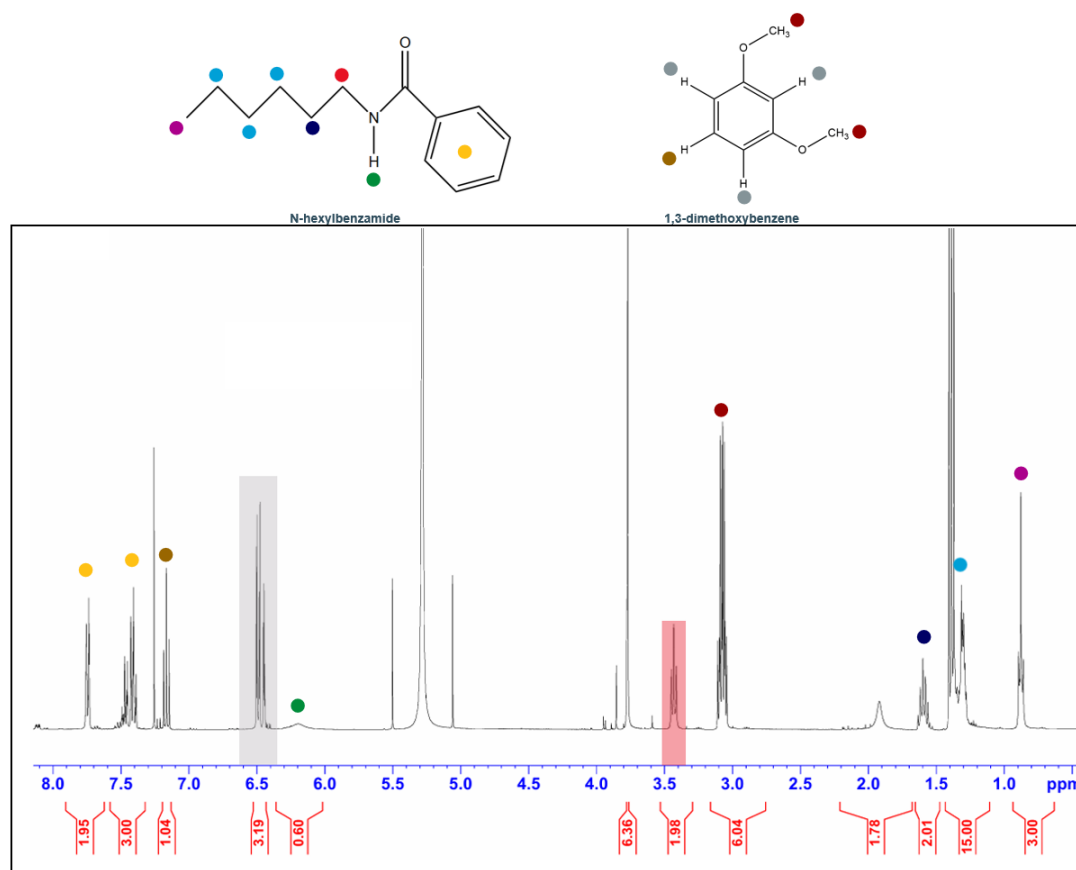


Figure 46: Illustrative ^1H NMR spectrum of acylation reaction in DCM with 1,3-dimethoxybenzene as internal standard, giving an acylation yield of 99%. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 1ml THF, 2h, 30°C , and 600 rpm.

5.2.1.2 Et₃N as HCl scavenger and ammonium salt formation

The role of Et₃N as a hydrochloric acid scavenger in the acylation reaction was investigated using a component-omission experiment. The acylation reaction is performed as described in Section 4.4.1, but in the absence of Et₃N. In the resulting ¹H NMR spectrum, signals corresponding to the product are highlighted in yellow, those corresponding to the reagents in blue, and overlapping product and reagent signals in green.

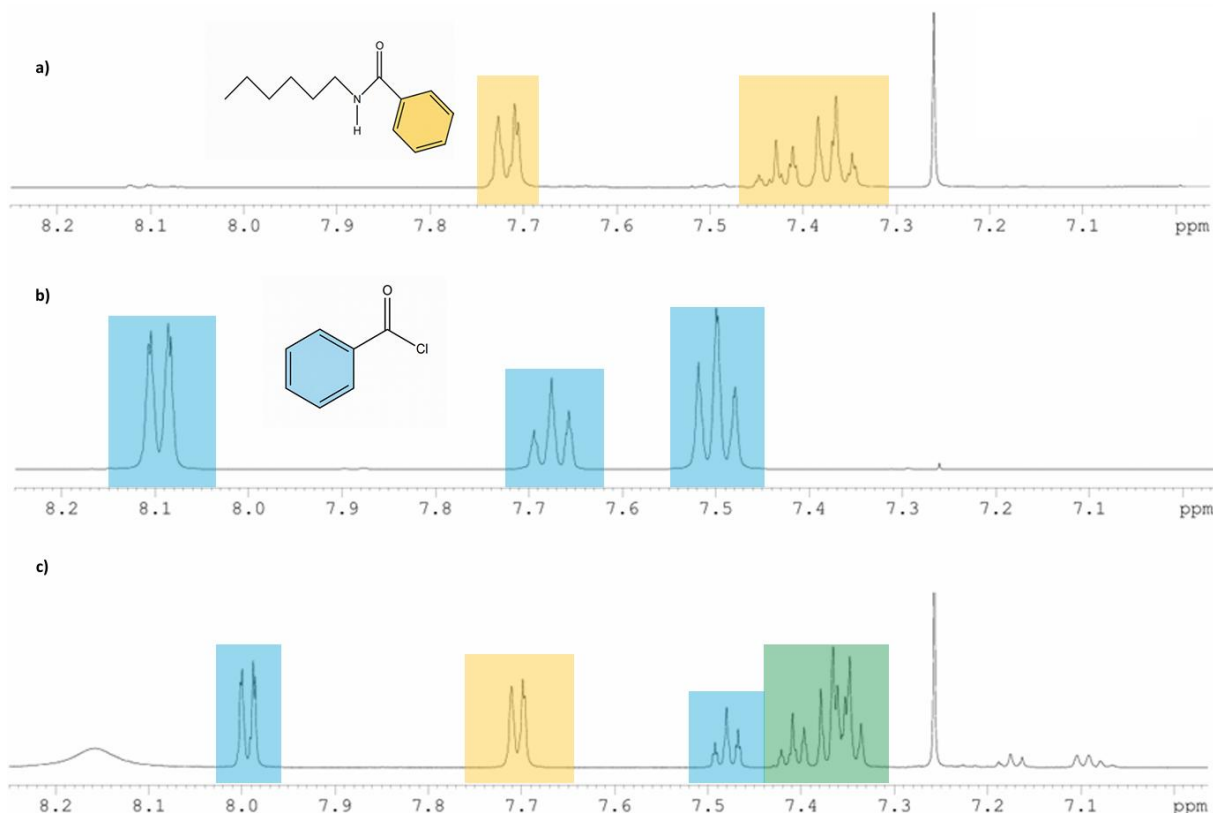


Figure 47: ¹H NMR of the aromatic region for the acylation performed in the absence of a hydrochloric acid scavenger, showing HCl inhibition. a) Reference spectrum of N-hexylbenzamide, b) reference spectrum of benzoyl chloride, c) reaction mixture obtained in the absence of Et₃N. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 1 ml THF, 2h, 30°C, and 600 rpm.

The acylation reactions in Figure 47 are performed in the absence of an HCl scavenger and reveal NMR signals in the aromatic region corresponding to both the product (N-hexylbenzamide) and starting material (benzoyl chloride). Remarkably, the two doublets in the product spectrum, each corresponding to two aromatic protons, exhibit approximately identical integration values, indicating an amide yield of approximately 50%.

These observations suggest that the acylation reaction initially proceeds successfully. However, the HCl generated during the reaction is not removed from the reaction mixture. The released HCl protonates the remaining hexylamine, forming its respective ammonium salt. In this protonated form, the nitrogen lone pair is no longer available for nucleophilic attack on the carbonyl carbon of benzoyl chloride, thereby inhibiting further acylation. As a result, the reaction stalls at approximately 50% conversion, while the remaining hexylamine is converted into its ammonium salt. When the amines are protonated prior to reaction by the addition of an equimolar amount of HCl, the amide yield decreases further to approximately 31% (Appendix 3: Additional NMR spectra). Nevertheless, some amide formation occurs because the

protonation equilibrium maintains a small amount of free amine in solution, which can subsequently undergo irreversible acylation to yield the corresponding amide.

Lastly, the possibility of storing the amine as an ammonium salt and subsequently regenerating the free amine in situ by adding Et_3N was investigated. This approach is attractive because amines are often volatile, air-sensitive, and associated with fishy odours, whereas their corresponding ammonium salts are non-volatile, less air-sensitive, and odourless [111]. In this experiment, hexylamine is first converted to its ammonium salt by adding an equimolar amount of HCl . Subsequently, a twofold excess of Et_3N relative to the amines is added to the acylation reaction to deprotonate the ammonium salt and scavenge the HCl formed during the reaction with benzoyl chloride. The results of this experiment show near quantitative yields of N-hexylbenzamide, thereby demonstrating the effectiveness of in situ deprotonation and acid scavenging (Appendix 3: Additional NMR spectra).

These findings demonstrate that the presence of a base is essential for preventing the formation of inactive ammonium salts and for driving the acylation reaction towards high conversions. Furthermore, the results highlight the feasibility of storing amines as stable ammonium salts, which can subsequently be regenerated when required for subsequent functionalisation.

5.2.1.3 Time screening

To evaluate the optimal reaction time and gain more insight into the kinetics of the acylation reaction, a time-screening experiment is performed.

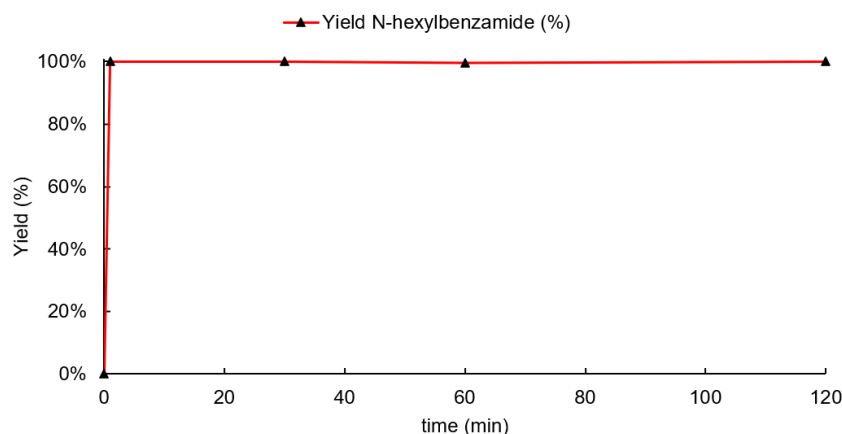


Figure 48: Yield of N-hexylbenzamide as a function of reaction time during acylation with benzoyl chloride, indicating an almost instantaneous reaction. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 1 ml THF, 30°C, and 600 rpm.

As indicated by the time screening experiment presented in Figure 48, the acylation reaction proceeds extremely rapidly. Near-complete conversion is already achieved at the first sampling point after 1 minute. The high reaction rate can be attributed to the nature of the acylating agent. Acyl halides, such as benzoyl chloride, are highly reactive due to the electron-withdrawing chloride substituent, which acts as an excellent leaving group. In contrast, other acylating agents, such as phthalic anhydride or succinic anhydride, are expected to react more slowly because of their lower intrinsic reactivity.

5.2.1.4 Inhibition studies

As the goal of this study is to perform a one-pot hydrogenation-functionalisation that avoids the difficult isolation and purification of the hydrogenated dHNBR, the influence of the hydrogenation catalyst on the acylation of hexylamine is investigated. Following hydrogenation, the reaction mixture contains the ruthenium catalyst precursor, phosphine ligand, and K^tBu base, which are not consumed during the reaction. Therefore, it is investigated whether Ru(cod)methylallyl₂, PPh₃, or K^tBu inhibits the acylation reaction.

To investigate this, the acylation reaction was performed in the presence of varying concentrations of Ru(cod)methylallyl₂ (0.2 mol% - 0.5 mol% - 1 mol % - 2 mol %) together with PPh₃ (0.4 mol% - 1 mol% - 2 mol % - 4 mol %) and various concentrations of K^tBu (2.5 mol% - 5 mol% - 10 mol % - 20 mol %). The resulting ¹H NMR spectra of this inhibition study are provided in Appendix 3: Additional NMR spectra.

In all cases, near-complete conversion was obtained, and no significant effect on the reaction outcome was observed. These results demonstrate that neither the individual components of the hydrogenation catalytic system nor their combination inhibits the acylation reaction under the conditions investigated.

5.2.1.5 Acylation as a follow-up reaction

As a next stage, the acylation reaction is evaluated as a follow-up reaction on the model compound. So, the substrate, hexanenitrile, is first hydrogenated to hexylamine, then 1.5 equivalents of Et₃N and 1 equivalent of benzoyl chloride are added to the same reaction mixture to perform the subsequent acylation to N-hexylbenzamide.

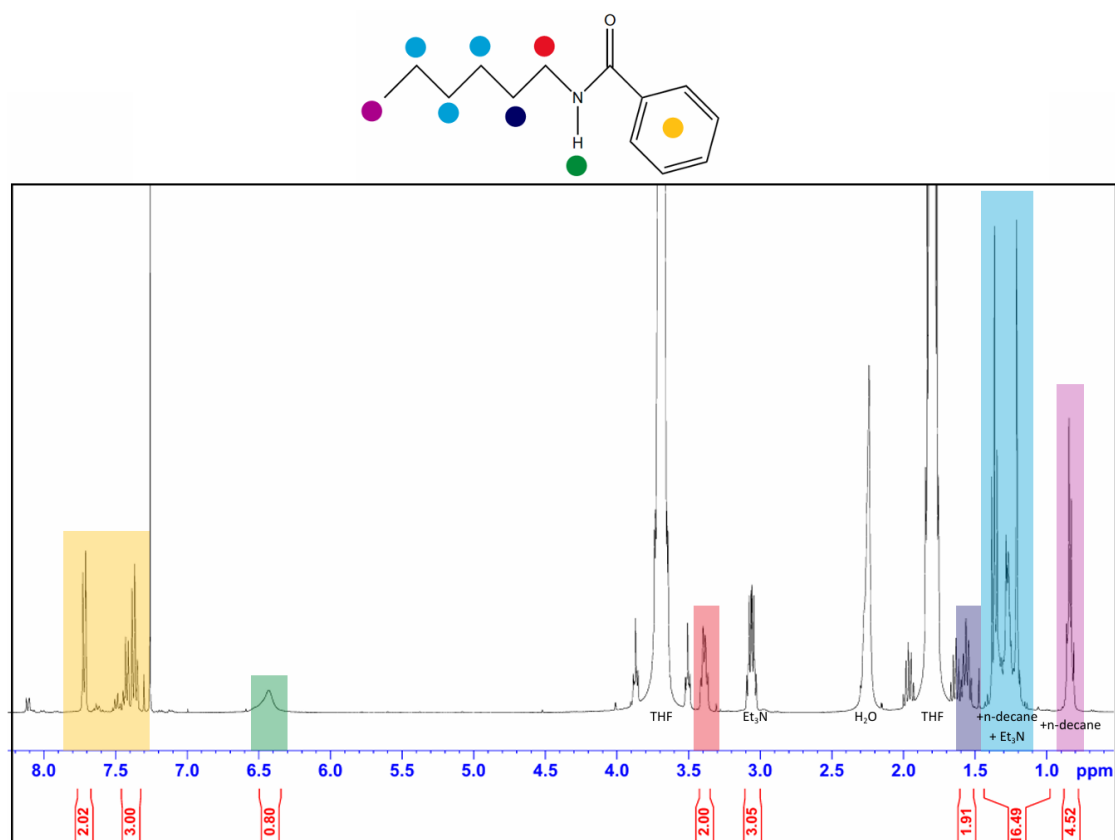


Figure 49: Successful follow-up acylation reaction with benzoyl chloride, confirmed by the formation of characteristic product signals in the ¹H NMR. Reaction conditions: 0.4 mmol substrate, 0.4 mmol benzoyl chloride, 0.6 mmol Et₃N, 2 ml THF, 2h, 30°C, and 600 rpm.

The results of the follow-up reaction once again demonstrate successful acylation under standard conditions (2 hours, 600 rpm, 30°C). All characteristic signals of N-hexylbenzamide can be assigned in the ^1H NMR spectrum obtained. In addition to the signals originating from THF, CHCl_3 , and the $\text{Et}_3\text{N}\cdot\text{HCl}$, two signals corresponding to n-decane are also observed. The presence of n-decane is expected as it was added as an internal standard during the preceding hydrogenation step for gas chromatography analysis. This slightly complicates the interpretation of the integration values. The CH_3 peak at 0.84 ppm contains contributions from the terminal CH_3 groups of both N-hexylbenzamide (0.4 mmol) and n-decane (0.1 mmol). Likewise, the broad signal between 1-1.4 ppm contains contributions from CH_2 groups of N-hexylbenzamide, n-decane, and $\text{Et}_3\text{N}\cdot\text{HCl}$. The experimentally observed integration values are in good agreement with these expected contributions. Together with the successful assignment of all characteristic product signals, these results provide strong evidence that the follow-up acylation reaction proceeded successfully.

5.2.2 One-pot hydrogenation-acylation of (d)HNBR

Following the successful acylation of the model compounds, the methodology is subsequently applied to the intermediate polymer substrate, methylamine-functionalised polyethylene. These experiments aim to evaluate whether the optimised acylation conditions can be translated to the polymer system while maintaining high conversion and efficient functionalisation. This section describes the acylation of methylamine-functionalised polyethylene and its partially defunctionalised analogue in a one-pot procedure, in which the hydrogenation and acylation are performed sequentially without intermediate work-up. This increases operational simplicity and time efficiency while reducing waste generation, solvent consumption, and energy demand, thereby improving both the sustainability and industrial applicability of the developed methodology. Different acylating agents, including benzoyl chloride, phthalic anhydride, and succinic anhydride, are used as proof of concept to demonstrate that a wide range of N-functionalised polyolefins are available.

5.2.2.1 Acylation with benzoyl chloride

FTIR spectroscopy of the HNBR substrate (blue, Figure 50), methylamine-functionalised intermediate (orange, Figure 50) and acylated polymer (green, Figure 50) indicate that the acylation reaction proceeded successfully after 2 hours at 30°C. As a first step, the disappearance of the nitrile absorption band at around 2236 cm^{-1} and the appearance of characteristic amine absorption bands were evaluated. Typical amine vibrations include the N-H stretch between $3400\text{--}3250\text{ cm}^{-1}$, the N-H bend between $1650\text{--}1580\text{ cm}^{-1}$, and the C-N stretch between $1250\text{--}1020\text{ cm}^{-1}$ [101]. These characteristic amine bands are clearly visible in the spectrum of the intermediate polymer, confirming successful hydrogenation.

The green spectrum in Figure 50 corresponds to the final amide-functionalised polymer. The observed absorption bands match the expected vibrations of the amide-containing polymer structure shown in Figure 50. Characteristic absorptions of this polymer include the N-H stretch between $3400\text{--}3250\text{ cm}^{-1}$, the amide I band ($1700\text{--}1600\text{ cm}^{-1}$) primarily associated with C=O stretching, and the amide II band ($1600\text{--}1500\text{ cm}^{-1}$) arising mainly from N-H bending. Additionally, the amide III band can be observed between $1310\text{--}1175\text{ cm}^{-1}$, predominantly due to C-N stretching [112]. All characteristic absorption bands are labelled and match the expected vibrational modes. Furthermore, the FTIR spectral features closely resemble those reported for amide-functionalised polymers in literature [17]. Therefore, the FTIR peak labelling

and its consistency with literature data provide convincing evidence that hydrogenation and subsequent functionalisation are successfully performed on the polymeric substrate under standard acylation conditions.

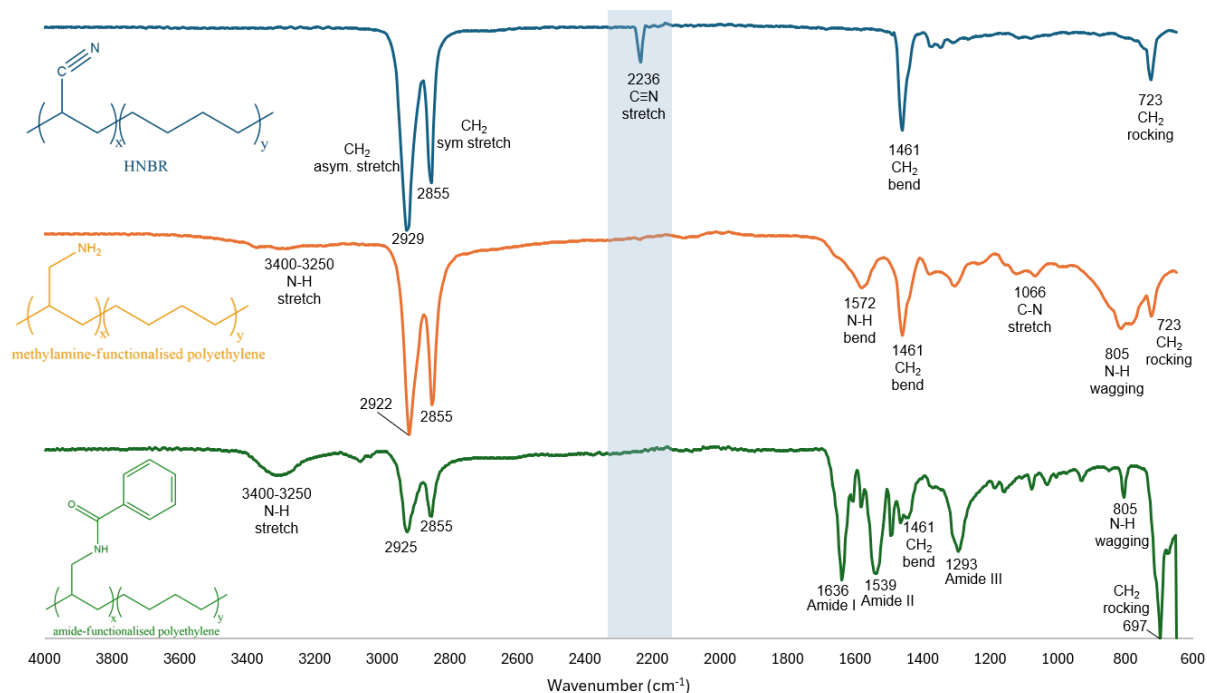


Figure 50: FTIR spectra of HNBR, amine- and amide-functionalised polyethylene, showing chemical transformation during hydrogenation and subsequent acylation. The disappearance of the nitrile stretch ($\text{C}\equiv\text{N}$, 2236 cm^{-1}) confirms hydrogenation, while the appearance of N-H vibrations and amide bands I-III confirm successful amine and amide functionalisation.

The success of the acylation reaction is further evaluated by ^1H NMR spectroscopy, as shown in Figure 51. The signals observed for the model compound N-hexylbenzamide closely correspond to those present in the spectrum of the amide-functionalised polyethylene shown at the bottom of the figure. Furthermore, no significant unidentified signals or signals attributable to residual benzoyl chloride or unreacted hexylamine are detected in either spectrum, indicating near quantitative acylation yields. Together with the FTIR results discussed above, these observations provide strong evidence that the amine functionalities present in methylamine functionalised polyethylene can be efficiently acylated under standard reaction conditions. Near-complete conversion is achieved after a 2h reaction at 30°C using 1 equivalent of benzoyl chloride and 1.5 equivalents of Et_3N relative to the initial amount of functional groups.

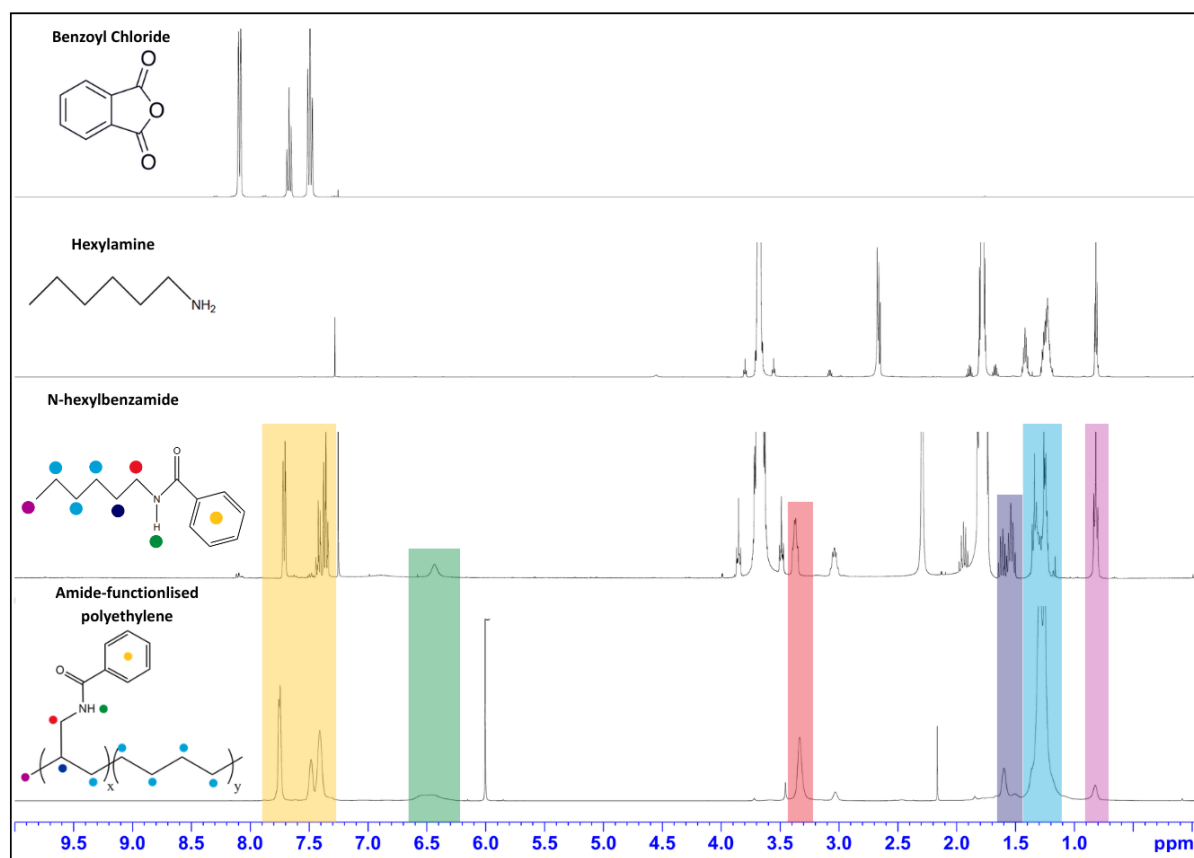


Figure 51: ^1H NMR spectra of benzoyl chloride, hexylamine, N-hexylbenzamide, and amide-functionalised polyethylene, indicating successful acylation, as confirmed by the formation of characteristic product signals. Reaction conditions: 0.25 mmol substrate, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 2 ml THF, 2h, 30°C, and 600 rpm.

5.2.2.2 Acylation with Succinic anhydride

The second acylating agent tested in this research is succinic anhydride. This compound is a cyclic anhydride that shows high reactivity towards nucleophilic amines and alcohols. Reaction with an amine-functionalised substrate results in the formation of an amide bond while simultaneously introducing a terminal carboxylic acid functionality into the substrate. This transformation was carried out to modulate the material's chemical and physical properties. The following section presents the spectroscopic evidence supporting successful acylation with succinic anhydride, with the main objective demonstrating that the intermediate methylamine functionalised polyethylene can be converted into a broad range of amides.

As a first step, hexylamine is acylated with an equimolar amount of succinic anhydride to form N-hexylsuccinamic acid. This acylation is performed under the same standard conditions as used for the acylation with benzoyl chloride, namely 2 hours at 30°C. The resulting ^1H NMR spectrum is shown in Figure 52. All characteristic signals corresponding to the product, N-hexylsuccinamic acid, can be assigned and are consistent with the observed peak integration values. Furthermore, no significant signals attributable to unreacted reagents or byproducts are observed. These results provide strong evidence that the acylation proceeded with near-complete conversion under the applied reaction conditions.

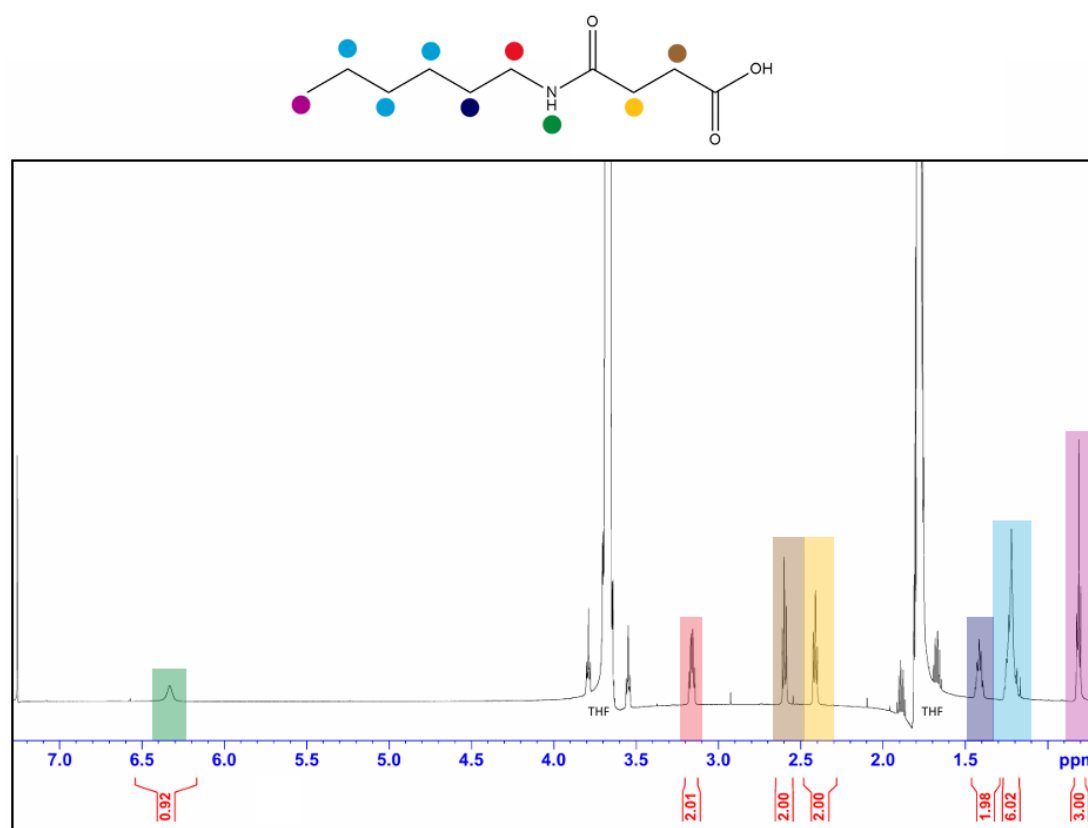


Figure 52: ^1H NMR spectrum of N-hexylsuccinamic acid with peak assignment and signal integration of product signals confirming successful acylation of hexylamine with succinic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol succinic anhydride, 1 ml THF, 2h, 30°C, and 600 rpm.

The FTIR data provide strong additional evidence for a successful synthesis of the amide-functionalised polyethylene with succinic anhydride. The obtained spectrum is assessed for the presence of characteristic absorption bands associated with the expected product polymer. Typical expected vibrations of the product polymer include the N-H stretch ($3400\text{--}3250\text{ cm}^{-1}$), N-H wagging ($910\text{--}665\text{ cm}^{-1}$), the carboxylic C=O stretch ($1710\text{--}1690\text{ cm}^{-1}$), the three amide bands ($1700\text{--}1600\text{ cm}^{-1}$, $1600\text{--}1500\text{ cm}^{-1}$, $1310\text{--}1175\text{ cm}^{-1}$), and the C-N stretch ($1250\text{--}1020\text{ cm}^{-1}$) [101]. All these characteristic absorption bands can be assigned in the FTIR spectrum shown in Figure 53, supporting the proposed product polymer structure.

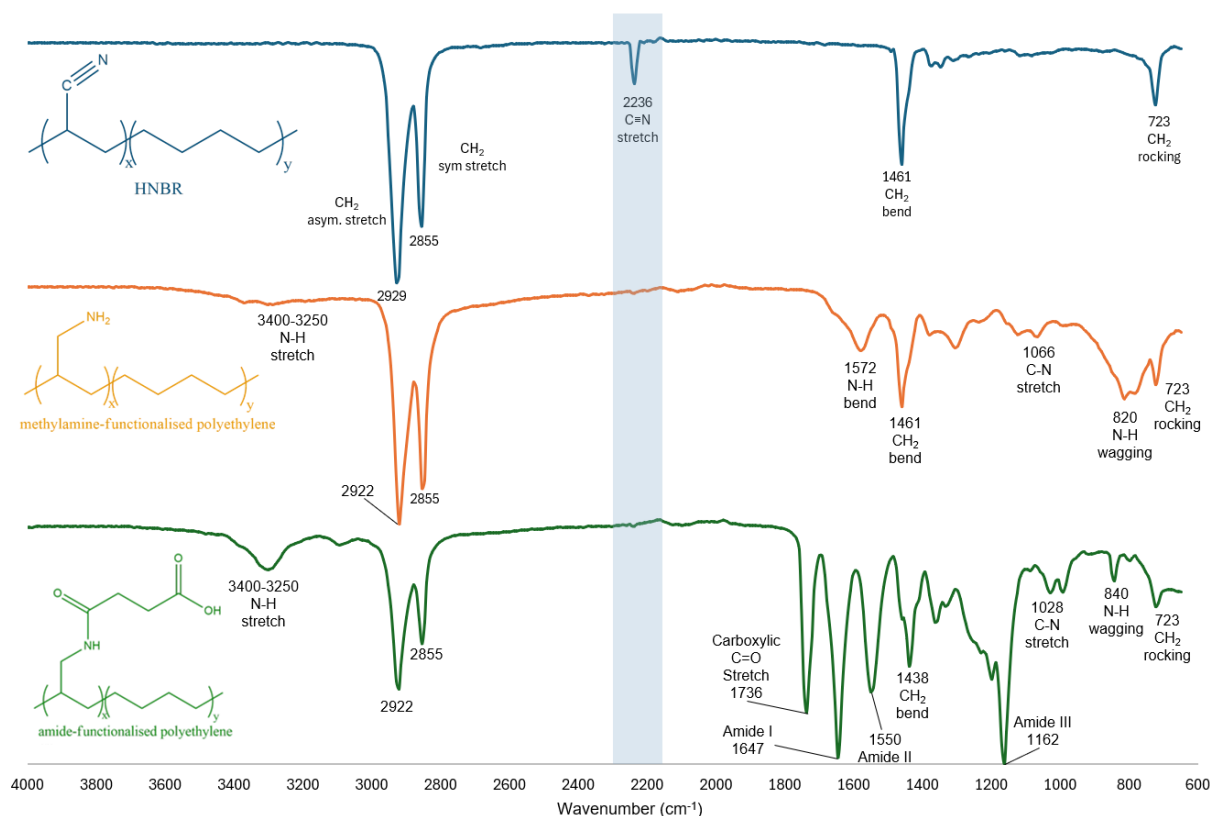


Figure 53: FTIR spectra of HNBR, amine- and amide-functionalised polyethylene, showing chemical transformation during hydrogenation and subsequent acylation. The disappearance of the nitrile stretch ($\text{C}\equiv\text{N}$, 2236 cm^{-1}) confirms hydrogenation, while the appearance of N-H vibrations and amide bands I-III and the carboxylic stretch confirms successful amine and amide functionalisation.

The successful acylation of the intermediate methylamine-functionalised polyethylene with succinic anhydride is further supported by the ^1H NMR shown in Figure 54. Characteristic product signals highlighted in the spectra of both the model compound, N-hexylsuccinamic acid, and the resulting amide-functionalised polyethylene. The strong correspondence between the two spectra indicates successful conversion of the pendant amine groups into the corresponding amides using an equimolar amount of succinic anhydride for 2 hours at 30°C . The absence of characteristic succinic anhydride, hexylamine or byproduct signals in the product spectra even indicates near-quantitative conversion of the amines to the amide groups bearing terminal carboxylic acid functionalities. The additional signals observed in the spectrum of amide-functionalised polyethylene originate from residual methanol and water from the work-up procedure.

Both the FTIR and the ^1H NMR data presented in Figure 53 and Figure 54 provide strong evidence for the successful acylation of methylamine-functionalised polyethylene with succinic anhydride. Near-complete conversion is achieved after 2h reaction at 30°C using an equimolar amount of succinic anhydride.

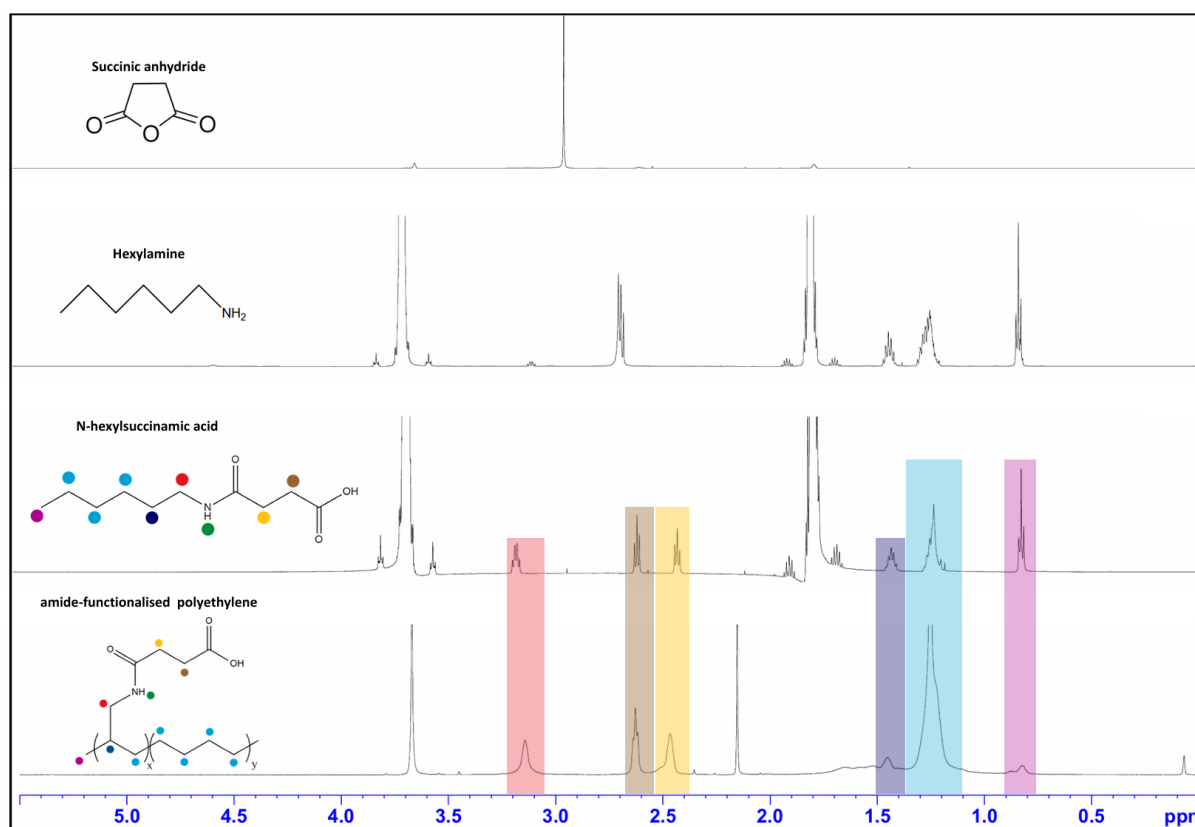


Figure 54: ^1H NMR spectra of succinic anhydride, hexylamine, N-hexylsuccinamic acid, and resulting amide-functionalised polyethylene. The highlighted peaks correspond to characteristic product protons, confirming successful acylation with succinic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol succinic anhydride, 2 ml THF, 2h, 30°C , and 600 rpm.

5.2.2.3 Acylation with phthalic anhydride

The final acylating agent tested in this study is phthalic anhydride. This cyclic anhydride is of vital importance for the chemical industry. It can undergo several important reactions, such as esterification and acylation, due to its highly electrophilic carbonyl groups. The phthalic anhydride structure allows nucleophiles such as alcohols and amines to easily attack and trigger a ring-opening and nucleophilic substitution [113].

For this part of the study, it is important to perform the acylation reaction with phthalic anhydride at low temperatures to prevent dehydration and ring-closure. If this ring closure occurs, the reaction is no longer a regular acylation but rather a phthalimide formation, which will be discussed in Section 5.3. To suppress ring closure, the standard acylating conditions are employed, namely 2 h at 30°C with 1 equivalent of phthalic anhydride. The reaction was first evaluated using hexylamine as a model compound before being applied to methylamine-functionalised polyethylene.

The ^1H NMR shown in Figure 55 provides significant evidence for successful acylation with phthalic anhydride. All characteristic signals of the expected product can be assigned, and the observed integration values are consistent with the proposed structure. Furthermore, no significant signals attributable to unreacted starting materials or byproducts are detected. These observations indicate that acylation proceeded successfully under the applied conditions while ring closure to the corresponding phthalimide is effectively suppressed.

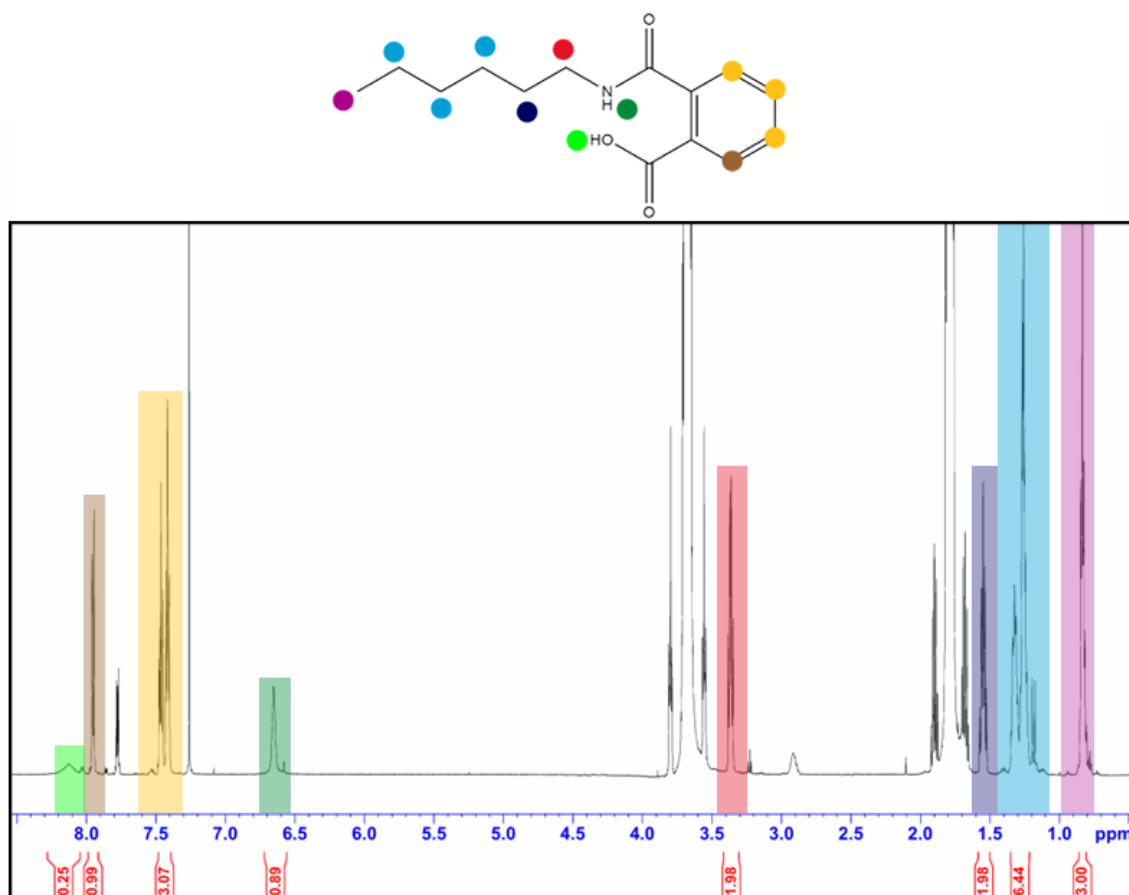


Figure 55: ^1H NMR spectrum of 2-(N-hexylcarbamoyl) benzoic acid with peak assignment and signal integration of product peaks confirming successful acylation of hexylamine with phthalic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol phthalic anhydride, 2 ml THF, 2h, 30°C, 600 rpm.

Following successful modification of the model compound hexylamine, the methodology was extended to methylamine-functionalised polyethylene to introduce analogous phthalic acid-derived functionalities onto the polymer backbone. The standard acylation conditions, consisting of a 2-hour reaction at 30°C, are maintained as the starting point for this functionalisation.

The FTIR spectrum of the product polymer (green, Figure 56) is examined for the presence of characteristic absorption bands corresponding to the proposed product polymer. Typical expected vibrations due to the phthalic-derived functionalities include the N-H stretch (3400-3250 cm^{-1}), the C=O stretch (1710-1690 cm^{-1}), the aromatic C-C stretch (1500-1400 cm^{-1}), the aromatic out-of-plane bending (900-375 cm^{-1}), and the C-N stretch (1250-1020 cm^{-1}) [101]. Both the C=O stretch and the N-H stretch are clearly visible in this spectrum. Moreover, the remaining characteristic absorption bands can also be assigned to the observed peaks. These observations provide significant evidence that phthalic anhydride successfully acylated the majority of the amines while suppressing unwanted ring closure under the applied reaction conditions of 30°C for 2h.

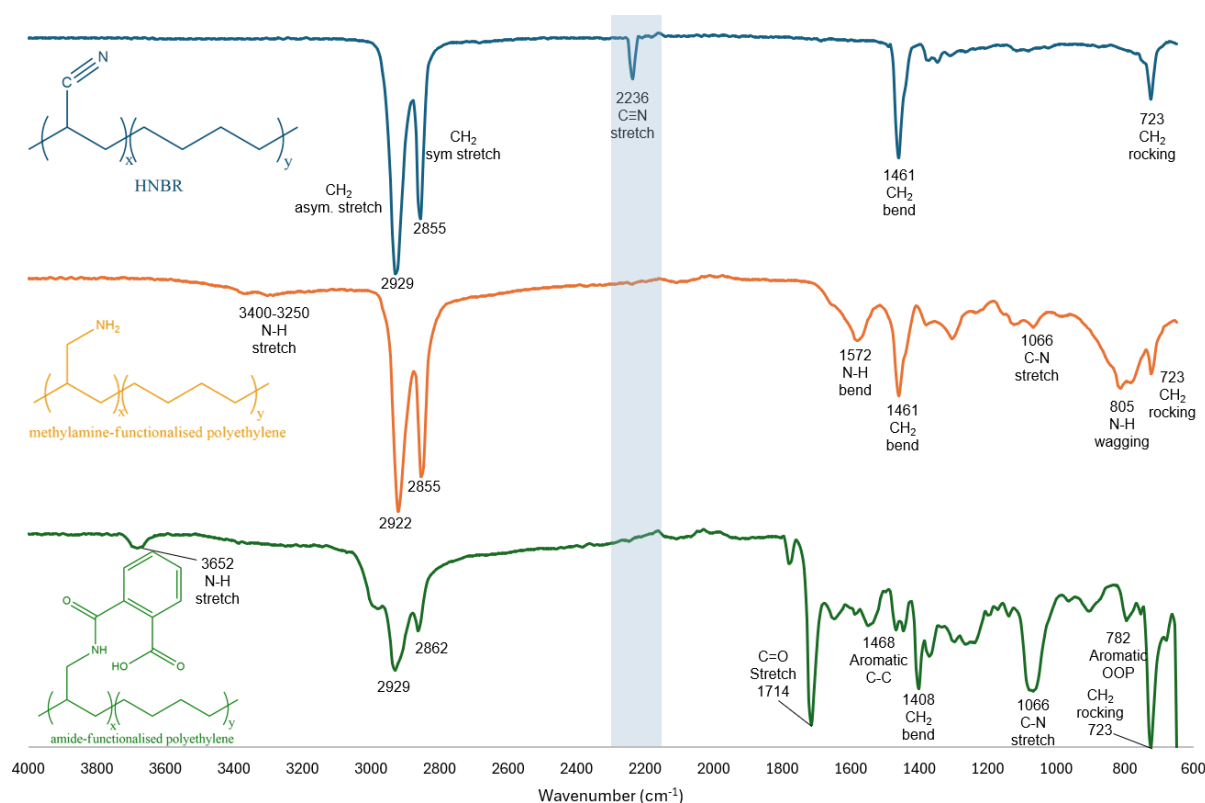


Figure 56: FTIR spectra of HNBR, amine- and amide-functionalised polyethylene, showing chemical transformation during hydrogenation and subsequent acylation. The disappearance of the nitrile stretch ($\text{C}\equiv\text{N}$, 2236 cm^{-1}) confirms hydrogenation, while the appearance of N-H vibrations and the carboxylic stretch confirms successful amine and amide functionalisation.

5.2.2.4 Acylation of hydrogenated dHNBR

Lastly, the one-pot hydrogenation-acylation is performed on the 85% defunctionalised HNBR. In the preceding retro-hydrocyanation step, 85% of the nitrile functionalities were converted to olefinic bonds through the precise addition of 0.85 equivalents of the sacrificial acceptor molecule, vinyl norbornene. The reaction conditions are roughly kept the same as for the regular methylamine-functionalised polyethylene acylation, so 1 equivalent benzoyl chloride, 1.5 equivalents Et_3N , 30°C , but a 24-hour reaction is employed, because dissolution of the defunctionalised polymer proved more challenging. The success of the hydrogenation is evaluated by the disappearance of the $=\text{C-H}$ OOP bending at 969 cm^{-1} , as shown in Figure 57. The disappearance of this absorption band indicates complete hydrogenation of the double bonds. Because the absorption band from the residual nitrile content of 3.5 mol% per C_2H_4 is too weak to reliably monitor its disappearance. Consequently, the success of the nitrile hydrogenation is evaluated indirectly through the subsequent acylation reaction.

The FTIR of the resulting amide-functionalised polyethylene (green, Figure 57) clearly displays the three characteristic amide absorption bands, including amide I ($1700\text{--}1600\text{ cm}^{-1}$) from the C=O stretching, amide II ($1600\text{--}1500\text{ cm}^{-1}$) mainly from N-H bending, and amide III due to C-N stretching ($1310\text{--}1175\text{ cm}^{-1}$)[101]. The presence of these characteristic bands, together with the strong resemblance of the spectrum to available literature spectra of similar amide-functionalised polyolefins [17], provide compelling evidence of the successful one-pot hydrogenation and acylation of $\text{dHNBR}_{3.5\%}$ under the defined conditions. The results demonstrate the synthesis of an amide-functionalised polyolefin with an amide content of approximately 3.5 mol% per C_2H_4 unit. These findings demonstrate that the second objective of this thesis, namely the synthesis of various N -functionalised polymers with precise control over functional-group content, has been achieved for amide-functionalised polyolefins.

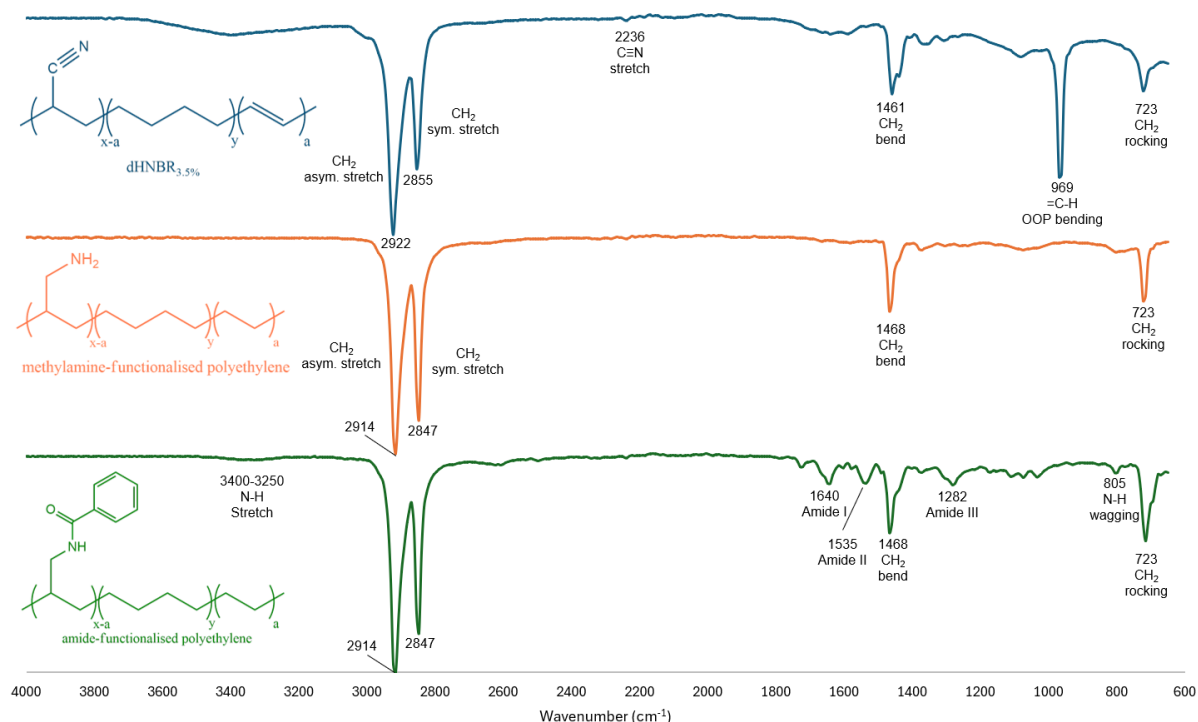


Figure 57: FTIR spectra of the one-pot hydrogenation-acylation of dHNBR containing 3.5 mol% nitriles per C_2H_4 unit, indicating successful hydrogenation and acylation due to the appearance of the amide vibrational modes and the disappearance of the nitrile stretch ($\text{C}\equiv\text{N}$, 2236 cm^{-1}) and $=\text{C-H}$ OOP bending (969 cm^{-1}).

5.3 Synthesis of Phthalimide-Functionalised Polyolefins by Phthalimide Formation

The second organic functionalisation, which is thoroughly investigated in this search to further functionalise the pendant amines of the intermediate, methylamine-functionalised polyethylene, is the phthalimide formation. In this reaction, a primary amine performs a nucleophilic attack on the carbonyl carbon of phthalic anhydride, which, after dehydration, yields the corresponding phthalimide. This transformation was carried out to modulate the chemical and physical properties of the material. The following section presents the spectroscopic evidence supporting successful phthalimide formation of the model compound and the polymeric substrate. The main objective of this section is to prove that the intermediate methylamine-functionalised polyethylene can be further functionalised into a phthalide-functionalised polymer.

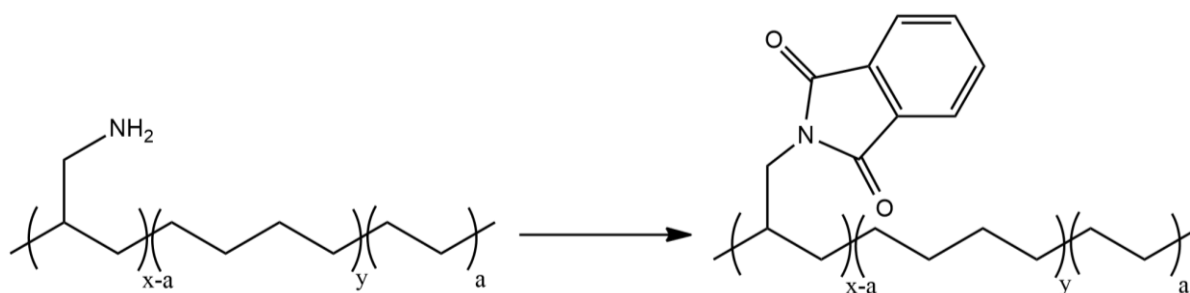


Figure 58 : Schematic representation of the objective of the phthalimide formation.

5.3.1 Phthalimide formation with hexylamine

The phthalimide formation is first investigated using hexylamine as a model compound, as it resembles the pendant amine groups present on methylamine-functionalised polyethylene. The reactions are carried out as described in Section 4.5.1 and analysed by NMR spectroscopy as outlined in Section 4.8. According to the literature, efficient cyclisation to phthalimides generally requires elevated temperatures, typically above 100°C [114]. Therefore, phthalimide formation is first analysed in a range of solvents at temperatures close to their boiling points. This will be further discussed in Section 5.3.1.1.

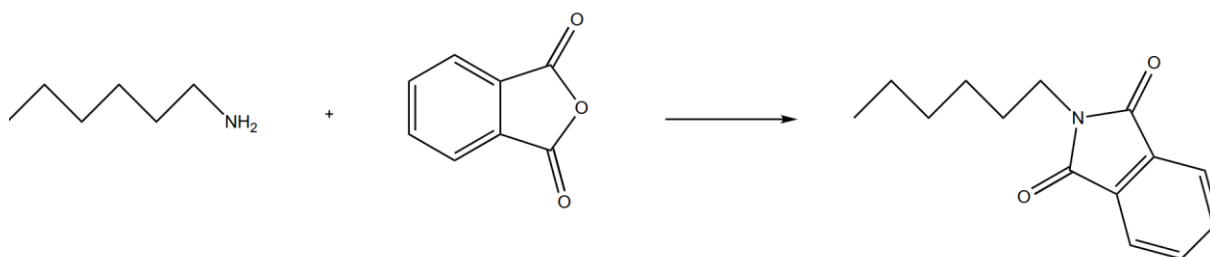


Figure 59: Model reaction for the investigation of the phthalimide formation.

Figure 60 illustrates the approach used to analyse the NMR data obtained from the phthalimide formation reactions. In these ^1H NMR spectra, all characteristic peaks corresponding to the product, N-hexylphthalimide can be clearly assigned, and the allocation is further supported by the observed peak integration values. The remaining signals originate from THF and residual CHCl_3 present in the deuterated solvent. No significant signals attributable to unreacted starting materials or byproducts are detected, indicating near-complete conversion of phthalic anhydride and a high selectivity towards the desired product. This conclusion is further supported by using 1,3-dimethoxybenzene as an internal standard in quantitative ^1H NMR analysis, which confirmed near-quantitative product formation (Appendix 3: Additional NMR spectra). Therefore, the spectrum shown in Figure 60 provides strong evidence for the successful conversion of hexylamine into N-hexylphthalimide.

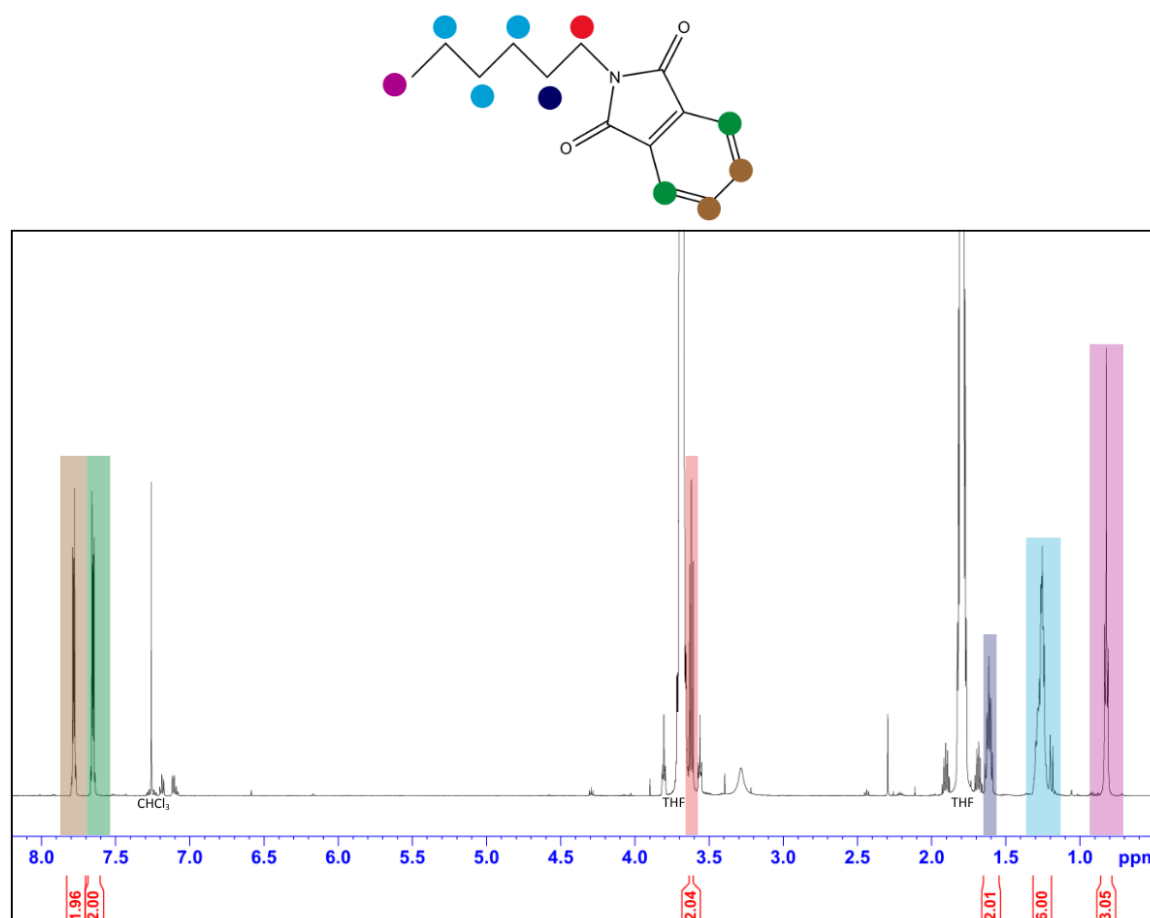


Figure 60: ^1H NMR spectrum of N-hexylphthalimide with peak assignment and signal integration of product peaks confirming successful phthalimide formation of hexylamine with phthalic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol phthalic anhydride, 1 ml THF, 24h, 150°C and 600 rpm

5.3.1.1 Solvent screening

To optimise the phthalimide formation protocol, the reaction is examined in different solvents under standardised conditions. Phthalimide formation eventually achieved high yields across all solvents listed below.

Tabel 1: Solvents and reaction temperatures used for the near quantitative phthalimide functionalisation

Solvent	Boiling point (°C)	Reaction Temperature (°C)
Xylene (dry)	140	130
PhCl (dry)	132	130
NBP	240	230
DMF	153	130
Dioxane (dry)	101	100
N-butylacetate	126	130
dichlorobenzene	173	170
THF (dry)	66	60 → 150*

* Reaction performed in a high-pressure reactor

The phthalimide functionalisation was initially evaluated at temperatures just below the boiling point of each solvent. Under these conditions, near-quantitative yields are obtained in most solvents, with the exception of THF (Appendix 3: Additional NMR spectra). This lower performance is most likely related to the significantly lower boiling point of THF compared to the other solvents. The initial reaction temperature of 60°C was likely too low to achieve successful dehydration and ring closure within the 24h reaction timeframe. However, when the reaction is performed in a high-pressure reactor, the reaction temperature could be increased to 150°C for 24 h, which afforded the corresponding phthalimides with near quantitative yields (Figure 60).

In all the above-listed solvents, only product and solvent signals are observed in the ¹H NMR spectra. This indicates that nearly all amines are converted into phthalimides under the applied conditions. This conclusion is further validated for the reaction in xylene using 1,3-dimethoxybenzene as an internal standard for quantitative ¹H NMR analysis, which confirmed near-quantitative yields (Appendix 3: Additional NMR spectra). All solvents investigated are aprotic. Protic solvents are avoided because they may hydrolyse phthalic anhydride, reducing the efficiency and yield of phthalimide formation.

5.3.1.2 Time screening

To gain further insight into the reaction progress, a time screening of the phthalimide formation is conducted. This investigation provides information on the rate of substrate conversion and formation of the corresponding phthalimides.

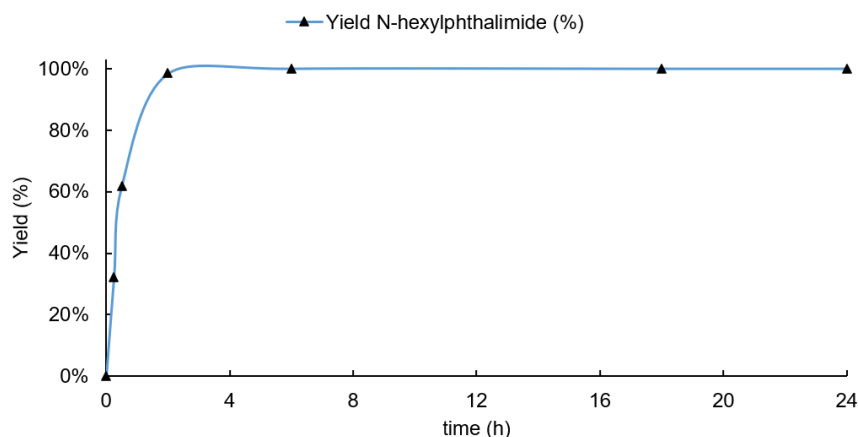


Figure 61: Yield of N-hexylphthalimide during the time screening experiment of the phthalimide formation with phthalic anhydride. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 1 ml THF, 150°C, and 600 rpm

The results of the time screening in Figure 61 show that phthalimide formation reaches near completion after approximately 2 hours, as the yield of N-hexylphthalimide plateaus, indicating that the product formed is stable under the reaction conditions.

A more detailed examination of the aromatic regions in the ^1H NMR spectra supports the reaction mechanism proposed in Figure 12 of the literature study. Spectrum A in Figure 62 corresponds to a reference acylation reaction with phthalic anhydride in which ring closure is suppressed, whereas spectra B, C, and D represent sample points from the time screening. The results suggest that the initial acylation occurs rapidly, with associated signals highlighted in yellow. In contrast, the subsequent dehydration step, which leads to ring closure and phthalimide formation, proceeds more gradually, with associated signals highlighted in blue. Over time, the NMR data of Figure 62 show a continuous decrease in signals associated with the uncyclised acylated intermediate (yellow), alongside a corresponding increase in phthalimide signals (blue), with complete conversion observed after roughly 2 hours, indicating complete conversion of the hexylamine into N-hexylphthalimide.

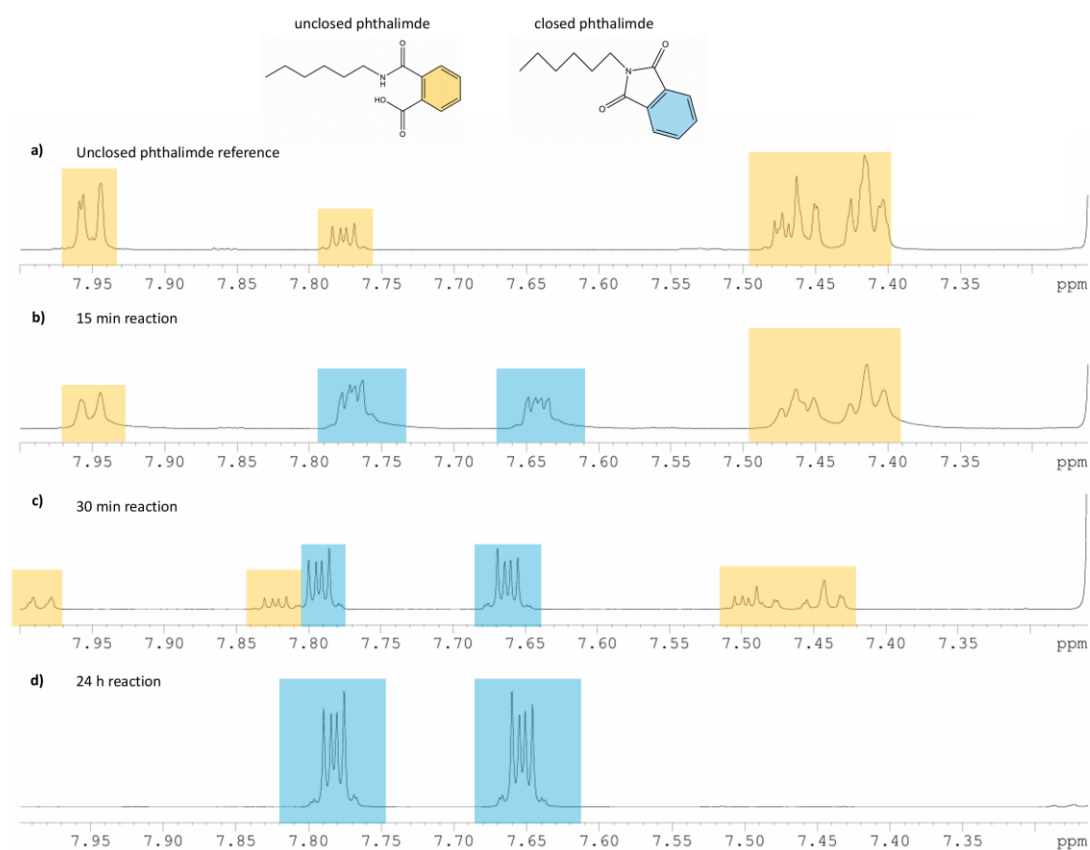


Figure 62: ^1H NMR of the progression of the phthalimide formation showing rapid acylation but slow dehydration and ring-closure. (a) uncyclised phthalimide reference, (b) sample after 15 min reaction, (c) sample after 30 min reaction, (d) sample after 24h reaction. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 1 ml THF, 150°C , and 600 rpm.

5.3.1.3 Ring-closure studies

As already suggested by the time-screening experiment, ring closure is an important phenomenon in phthalimide formation and is the rate-limiting step. This dehydration is heavily temperature dependent. When phthalimide formation is desirable, the reactions are performed in THF at 150°C for 24 hours. However, when ring closure must be avoided, the reactions are carried out in THF at 30°C for 2 hours. To gain more insight into this ring-closure phenomenon, the influence of temperature is analysed for both reactions.

Firstly, the ring-closure during phthalimide formation is investigated. This reaction is typically carried out in THF at 150°C and 600 rpm for 24 hours. Subsequently, the reaction temperature is varied to determine the temperature at which significant amounts of the uncyclised intermediate remain present in the reaction mixture. As shown in Figure 63, substantial amounts of uncyclised intermediate are observed once temperatures below 100°C are employed. Further lowering the temperature leads to a corresponding decrease in phthalimide yield and an increase in the amount of uncyclised acylated intermediate.

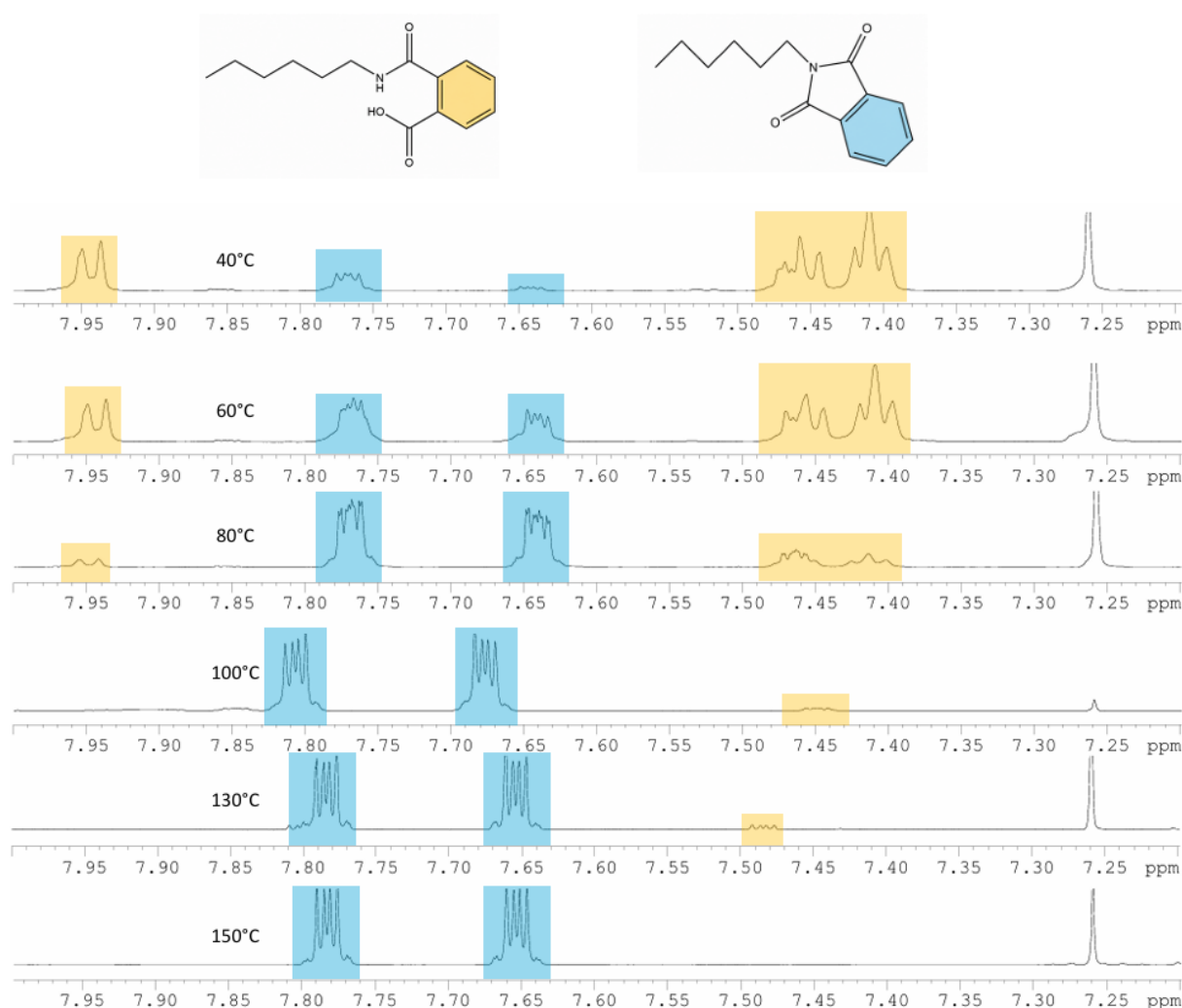


Figure 63: ^1H NMR of the aromatic region displaying temperature dependency of ring-closure during phthalimide formation of hexylamine with phthalic anhydride for a 24h reaction. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 24h, and 600 rpm.

In the acylation reaction with phthalic anhydride, ring closure is undesirable because the resulting phthalimide no longer contains the free carboxylic acid functionality. Retaining this carboxylic acid group may be advantageous for certain applications, for example, by enhancing interactions with polar dyes. Therefore, the temperature range over which the acylation can proceed without significant cyclisation was investigated. This information is particularly relevant for product dissolution, which often requires elevated temperatures. The stacked ^1H NMR spectra of the aromatic region indicate that significant cyclisation occurs at temperatures of 60 °C and above. Consequently, temperatures must be maintained below 60°C throughout the synthesis of uncyclised phthalimide derivatives.

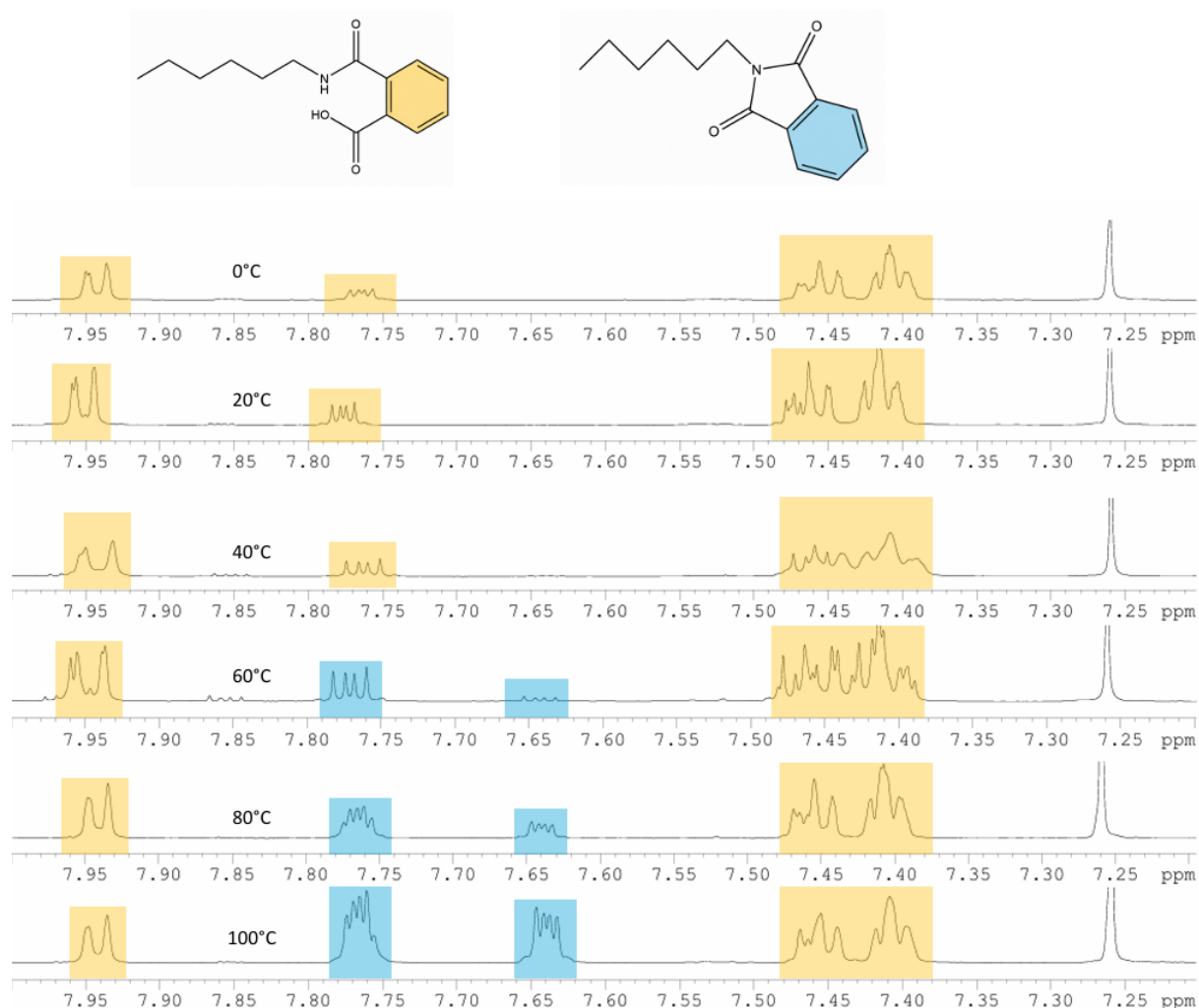


Figure 64: ^1H NMR of the aromatic region displaying the temperature dependency of ring-closure during acylation reaction of hexylamine with phthalic anhydride for the 2h reaction. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 2h, and 600 rpm

5.3.1.4 Inhibition studies

The phthalimide formation is a consecutive reaction with the hydrogenation step. To facilitate synthesis, it would be highly desirable to load phthalic anhydride directly into the reactor without intermediate workup of the hydrogenated product. Therefore, it must be thoroughly investigated whether any of the hydrogenation components inhibit phthalimide formation.

Firstly, the possible inhibition of the residual $\text{Ru}(\text{cod})\text{methallyl}_2$ and PPh_3 from the catalytic system is investigated. Fortunately, neither 0.5 mol% ruthenium with 1 mol% phosphine ligand

nor 1 mol% ruthenium with 2 mol% ligand results in noticeable inhibition of the reaction. Subsequently, the inhibiting effect of 5 and 10 mol% K₂OtBu is investigated, but the presence of this component also shows no significant influence on the reaction yield. These results support the feasibility of a one-pot hydrogenation–functionalisation approach. The corresponding ¹H NMR spectra of the inhibition study are presented in Appendix 3: Additional NMR spectra.

5.3.1.5 Follow-up reaction

As a last step before moving on to the polymeric substrate, the phthalimide formation is investigated as a one-pot follow-up reaction. Here, the substrate hexanenitrile is first hydrogenated to hexylamine to subsequently further functionalise it to N-hexylphthalimide.

The ¹H NMR spectrum of the follow-up reaction indicates near-quantitative conversion of the primary amines into phthalimides after a 24h reaction at 150°C in THF. All characteristic signals of N-hexylphthalimide can be assigned in the spectrum, and the proposed assignments are further supported by the observed integration values, which are in good agreement with the expected proton ratios. In addition to the product and solvent signals, two n-decane peaks are observed, which contribute to the CH₂ and CH₃ signals. The n-decane peaks also match approximately with their expected integration values based on the amount of internal standard added. Together, the signal assignment and integration provide strong evidence of the successful one-pot conversion of hexanenitrile to N-hexylphthalimide.

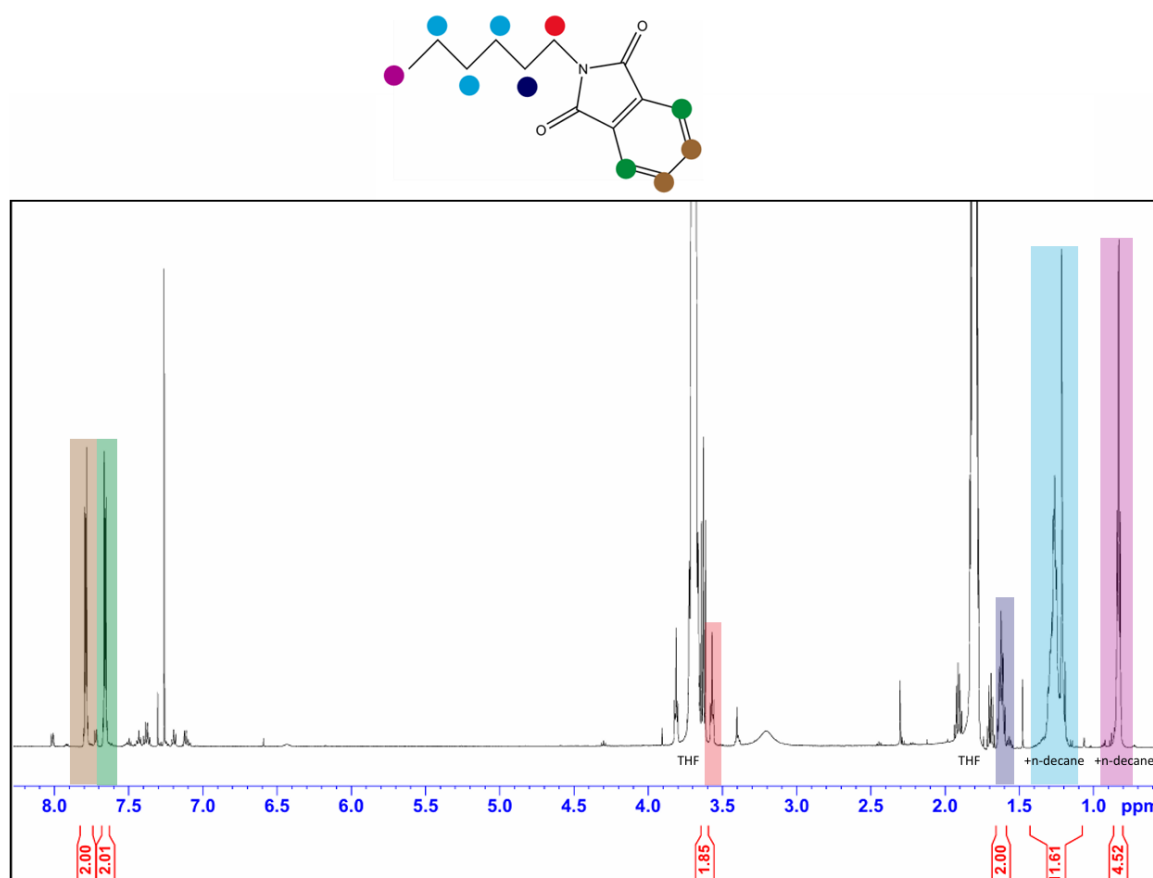


Figure 65: Successful follow-up phthalimide formation reaction with phthalic anhydride, confirmed by the formation of characteristic product signals in the ¹H NMR. Reaction conditions: 0.4 mmol substrate, 0.4 mmol phthalic anhydride, 2 ml THF, 24h, 150°C and 600 rpm.

5.3.1 One-pot hydrogenation-phthalimide formation of (d)HNBR

Following the successful phthalimide formation of the model compounds, the methodology is subsequently applied to the intermediate polymeric substrate, methylamine-functionalised polyethylene. These experiments are conducted to evaluate whether the optimised phthalimide formation conditions can be translated to the polymer system while maintaining high conversion and efficient functionalisation. This section describes the phthalimide formation of methylamine-functionalised polyethylene and a partly defunctionalised form using phthalic anhydride in a one-pot hydrogenation-functionalisation protocol. By avoiding intermediate isolation and purification, this approach reduces the waste generation, solvent consumption, and energy demand, thereby improving both the sustainability and industrial applicability of the developed method.

5.3.1.1 Phthalimide formation with phthalic anhydride

The synthesis of the phthalimide-functionalised polymers is analysed using both FTIR and NMR spectroscopy. The FTIR spectra, shown Figure 66, are examined for the presence of characteristic absorption bands corresponding to the phthalimide structure. Typical expected vibrations for phthalimides include the imide stretch ($1750\text{--}1670\text{ cm}^{-1}$), aromatic C-C stretch ($1500\text{--}1400\text{ cm}^{-1}$), the CN stretch ($1250\text{--}1020\text{ cm}^{-1}$), and aromatic out-of-plane bending ($900\text{--}375\text{ cm}^{-1}$). All these relevant absorption peaks can be assigned in the recorded FTIR spectrum and are labelled in Figure 66. Therefore, this spectrum provides strong evidence that the pendant amines of the polymers are converted to phthalimides with a near-quantitative yield. These results are obtained with 1 equivalent of phthalic anhydride in a 24h reaction at 150°C in 2 ml THF.

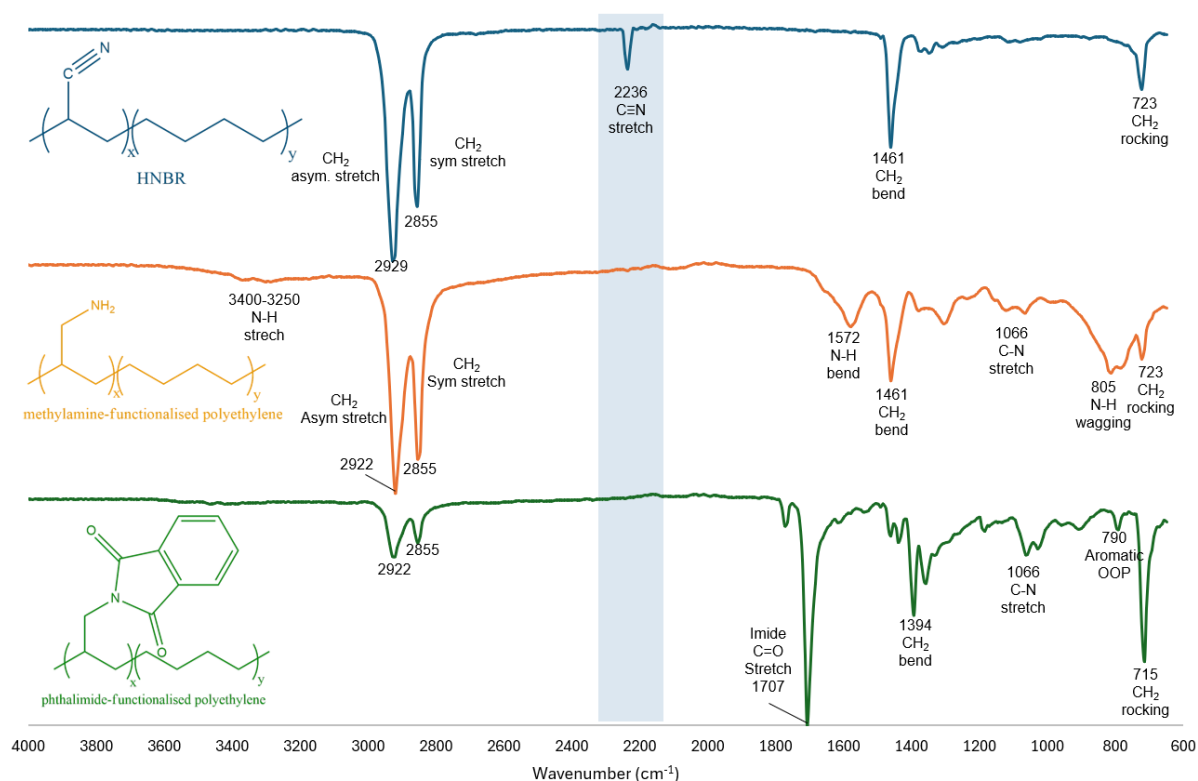


Figure 66: FTIR spectra of HNBR, amine- and phthalimide-functionalised polyethylene, showing chemical transformation during hydrogenation and subsequent phthalimide formation. The disappearance of the nitrile stretch ($\text{C}\equiv\text{N}$, 2236 cm^{-1}) confirms complete hydrogenation, while the appearance of N-H vibrations and the imide stretch (1707 cm^{-1}) confirms successful amine and phthalimide formation.

The successful synthesis of the phthalimide-functionalised polyethylene is further evaluated with ^1H NMR spectroscopy, as illustrated in Figure 67. The characteristic signals of the model compound, N-hexylphthalimide, closely correspond with those observed from the phthalimide-functionalised polyethylene. The stacked spectra further demonstrate that the observed product signals do not coincide with those originating from unreacted starting materials. Together with the FTIR results, these observations provide strong evidence for a near-quantitative conversion of the primary amines into phthalimides under the applied reaction conditions.

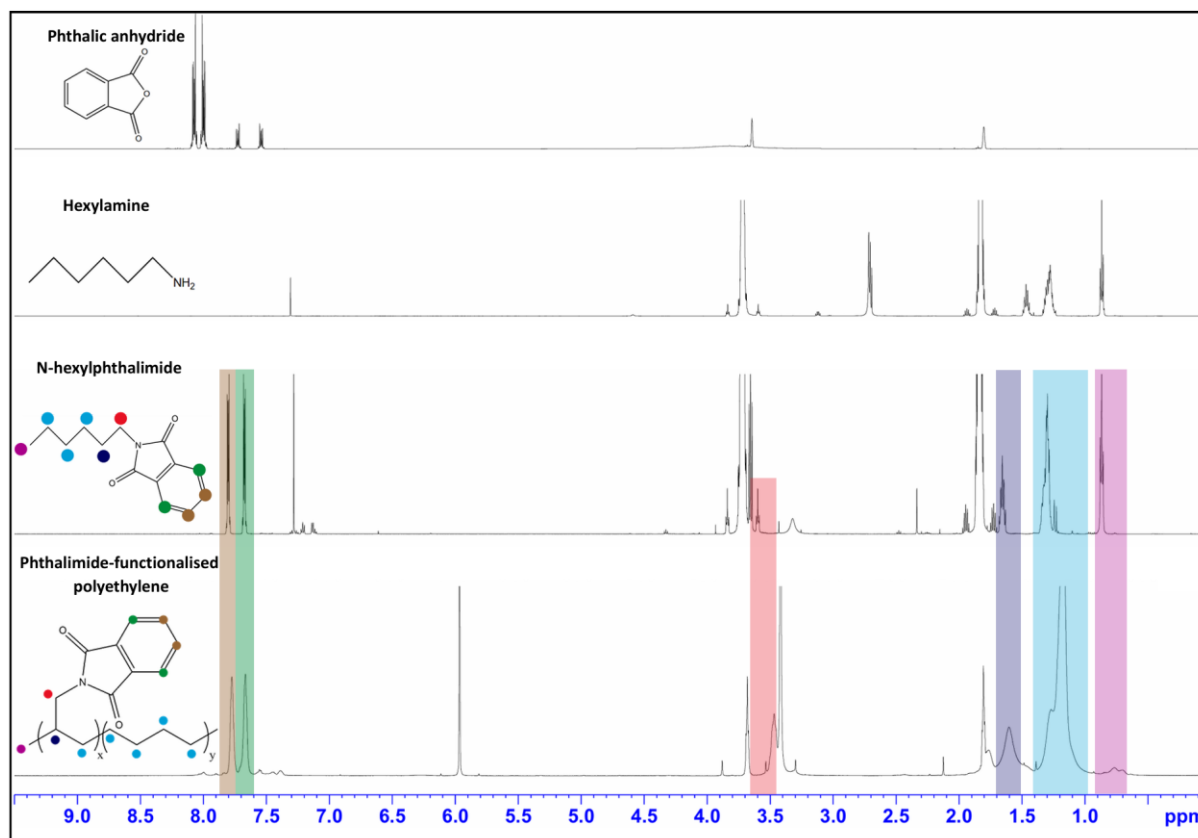


Figure 67: ^1H NMR spectra of phthalic anhydride, hexylamine, N-hexylphthalimide, and the resulting phthalimide-functionalised polyethylene. The highlighted peaks correspond to characteristic protons of the products, confirming successful acylation with phthalic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol phthalic anhydride, 2ml THF, 24h, 150°C, and 600 rpm

5.3.1.2 Phthalimide formation of hydrogenated dHNB_{3.5%}

Lastly, the one-pot hydrogenation-phthalimide formation is performed on dHNB_{3.5%}. Around 15% of the nitriles remain on the substrate after retro-hydrocyanation, while 85% are converted into olefinic bonds by the precise dosage of 0.85 equivalents of the sacrificial acceptor molecule, vinyl norbornene. The success of the hydrogenation is evaluated by the disappearance of the =C-H OOP bending vibration at 969 cm⁻¹, which indicates complete hydrogenation of the olefinic bonds. The nitriles are assumed to be hydrogenated as well.

The phthalimide formation is subsequently carried out under the same standard reaction conditions previously employed for methylamine-functionalised polyethylene, namely using 1 equivalent of phthalic anhydride in THF at 150°C for 24h. Ultimately, the phthalimide synthesis is evaluated by the appearance of the characteristic phthalimide absorption bands in the FTIR spectrum. Typical phthalimide vibrations are the imide C=O stretch (1750-1670 cm⁻¹), the CN stretch (1250-1020 cm⁻¹), aromatic C-C stretch (1500-1400 cm⁻¹), and aromatic out of plane bending (900-375 cm⁻¹)[101]. These characteristic absorption bands can be assigned in Figure 68, and the spectrum closely resembles literature spectra of similar phthalimide-functionalised polyolefins [17]. Therefore, it can be concluded that the amines are effectively converted into phthalimides, yielding a phthalimide-functionalised polyethylene containing approximately 3.5 mol% phthalimides per C₂H₄ unit. Furthermore, the successful phthalimide formation provides indirect evidence for the preceding nitrile hydrogenation. Most importantly, these findings further demonstrate that the second objective of this thesis, namely the synthesis of various N-functionalised polymers with precise control over functional-group content, has been successfully achieved for phthalimide-functionalised polyolefins.

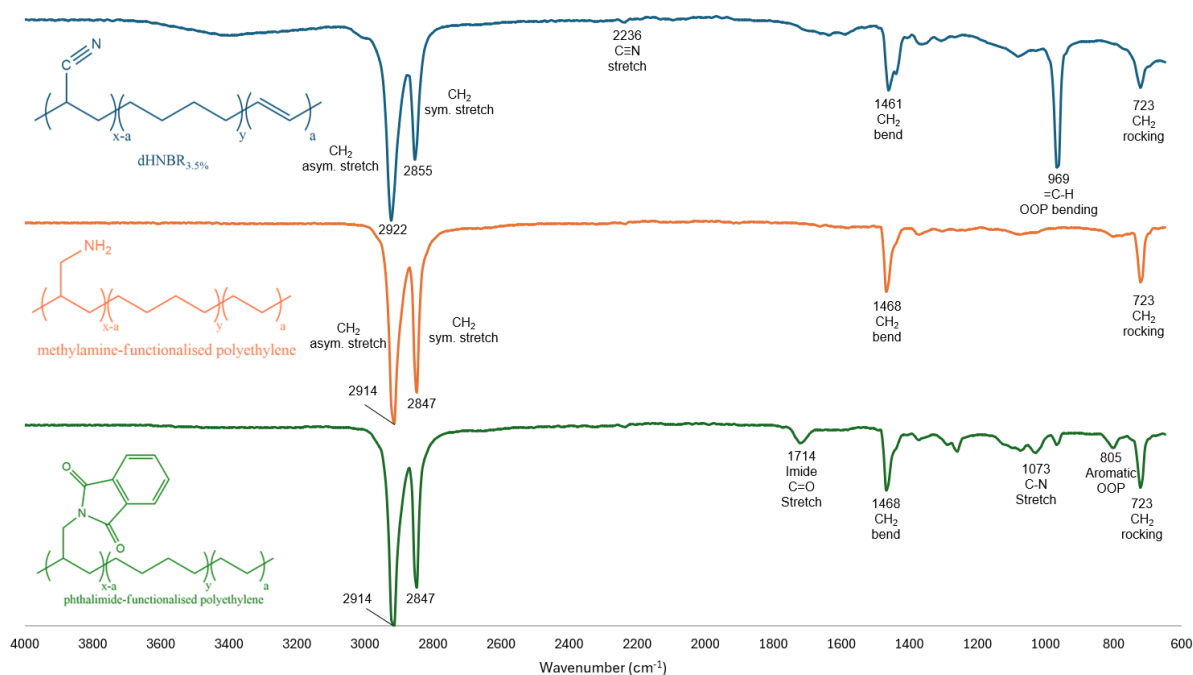


Figure 68: FTIR spectra of dHNB_{3.5%}, methylamine-functionalised polyethylene, and phthalimide-functionalised polyethylene showing chemical transformation of the one-pot hydrogenation-phthalimide formation reaction. Disappearance of the nitrile stretch (C≡N, 2236 cm⁻¹) and =C-H OOP (969 cm⁻¹) confirms hydrogenation, while appearance of N-H vibrations and the imide stretch (1714 cm⁻¹) confirms successful amine and amide functionalisation.

6 CONCLUSION

This thesis establishes a novel and versatile approach for the synthesis of N-functionalised polyolefins through controlled post-polymerisation modification of the inexpensive and commercially accessible substrate poly(acrylonitrile-co-butadiene)/ NBR. By combining retro-hydrocyanation, hydrogenation, and subsequent functionalisation reactions, this work successfully synthesises structurally diverse amide- and phthalimide- functionalised polyethylenes with precise control over the functional group content under comparatively mild conditions. In doing so, this methodology overcomes several longstanding challenges associated with the synthesis of N-functionalised polyolefins, including the need for harsh conditions, the use of expensive reagents, and limited control over functional group incorporation. Therefore, the new methodology represents a significant advance towards the controlled and accessible synthesis of a wide range of N-functionalised polyolefins with strong potential for enhanced mechanical properties compared to conventional polyolefins.

Initial model-compound reactions provided insight into the differing hydrogenation behaviour of nitrile and olefinic functionalities and identified an effective ruthenium-based catalytic system capable of hydrogenating both functional groups present within the polymeric NBR substrate. Subsequent application of this catalytic methodology to NBR and HNBR substrates demonstrates that efficient hydrogenation of nitrile and olefinic bonds can be achieved by adjusting reaction times and catalyst loadings to account for intrinsic polymer processing limitations. NMR and FTIR spectroscopy consistently confirmed the near-complete conversion of the targeted functionalities, thereby validating the robustness and applicability of the developed catalytic platform to polymeric substrates.

This work further demonstrates that the intermediate methylamine-functionalised polyethylene serves as a highly versatile platform for subsequent post-polymerisation functionalisation. Both acylation and phthalimide formation proceeded efficiently through a one-pot hydrogenation-functionalisation protocol without intermediate work-up, improving simplicity, time efficiency, and industrial applicability. These one-pot strategies starting from either conventional or precisely defunctionalised polymeric substrates enable the synthesis of structurally distinct N-functionalised polyolefins with precise control over both the degree and nature of functionalisation. The successful transformation of the pendant amine groups into structurally diverse amide and phthalimide functionalities with near-quantitative yields further demonstrates the versatility and broad applicability of the developed methodology.

Importantly, this thesis demonstrates that the commercially available NBR and derived HNBR constitute an effective and highly adaptable precursor for the controlled incorporation of nitrogen-containing functionalities into polyolefin architectures. The ability to tune the functional group content through catalytic retro-hydrocyanation prior to functionalisation represents a significant conceptual advancement in the synthesis of polar-functionalised polyolefins with tunable and potentially enhanced properties.

Overall, this work establishes a powerful and accessible methodology for the preparation of structurally diverse N-functionalised polyolefins from the inexpensive industrial feedstock, poly(acrylonitrile-co-butadiene). Beyond providing proof of concept for the synthesis of four structurally distinct N-functionalised polyolefins, the developed methodology expands the synthetic toolbox available for polyolefin functionalisation while tackling several longstanding

challenges associated with the controlled incorporation of nitrogen-containing functionalities into polyolefin architectures. In doing so, this thesis lays the foundation for the future development of advanced polyolefin materials through controlled post-polymerisation modification strategies and represents a significant step toward broader accessibility and commercialisation of N-functionalised polyolefins.

7 FUTURE OUTLOOK

The results of this thesis establish a novel synthetic methodology for N-functionalised polyolefins and provide a strong foundation for future research into the synthesis of similar polymers. The developed strategy, consisting of a retro-hydrocyanation, hydrogenation and subsequent functionalisation, has proven to be a powerful and versatile platform for the synthesis of various N-functionalised polyolefins. At present, the successful application of this methodology has been demonstrated for several structurally distinct amide- and phthalimide-functionalised polyethylenes. Further studies could expand this methodology to other functional groups derived from primary amines, including secondary and tertiary amines, pyrazoles and oxygen-containing functionalities such as carbonyl groups and carboxylic acids.

Future studies should focus in particular on detailed mechanical testing and characterisation of all synthesised polymers in this thesis. Because many of the synthesised polymers show great potential for improved properties based on available literature data of similar N-functionalised polymers [17]. The amide-functionalised polyethylenes show great potential for improved printability and dyeability. Furthermore, the phthalimide-functionalised polyethylene should have increased toughness and tensile strength due to aromatic stacking of the functional groups. Moreover, the methylamine-functionalised polyethylene should have increased adhesion and wettability due to its highly polar nature. However, currently these are just speculations based on the available literature on N-functionalised polyolefins, and these polymers should undergo extensive mechanical testing and characterisation to determine whether these properties, in fact, significantly improve and thereby bypass the need for harmful performance-enhancing additives.

The hydrogenation step, which in this research was optimised using Ru(cod)methylallyl₂, can be extended to less expensive, more earth-abundant metals. During initial hydrogenation experiments, some in-house-synthesised manganese catalysts were tested. These catalysts could effectively hydrogenate nitriles, but failed to hydrogenate olefinic bonds (results presented in Appendix 4: Manganese as a catalyst). Future research should focus on further development and fine-tuning of such catalysts. Besides manganese, other earth-abundant metals, such as Fe, Co, and Ni, are known to form effective nitrile hydrogenation catalysts and might be promising to look deeper into as well, to lower the overall cost of the reaction and increase the industrial applicability [115].

Lastly, the recyclability of the newly synthesised polymers should be thoroughly investigated to evaluate whether material loops can be closed and whether these materials can contribute to more sustainable polymer technologies. In addition, the developed methodology provides a promising foundation for future scale-up towards industrial implementation of N-functionalised polyolefins. In particular, these materials may find applications in high-performance coatings, adhesives, compatibilisers, packaging materials, and advanced engineering plastics, where improved polarity, adhesion, printability, dyeability, and mechanical performance are highly desirable. Furthermore, the ability to introduce diverse functional groups directly into the polyolefin backbone in a controlled manner could reduce reliance on external, often harmful, performance-enhancing additives and thereby contribute to the development of more sustainable and recyclable polymer systems.

Overall, the results presented in this thesis not only provide a versatile synthetic platform for the preparation of N-functionalised polyolefins but also open new opportunities for the development of new polar-functionalised polyolefins with enhanced properties and broader industrial applicability, which might close material loops and thereby reduce reliance on harmful performance-enhancing additives.

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9 APPENDIX

Appendix 1: Inventory of chemical products

Product	Supplier	Purity (%)
1,1'-Bis(difenylfosfino)ferrocene	TCI	/
1,4-Bis(diphenylphosphino)butane	Fluorochem	/
2,2'-Bis(difenylfosfino)-1,1'-binaftyl	Strem Chemicals	98%
1,3-dimethoxybenzene	TCI	>97.0%
1,4- Dioxane (extra dry)	Thermo Scientific	99.5%
2-MethylTetrahydrofuran (extra dry)	Thermo Scientific	>99.5%
1,3,5-Trimethoxybenzene	TCI	>97.0%
Acetonitrile (extra dry)	Thermo Scientific	>99.9%
Bis[(2-diphenylphosphino) phenyl] ether	Thermo Scientific	98%
Benzene-d ₆	Thermo Scientific	99.6%
Benzonitrile	Fischer Chemical	>99%
Benzoylchloride	Alfa Aesar	>99.9%
Bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II)	Thermo Scientific	/
Carbonylchlorohydridotris(triphenylphosphine) ruthenium(II)	Sigma-Aldrich	/
Cesium carbonate	Sigma-Aldrich	99%

Chloroform-d8	Across Organics	99.6%
Chlorobenzene (extra dry)	Thermo Scientific	99.5%
Cyclopentyl methyl ether (extra dry)	Thermo Scientific	99.5%
n-Decane	TCI	>99.9%
Deuterium oxide	Thermo Scientific	99.8%
Dichloromethane (extra dry)	Thermo Scientific	99.8%
Dichlorobenzene	Thermo Scientific	>98.0%
Dichloro(benzene)ruthenium(II) dimer	TCI	/
Dichlorotris(triphenylphosphine)ruthenium(II)	TCI	>90%
Dihexylamine	Sigma-Aldrich	97%
Dimethylformamide	Fischer Chemical	99.6%
Dimethylsulfoxide	Fisher Chemical	>=99.9%
Ethyl acetate	Fisher Chemical	>98%
Hexanenitrile	TCI	97%
Hexylamine	Thermo Scientific	99%
Hydrochloric acid	Fisher Chemical	37%
Hydrogen	Air Liquide	>99.99%
Hydrogenated Nitrile Butadiene Rubber	Synthesized in-house from / Sigma-Aldrich precursor	

Methanol	Fisher Chemical	99%
Mn-2	Synthesized in-house	/
N-Butyl acetate	Thermo Scientific	>99%
N-Butyl-2-pyrrolidone	Carl Roth GmbH	>99.5%
Nickel(II) 2,4-pentanedionate	Thermo Scientific	95%
Nitric acid	Fischer Chemical	70%
Nitrile Butadiene Rubber	Sigma-Aldrich	/
Nitrogen	Air Liquide	>99.99%
n-Octane	Carl Roth GmbH	>99%
Phthalic anhydride	Fisher Chemical	>99%
Potassium tert-butoxide	Acros Organics	>98.0%
Succinic anhydride	Thermo Scientific	99%
Sodium tert-butoxide	Thermo Scientific	99%
Tetrachloroethane	Alfa Aesar	>98%
Tetrachloroethane-d ₂	Thermo Scientific	99.5%
Tetrahydrofuran (extra dry)	Thermo Scientific	99.5%
Trans-4-octene	Thermo Scientific	99.5%
Tricyclohexylphosphine	Thermo Scientific	98%
Triethylamine	Thermo Scientific	99%

Tris(4-fluorophenyl) phosphine	Thermo Scientific	98%
Tris(4-methoxyphenyl) phosphine	Thermo Scientific	98%
Triphenylphosphine	Thermo Scientific	99.9%
Toluene (dry)	Thermo Scientific	99.85%
Toluene-d ₈	Thermo Scientific	99.6%
O-Xylene (dry)	Thermo Scientific	99%

Appendix 2: Chemical structures Ru-catalyst precursors and phosphine-ligands

Ruthenium catalyst precursors

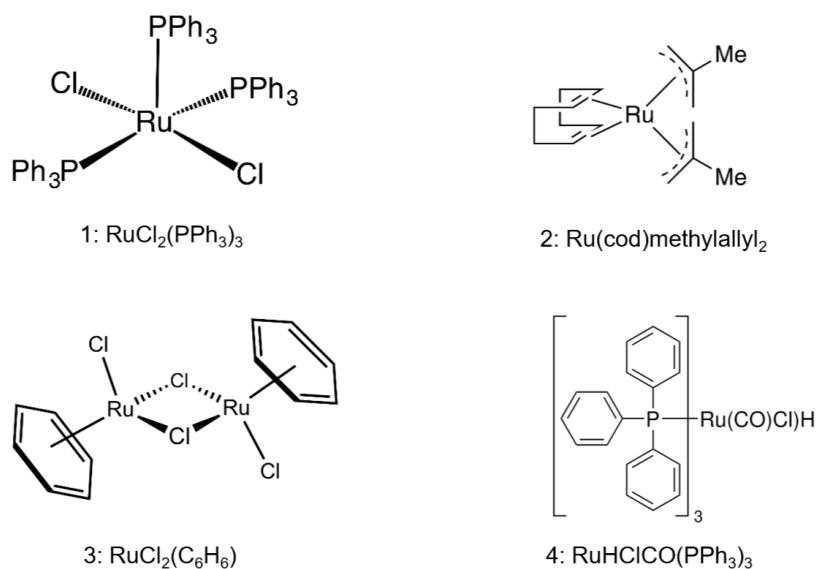


Figure 69: Chemical structures of Ruthenium catalyst precursors

Phosphine ligands

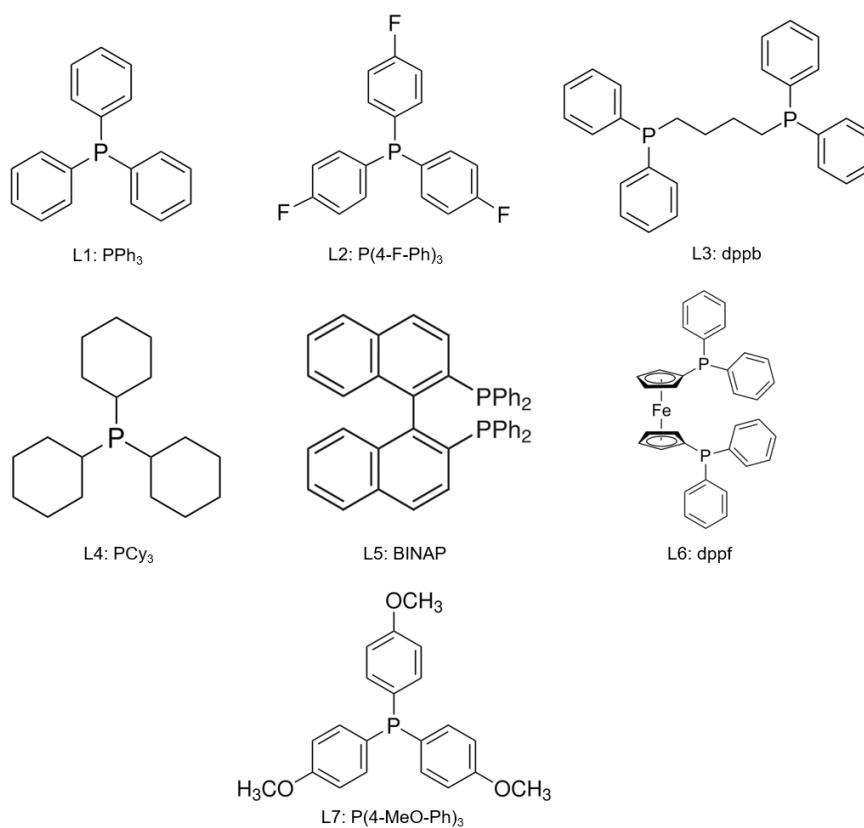


Figure 70: Chemical structure of phosphine ligands

Appendix 3: Additional NMR spectra

Acylation

Solvent-screening

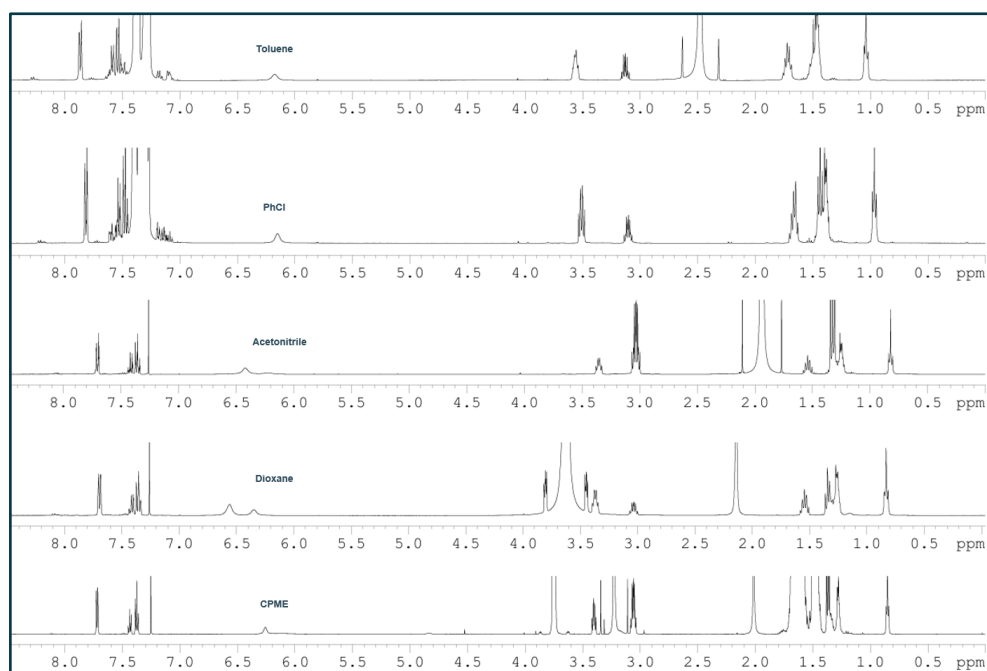


Figure 71: Solvent screening acylation reaction showing near-quantitative yields in all aprotic solvents. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et₃N, 1 ml solvent, 2h, 30°C, and 600 rpm

Salt studies

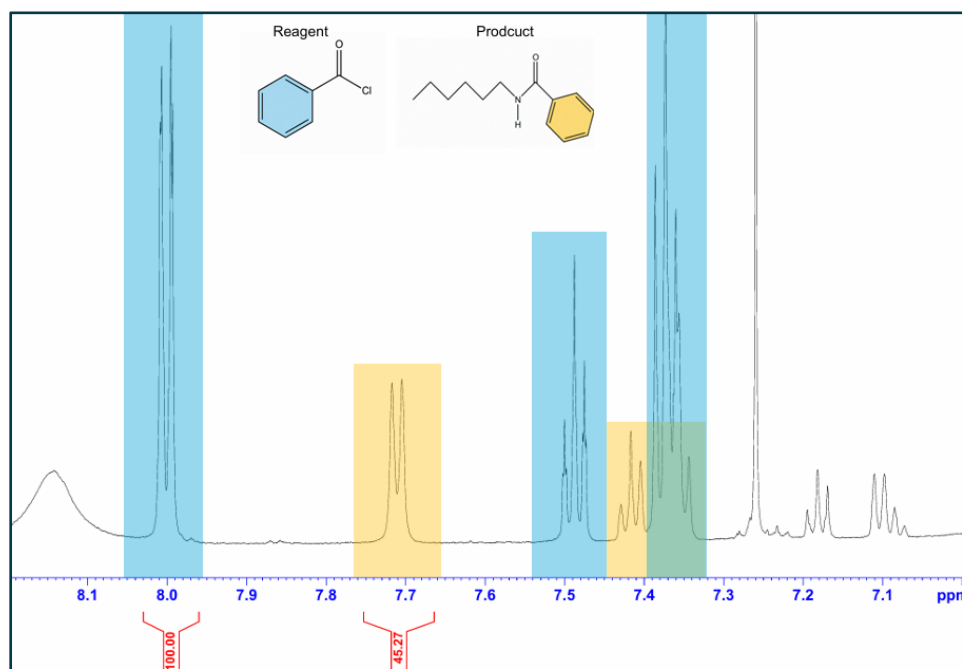


Figure 72: ¹H NMR of aromatic region of acylation with prior ammonium salt formation, giving a yield of 31% N-hexylbenzamide. Reagent peaks highlighted in blue, product peaks in yellow, and overlapping peaks in green. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.25 mmol HCl, 1 ml solvent, 2h, 30°C, and 600 rpm

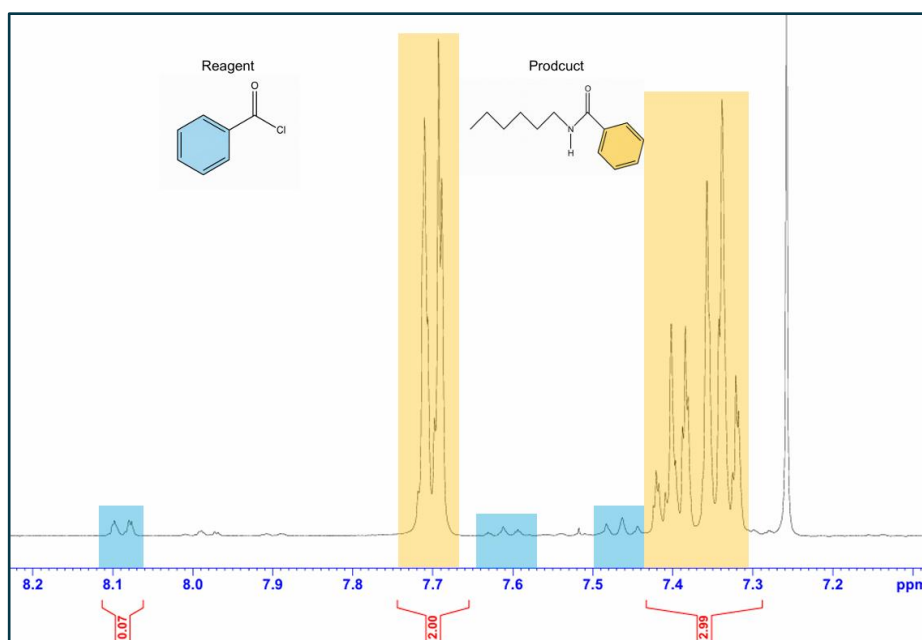


Figure 73: ^1H NMR of aromatic region of acylation, where the free amine is regenerated through reaction of ammonium salt with Et_3N , giving a yield of >96% N-hexylbenzamide. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.25 mmol HCl, 0.750 mmol Et_3N , 1ml THF, 2h, 30°C , and 600 rpm.

Acylation Inhibition studies

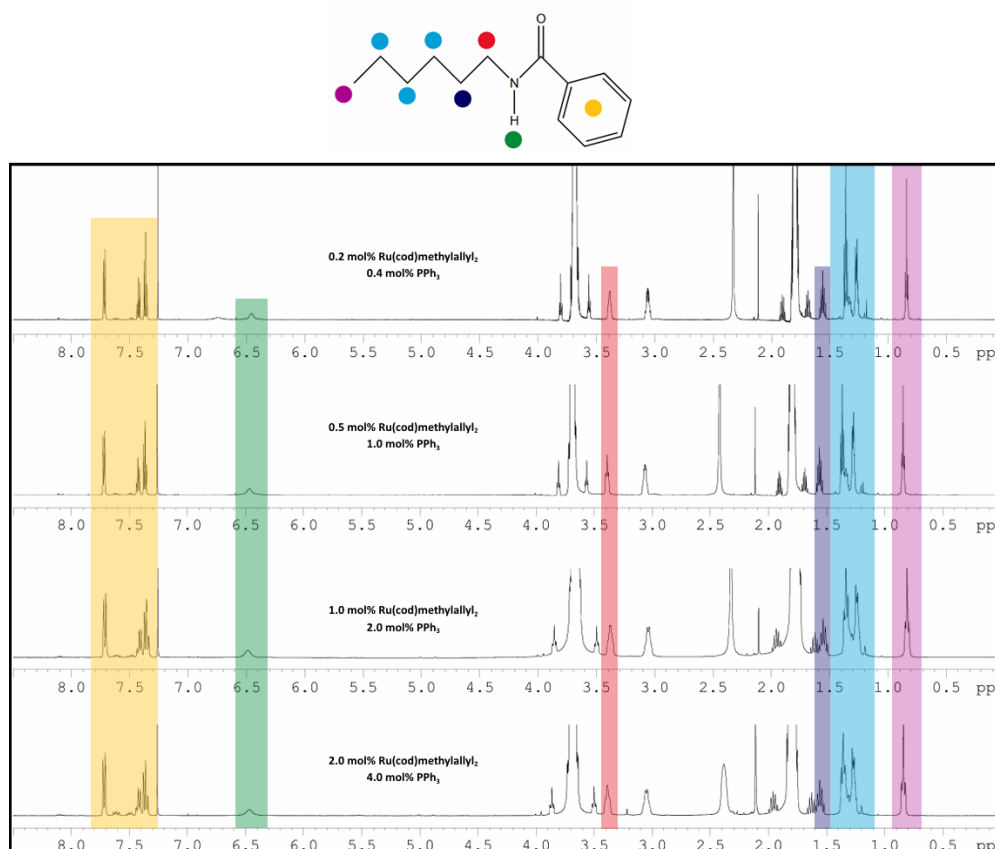


Figure 74: $\text{Ru}(\text{cod})\text{methylallyl}_2$ and PPh_3 show no inhibiting effect on the acylation. The highlighted peaks indicate characteristic protons of the product N-hexylbenzamide, indicating successful phthalimide formation with phthalic anhydride. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 1ml THF, 2h, 30°C , and 600 rpm.

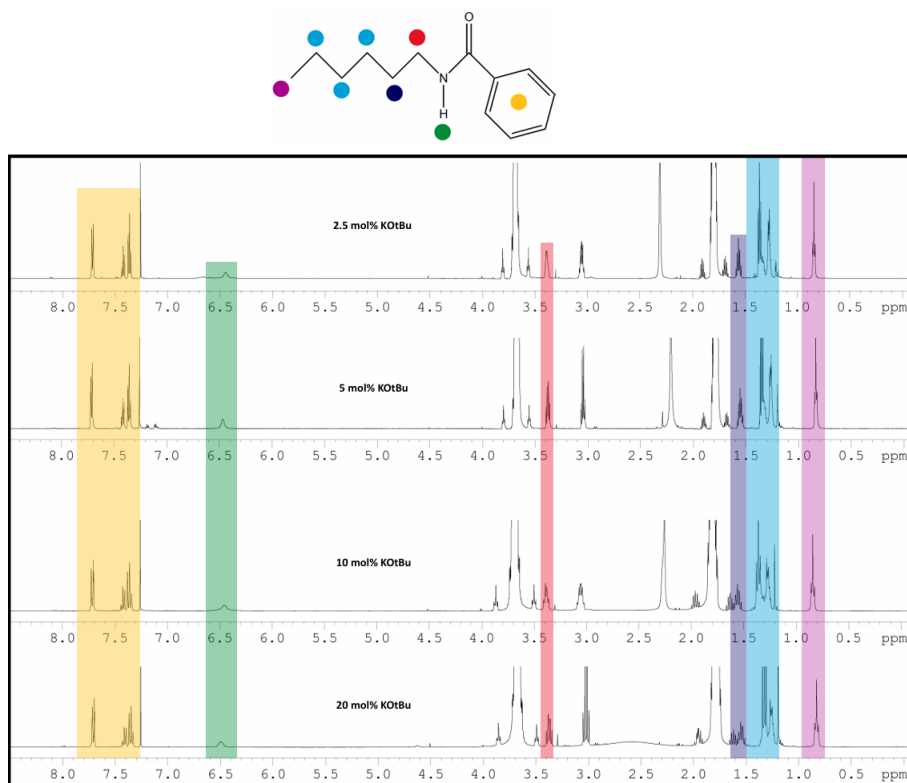


Figure 75: ^1H NMR indicates that KOtBu has no inhibiting effect on the acylation reaction. The highlighted peaks indicate characteristic protons of the product N-hexylbenzamide, indicating successful acylation with benzoyl chloride. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol benzoyl chloride, 0.375 mmol Et_3N , 1ml THF, 2h, 30°C , and 600 rpm.

Phthalimide formation

Internal standard for yield calculation

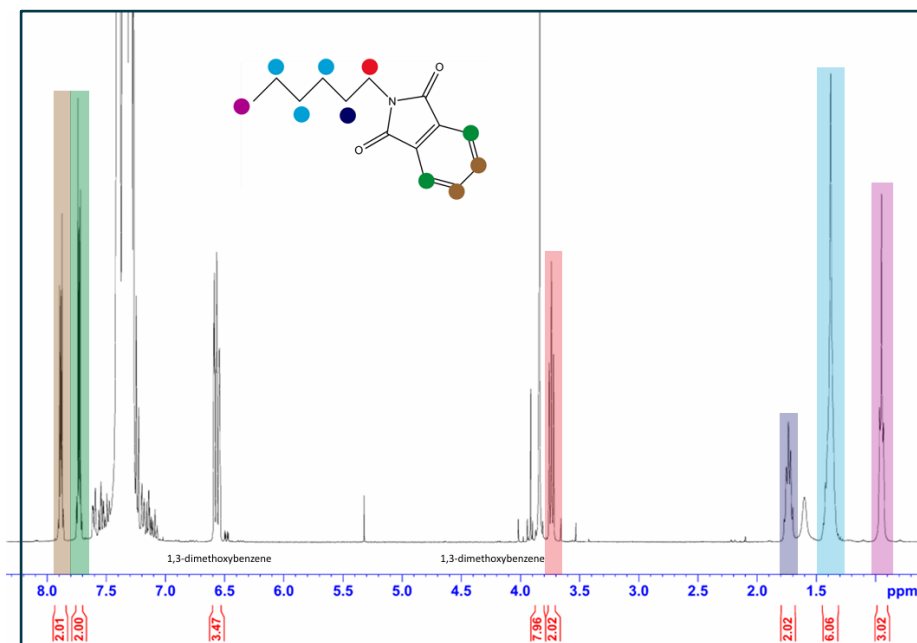


Figure 76: ^1H NMR spectrum of phthalimide formation in Xylene with 1,3-dimethoxybenzene as internal standard, giving an almost quantitative yield of 95%. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 1ml Xylene, 24h, 130°C , and 600 rpm.

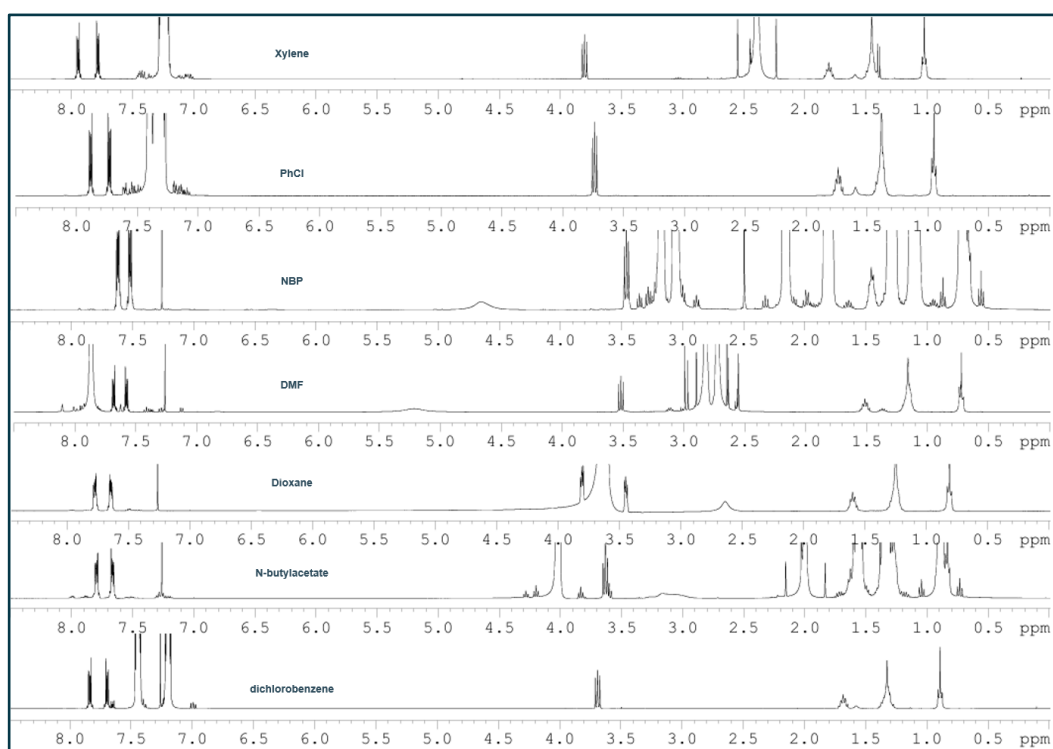


Figure 77: Solvent screening phthalimide formation, showing near-quantitative yields in all aprotic solvents with elevated boiling points. Reaction conditions: 0.25 mmol hexylamine, 0.25 mmol phthalic anhydride, 1 ml solvent, 24h, and 600 rpm.

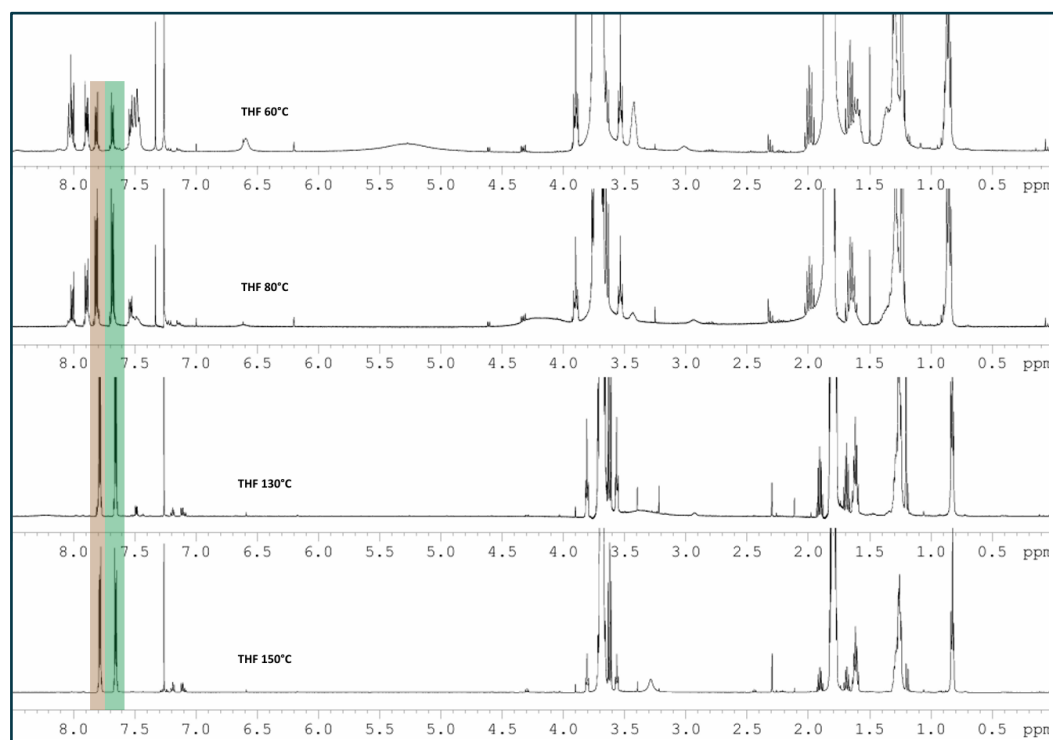


Figure 78: Phthalimide formation in THF at various temperatures, indicating increasing yield of phthalimides with increasing temperature, with a near quantitative yield at 150°C. Reaction conditions: 0.4 mmol hexylamine, 0.4 mmol phthalic anhydride, 2ml THF, 24h, and 600 rpm.

Inhibition studies

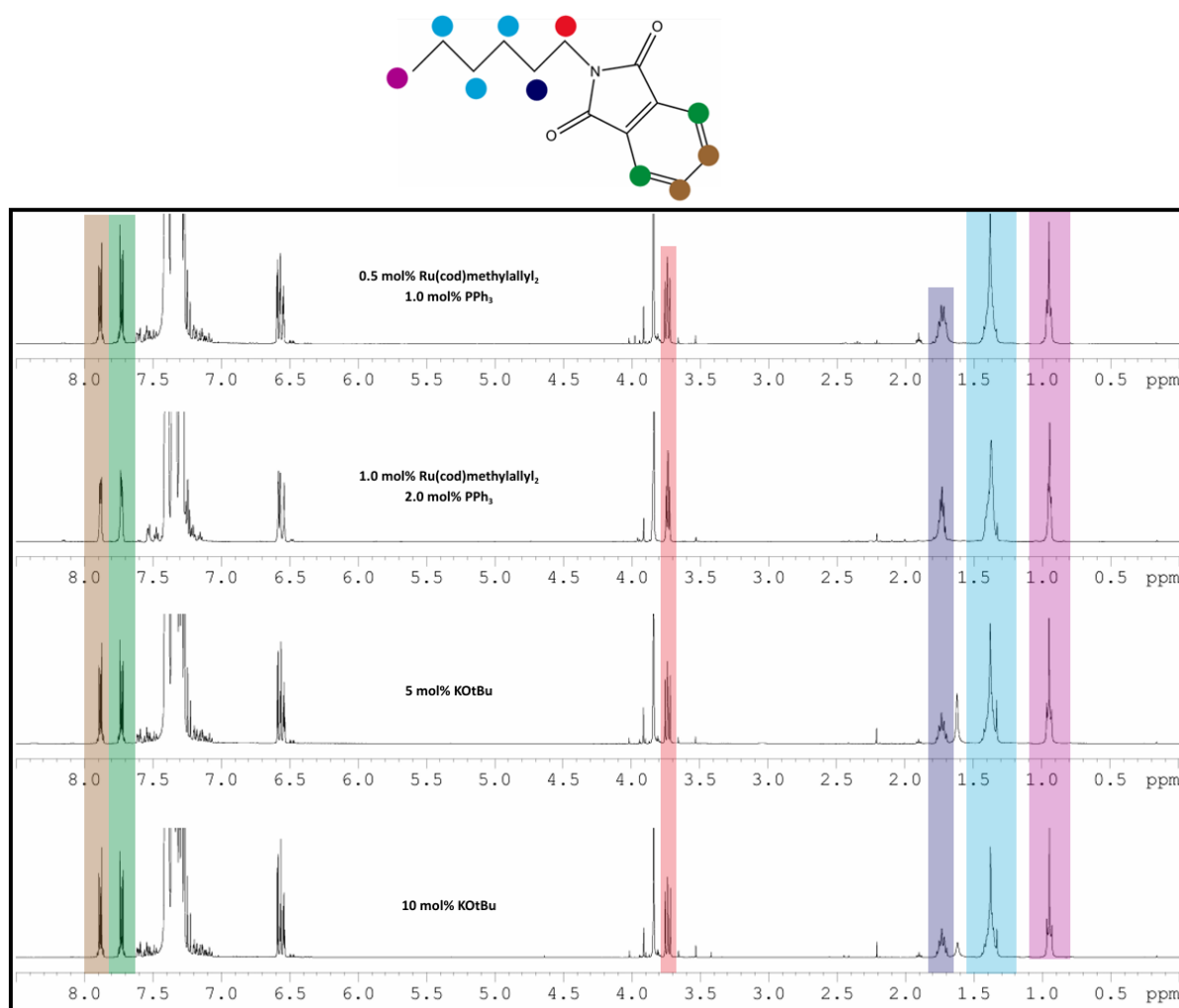


Figure 79: Inhibition study of $\text{Ru}(\text{cod})\text{methylallyl}_2$, PPh_3 , and KOtBu on phthalimide formation, showing the resulting ^1H NMR spectrum of N-hexylphthalimide. The highlighted signals correspond to characteristic protons of the product, confirming successful phthalimide formation through reaction with phthalic anhydride. Reaction conditions: 0.25 mmol substrate, 0.25 mmol phthalic anhydride, 1 ml PhCl , 24 h, 130 $^\circ\text{C}$, 600 rpm.

Appendix 4: Manganese as a catalyst

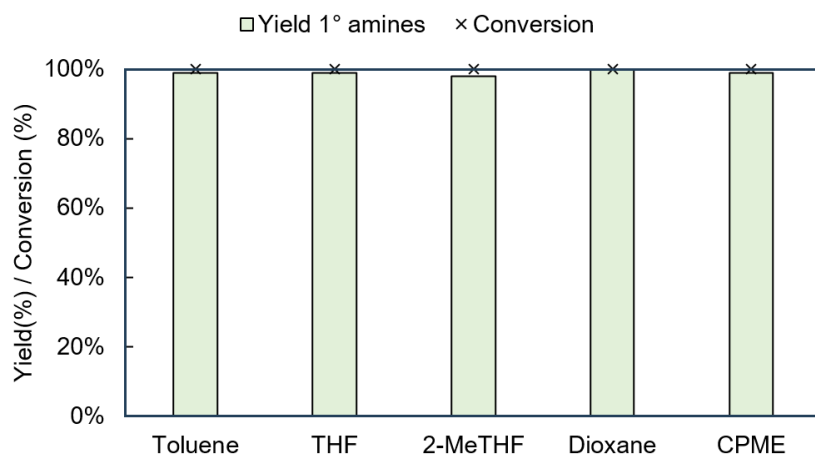


Figure 80: Complete nitrile hydrogenation according to the following conditions: 2 ml solvent (dry), 0.4 mmol hexanenitrile, 50 bar H₂, 2 mol% Mn-2, 20 mol% tBuOK, 100°C, 18h.

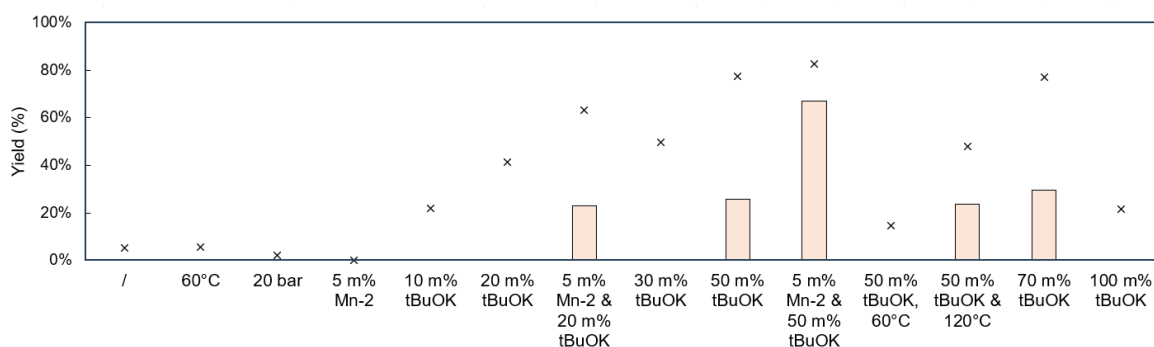


Figure 81: Poor olefinic double bond hydrogenation with Mn-2 catalyst. Standard conditions: 2 mL toluene (dry), 0.4 mmol (E)-4-octene, 50 bar H₂, 2 mol% Mn-2, 100°C, 18h.

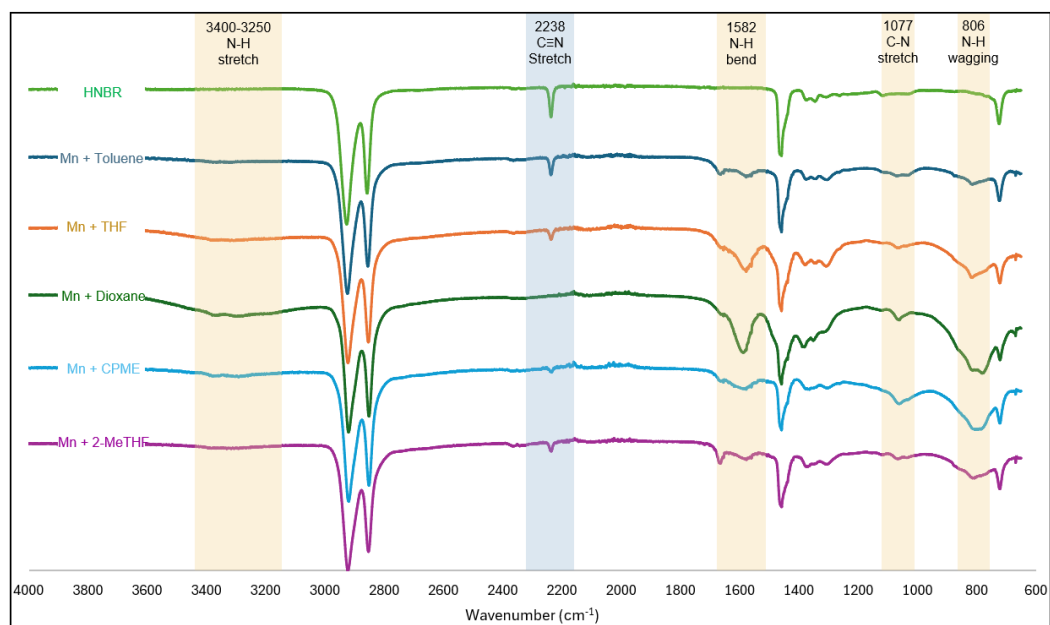


Figure 82: Solvent-screening HNBR according to the following conditions: 2 ml solvent (dry), 0.4 mmol hexanenitrile, 50 bar H₂, 2 mol% Mn-2, 20 mol% tBuOK, 100°C, 18h.

