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Sustainable synthesis of bio-based Poly(HydroxyUrethane)s (PHUs)

Guanfei Shen

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Guanfei SHEN

Sustainable Synthesis of Bio-based Poly(HydroxyUrethane)s (PHUs)

Devant le jury composé de :

Sylvain CAILLOL	Directeur de recherche CNRS, Montpellier	Rapporteur
Micheline DRAYE	Prof., Univ. Savoie Mont Blanc	Rapporteuse
Lorraine CHRIST	MdC, Université Claude Bernard Lyon 1	Examinatrice
Nadim EID	Ingénieur de Recherche, Arkema	Examineur
Yves QUENEAU	Directeur de recherche CNRS, Lyon	Président
Bruno ANDRIOLETTI	Prof., Université Claude Bernard Lyon 1	Directeur de thèse

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Résumé

La crise énergétique et l'utilisation des ressources fossiles qui entraînent des pollutions de plus en plus graves nécessitent un changement de paradigme. Par conséquent, le développement de produits chimiques plus respectueux de l'environnement et de procédés plus efficaces qui pourraient limiter l'utilisation d'intermédiaires et de processus toxiques a suscité de grands espoirs au cours des dernières décennies. Parmi les différentes stratégies pouvant être mises en œuvre dans ce but, la substitution des réactifs/monomères toxiques souvent utilisés dans la chimie des polyuréthanes (PUs) a stimulé de nombreuses innovations conduisant au développement de la version hydroxylée des PUs, les poly(hydroxyuréthane) (PHUs).

Les plastiques souvent non biodégradables provenant de sources fossiles ont entraîné de graves problèmes dans les écosystèmes naturels. Néanmoins, les polymères biosourcés sont considérés comme moins nocifs pour la santé humaine et l'environnement que leurs homologues à base de pétrole. Différents types de polymères biosourcés tels que le polylactide (PLA), les polyhydroxyalkanoates (PHA), le polyéthylène 2,5-furandicarboxylate (PEF), l'amidon modifié (PSM) et bien d'autres ont été développés dans le passé.

Dans le chapitre 1 de ce manuscrit, nous présentons l'histoire du développement des PUs. Compte tenu des avantages et des inconvénients des PUs, les chercheurs ont développé une nouvelle voie d'accès plus sûre aux polyuréthanes, ne nécessitant pas l'utilisation d'isocyanates (NIPUs pour Non Isocyanates PolyUrethanes) pour remplacer les PUs traditionnels. Parmi toutes les voies de synthèse possible pour accéder aux NIPUs, la polyaddition est la plus prometteuse permettant la préparation de PHUs (PolyHydroxyUrethanes). De nombreux paramètres (température, solvant, additifs, activité du carbonate cyclique et des diamines) peuvent affecter la réaction.

Les recherches sur les PHUs biosourcés s'intéressent principalement aux huiles végétales et à leurs dérivés. De plus, seules quelques monomères biosourcés ont été

utilisés dans la synthèse durable des PHUs. Parallèlement, des molécules biosourcées comme le cyclocarbonate de glycérol (glycerol carbonate, GC) ou des molécules plateformes comme le 5-hydroxyméthylfurfural (HMF), le furfural (FF), l'acide 2,5-furandicarboxylique (FDCA) ou différents diols ont été pleinement développées au cours des dernières décennies.

De plus, l'utilisation de solvants verts comme milieu réactionnel pour la mise en œuvre de réactions chimiques est plus respectueuse de la santé humaine et de l'environnement. Récemment, un solvant vert de type solvant eutectique profond (Deep Eutectic Solvent, DES) a suscité de nombreux espoirs car les DES présentent une excellente capacité de dissolution et pourraient jouer un rôle de catalyseur dans les systèmes réactionnels. La plupart des DES sont non toxiques, biodégradables, bon marché et faciles à préparer. A titre d'exemple, le DES (ChCl/Urée) a été proposé pour la première fois en 2003 et est depuis largement étudié.

Dans le chapitre 2 de cette thèse, nous décrivons une nouvelle méthode de synthèse de PHUs respectant de nombreux principes de la chimie verte (taux de carbone renouvelable, solvant «vert», absence d'additifs). Même les amines primaires α -méthylée, réputées comme étant faiblement réactives ont cette fois pu être mises en œuvre pour la préparation de PHUs. Ceci a été rendu possible par l'utilisation du DES ChCl/Urée qui est utilisé à la fois comme solvant « vert » et comme catalyseur. De plus, le haut pouvoir solvant et dissociant du DES permet la synthèse de polymères présentant un Mn assez élevé. Enfin, comme le bis-carbonate utilisé comme réactif clé contient un cœur FDCA qui est connu pour favoriser la biodégradabilité, il est attendu que cette approche permette le développement de PHU biodégradables.

Dans le chapitre 3 de la thèse, le 2,2-bifuryl-5,5-dicarboxylate (BFDCA-Bis-CC) et la diamine (5,5'-(propane-2,2-diyl) bis(furan-5,2-diyl))méthénamine (PBFA) sont issus de la biomasse. Nous avons proposé le DES (ChCl/Urée) comme solvant vert alternatif au solvant traditionnel (DMF) dans la réaction d'aminolyse entre le BFDCA-Bis-CC et les diamines. Comme précédemment, les amines faiblement réactives se sont avérées

suffisamment nucléophiles dans ces conditions. Une large gamme de PHUs a été obtenue, certains d'entre eux présentant d'excellentes propriétés thermodynamiques.

Dans le chapitre 4 de la thèse, nous avons synthétisé une série de monomères bifonctionnels préparés par transestérification du furanoate de diméthyle avec différents diols biosourcés. Dans une seconde étape, les esters méthyliques ont pu être transestérifiés par le carbonate de glycérol pour conduire au monomère réactif totalement biosourcé. Sur la base des travaux précédents, nous avons pu synthétiser une nouvelle série de PHU à partir du bis-cyclocarbonate biosourcé dans un DES.

Dans l'ensemble, nous avons développé une série de bis-cyclocarbonates furaniques entièrement biosourcés à partir du FDCA, de l'acide 2,2-bifuryl-5,5-dicarboxylique (BFDCA), du carbonate de glycérol et de diols selon les principes de la chimie verte, en évitant l'utilisation de produits chimiques (monomères, solvants) toxiques. Ainsi, nous avons développé l'utilisation de DES (ChCl/Urée) dans la réaction d'aminolyse pour synthétiser des PHUs. Même les amines primaires α -méthylées se sont révélées réactives dans des conditions relativement douces grâce à l'activité catalytique jouée par le DES. Nous avons également synthétisé des PHUs entièrement biosourcés à partir de BFDCA-Bis-CC et de PBFA. Les PHUs peuvent présenter des propriétés thermodynamiques classiques de PUs et donner une perspective encourageante aux polymères PHUs biodégradables. Nous espérons que ces premiers résultats inspireront d'autres chercheurs et ouvriront un nouveau champ d'application pour concevoir des voies durables et efficaces dans la réaction d'aminolyse à la synthèse des PHUs.

Mots clés : PolyHydroxyUréthane - Biosourcé - Acide 2,5-Furandicarboxylique - Acide 2,2-bifuryl-5,5-dicarboxylique - Diols - Carbonate de glycérol - Solvants eutectiques profonds - Aminolyse.

Abstract

With the depletion of the fossil energy and the more and more serious environment pollution, searching for a renewable energy and raw materials and achieving a more sustainable development become increasingly necessary. Among the different strategies that can be implemented towards this goal, the substitution of the toxic reagents/monomers often used in the polyurethanes (PUs) chemistry has stimulated much innovation leading to the development of the hydroxylated version of PUs, namely the poly(hydroxyurethane)s (PHUs).

The traditional non-biodegradable plastics originating from fossil sources have resulted in serious troubles in natural ecosystems. Nevertheless, bio-based polymers are believed to be less harmful for the human health and environment than their oil-based counter parts. Different types of bio-based polymers such as polylactide (PLA), polyhydroxyalkanoates (PHA), polyethylene 2,5-furandicarboxylate (PEF), plastarch material (PSM) and many others have been developed in the past.

In the chapter 1 of this thesis, we displayed the development history of PUs. In view of the merits and drawbacks of PUs, researchers developed new and safer non-isocyanate polyurethanes (NIPUs) alternative to replace the traditional PUs. Among all the routes to synthesize the NIPUs, the polyaddition is the most promising, giving the so-called PHUs. Many parameters (temperature, solvent, additives, activity of cyclic carbonate and diamines) can affect the reaction.

Bio-based PHUs research mainly focused on vegetable oils and their derivatives. In addition, only a few bio-based monomer molecules were applied in the sustainable synthesis of PHUs. Meanwhile, the bio-based glycerol cyclocarbonate (GC) and platform molecules (5-hydroxymethylfurfural (HMF), furfural (FF), 2,5-furandicarboxylic acid (FDCA), and diols have been fully developed in the recent 30 years.

Using a green solvent as medium for implementing chemical reaction is more friendly

for human health and environment. Recently, a green solvent consisting of deep eutectic solvents (DES) has aroused wide concern, as they exhibit excellent ability to dissolve materials and could play a catalyst role in reaction systems. Most DESs are non-toxic, bio-degradable, cheap, easily prepared. The ChCl/Urea DES was first proposed in 2003 and is widely studied for many popular applications.

In this thesis chapter 2, we disclose a highly efficient and sustainable method to synthesize PHUs, even with the poorly reactive, sterically hindered diamines. Our study indicates that the DES (ChCl/Urea) acts not only as a solvent but also as a catalyst. High molecular weight PHUs could be obtained thanks to the strong solubility character of the solvent. All the PHUs prepared contains the FDCA moiety. Knowing that the furanic ring is favorable for biodegradability, it is expected that our approach will be useful for the development of bio-degradable PHUs.

In the thesis chapter 3, the conventional solvent of DMF was replaced by the green solvent DES for the aminolysis reaction. After the reaction, different diamines afforded a large range of PHUs displaying different *M_w* that could exhibit excellent thermodynamic properties. The PHUs were synthesized using 2,2-bifuryl-5,5-dicarboxylate cyclic carbonate (BFDCA-Bis-CC) and the bio-based (5,5'-(propane-2,2-diyl) bis(furan-5,2-diyl))methenamine (PBFA) diamine in DES.

In the thesis chapter 4, access to eight bio-based diols connecting 5-(methoxycarbonyl)furan-2-carboxylic acid (Me-FDCA) is described. The screening of the different catalysts used to afford the GC-diols-FDCA from Me-diols-FDCA through transesterification is addressed. Finally, GC-hexylene glycol-FDCA and a GC-decene glycol-FDCA were obtained in 35% yield. In addition, the syntheses and characterization of PHUs from the bis-cyclocarbonate and different diamines in DES are reported.

All in all, we developed a series of fully bio-based furanic bis-cyclocarbonate from FDCA, 2,2-bifuryl-5,5-dicarboxylic acid (BFDCA), GC, and diols using the green

chemistry principles, avoiding the toxic chemicals and harsh reaction conditions. We introduced the DES (ChCl/Urea) as a solvent and catalyst to promote the aminolysis reaction and synthesize PHUs. Even α -methyl primary amines were proven reactive using mild reaction conditions thanks to the catalytic activity of the DES. We also achieved the synthesis of fully bio-based PHUs from BFDCA-Bis-CC and PBFA. We hope that our investigations will inspire other researchers to open a new scope in the design of sustainable and efficient routes in the aminolysis reaction to synthesize PHUs.

Key words: PolyHydroxyUrethane, Bio-based, 2,5-Furandicarboxylic acid, 2,2-bifuryl-5,5-dicarboxylic acid, Diols, Glycerol carbonate, Deep Eutectic Solvents, Aminolysis.

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ABBREVIATIONS

Abbreviation	Name
1,3-BDO	1,3-butanediol
1,3-PDO	1,3-propanediol
1,4-BDO	1,4-butanediol
2,3-BDO	2,3-butanediol
5CC	Five-membered CC
6CC	Six-membered CC
7CC	Seven-membered CC
8CC	Eight-membered CC
BAMF	2,5-bis(aminomethyl)furan
BFDCA	2,2-bifuryl-5,5-dicarboxylic acid
BHMF	5,5'-bihydroxymethyl furil
BHMH	Tetraol 5,5'-bihydroxymethyl hydrofluoric
BPFA	5,5'-Isopropylidenedifurfurylamine
Catal.	Catalyst
CC	Cyclic carbonate
ChCl	Choline chloride
CHDA	1,3-cis-bis(aminomethyl)cyclohexane
CMR	Carcinogenic, mutagenic, and reprotoxic
DA6	1,6-hexanediamine
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	N,N'-dicyclohexylcarbodiimide
DES	Deep eutectic solvent
DFF	2,5-diformylfuran
DHMF	5,5'-dihydroxymethyl furoin
DMAP	4-dimethylaminopyridine
DMC	Dimethyl carbonate
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
EDG	Electron donating group
EDR-148	Ethylene glycol bis(2-aminoethyl) ether
EG	Ethylene glycol
ERG	Electron-releasing group
EWG	Electron-withdrawing group
FAM	Furfuryl amine
FDCA	2,5-furandicarboxylic acid
FF	Furfural
FFCA	5-formyl- 2-furancarboxylic acid
FDCA-mCC	Furandicarboxylate-mono-cyclocarbonate
GC	Glycerol carbonate
GPC	Gel permeation chromatography

HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HDESs	Hydrophobic DESs
HDI:	Hexamethylene diisocyanate
HEMA	2-hydroxyethyl methacrylate
HMDI	Methylene-bis(4-cyclohexylisocyanate)
HMF	5-hydroxymethylfurfural
HMFCFA	5-hydroxymethyl-2 furandicarboxylic acid
H-NIPU	Hybrid Non-Isocyanate PolyUrethane
Ils	Ionic liquids
IPDA	Isophorone diamine
IPDI	Isophorone diisocyanate
m-CPBA	m-chloroperoxybenzoic acid
MDI	Diphenylmethane diisocyanate
MMA	Methyl methacrylate
MS	Mass spectrometry
MTBD	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene
MXDA	m-xylylenediamine
NaDESs	Natural deep eutectic solvents
NIPU	Non-Isocyanate PolyUrethane
NMR	Nuclear Magnetic Resonance
PBFA	(5,5'-(propane-2,2-diyl)bis(furan-5,2-diyl))dimethanamine
PBT	Polybutylene terephthalate
PC	Propylene carbonate
PDI	Polydispersity
PEF	Poly(ethylene 2,5-furandicarboxylate)
PEG	Poly ethoxylate glycol
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PHU	PolyHydroxyUrethane
PLA	Poly lactide
PSM	Plastarch material
PTT	Polypropylene terephthalate
PU	PolyUrethane
scCO ₂	Supercritical CO ₂
SCF	Super critical fluid
SEC	Size-exclusion chromatograms
SUPRADESs	Supramolecular deep eutectic solvents
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TDI	Toluene diisocyanate
TEA	Triethylamine
TETA	Triethylenetetramine
T _g	Transition temperature
TGA	Thermogravimetric analyses
THEDESs	Therapeutic DESs
Tol.	Toluene
VOCs	Volatile organic compounds

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General introduction

General introduction

Plastics play a pivotal role in our life, and the polyurethanes (PUs) are the 6th most widely used. They are applied in furnishing, cars, clothing, shoes, elastomers, coatings, wall and roofing insulation. Nevertheless, the use toxic isocyanate for their synthesis and decomposition producing toxic HCN or aromatic amines. Therefore, researchers developed a series of pathways to replace the traditional PUs, including polycondensation, rearrangement, ring-opening polymerization, and polyaddition. The polyaddition through aminolysis reaction give the most brightly perspective to synthesize non-isocyanate polyurethanes (NIPUs) compared with the other three methods. The aminolysis reaction between bis-cyclocarbonates and diamines giving the named poly(hydroxyurethane)s (PHUs), and greener methods to synthesize the cyclocarbonates have been developed. Many researchers work indicated that the structure of cyclocarbonates and diamines, temperature, additives etc. can affect the reaction.

The bio-based molecules have been developed to replace the fossil-based chemicals, and some of them can be produced from biomass in the industry. Glycerol as a by-product of industrial bio-diesel is produced in large quantities, and furfural (FF) market volume is limited because of its' monofunctional group. The glycerol carbonate (GC) from the glycerol have been developed, and we developed a series of pathways to synthesize 2,5-furandicarboxylic acid (FDCA) and 2,2-bifuryl-5,5-dicarboxylate cyclic (BFDCA) from FF and its' derivatives.

Deep eutectic solvent (DES) is one of the most attractive green solvents in recent 20 years. Although it can be applicated in many reaction types because of its excellent solubility, it is mainly used in free-radical polymerization.

All the work in the thesis including three parts. Firstly, we synthesized fully bio-based furan-2,5-dicarboxylate bis cyclic carbonate (FDCA-Bis-CC) through the transesterification, introduced the DES (ChCl/Urea) as solvent and catalyst to

aminolysis reaction. After the reaction, we received good M_n (number-average molecular weight) PHUs. Secondly, we used different types of diamines to aminolysis of 2,2-bifuryl-5,5-dicarboxylate cyclic carbonate (BFDCA-Bis-CC) in DES (ChCl/Urea), and received a wide range of M_w (mass average molar mass) PHUs. Thirdly, we afforded a series of bio-based diols connected 5-(methoxycarbonyl)furan-2-carboxylic acid (Me-FDCA), and then we obtained the Bis-CC from the hexylene glycol, isosorbide, and decene glycol connected Me-FDCA with GC through transesterification.

After a general conclusion, all procedures and experimental data are displayed in the experimental section.

Chapter 1

Chapter 1 Bibliography

1 Introduction

Polyurethanes (PUs), obtained by the polyaddition reaction of diols and diisocyanates, were invented back in 1930's by Otto Bayer and co-workers from the works of Würtz, who discovered the reaction between isocyanate and alcohol affording urethane groups in 1849. ^[1] In light of their excellent properties, PUs became a major polymer family that found applications in various areas such as furnishing, cars, clothing, shoes, elastomers, coatings, wall and roofing insulation, etc... ^[2-3] The share of PUs ranks 6th among all polymers on the European market in 2011 (Figure 1), with an annual worldwide production of around 18 million tons in 2016. ^[4] Conventionally, PUs originate from the polyaddition of a diol (or polyol) onto a diisocyanate (or polyisocyanate). The latter is directly synthesized by reaction of the corresponding amine with phosgene, which is highly toxic. ^[5] Until recently, PUs is either put into landfills or burnt at the end of life, but the PUs' combustion releases poisonous isocyanates and their degradation produces toxic amines. ^[6]

Environmentally friendly (sustainable) chemical products and procedures have been developed in academia and industry for 40 years, mainly because of the growing global awareness related to the urgent need to protect the environment and the depletion of fossil feedstocks. ^[7-8] In addition, for safety and health reasons, it is highly urgent to proscribe the use of toxic reagents such as the phosgene for the synthesis of isocyanates that are key intermediates for the synthesis of PUs. ^[9] Recently, it has

¹ Bayer, O. *Angew. Chem.* **1947**, *59*, 257–272.

² Delebecq, E.; Pascault, J. P.; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80–118.

³ Szycher, M. *Handbook of polyurethanes*. CRC Press, Boca Raton, FL. **1999**.

⁴ Cornille, A.; Auvergne, R.; Figovsky, O.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2017**, *87*, 535–552.

⁵ Gupta, S.; Upadhyaya, R. *Int. J. Pharm. Res. Bio-Sci* **2014**, *3*, 20–28.

⁶ Benbow, A. W.; Cullis, C. F. *Combust. Flame* **1975**, *24*, 217–230.

⁷ Anastas, P. T. *Green Chem.* **2003**, *5*, 29–34.

⁸ Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301–312.

⁹ Kreye, O.; Mutlu, H.; Meier, M. A. R. *Green Chem.* **2013**, *15*, 1431–1455.

been shown that using renewable resources, non-toxic, and lower energy processes could solve the environmental and energy crisis. ^[10]

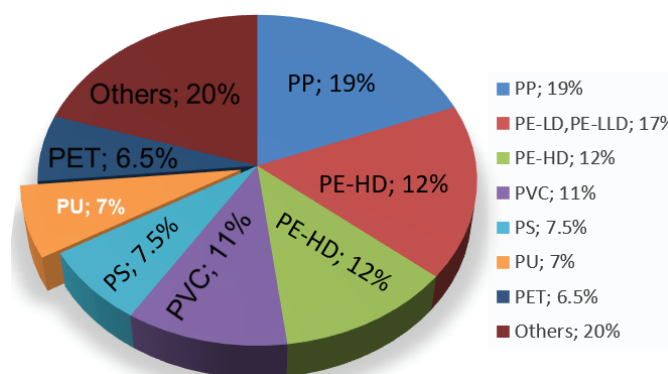


Figure 1. Main polymer materials in the European plastic market in 2011

2 PolyUrethane (PU)

Initially, PUs were first developed as an alternative for rubber during the period of World War II. Interestingly, PUs can be synthesized from a diversity of polyols and isocyanates. As a consequence, PUs have become very popular polymers found in a large range of applications. For instance, PU coatings were specifically applied by impregnating paper and garments in order to confer resistance to mustard gas and corrosion. ^[11] They were also involved in chemically resistant coating for masonry, metal, and high gloss finishes in airplanes and wood. ^[12] Using different formulations to produce PUs for specific industrial purposes, in the mid-50s, they were usually found in coatings, rigid foams, elastomers, and adhesives. ^[13] Towards the late 50s, the flexible PU foams could produce convenient and comfortable cushions for commercial uses. Using cheap polyether polyols to produce flexible foams found uses in several upholstery and automotive uses which are available at present. ^[11] Subsequently, these polymers could be used in various applications, increasing

¹⁰ Carré, C.; Ecochard, Y.; Caillol, S.; Avérous, L. *ChemSusChem* **2019**, *12*, 3410–3430.

¹¹ Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R. *RSC Adv.* **2016**, *6*, 114453–114482.

¹² Seymour, R. B.; Kauffman, G. B. *J. Chem. Educ.* **1992**, *69*, 909–912.

¹³ Petrović, Z. S.; Ferguson, J. *Prog. Polym. Sci.* **1991**, *16*, 695–836.

processing techniques, additives types, and formulations. ^[14] The materials contain the durability and toughness abilities of metal and the elasticity property of rubber, so they are suitable to replace the rubber, metal, and plastics in some engineered products. ^[15] They are popularly used in automotive, textiles, building and construction, bio-medical applications, and other industries due to their excellent strength, elongation, hardness, and modulus properties. ^[16-17]

2.1 The pathway to the PUs synthesis

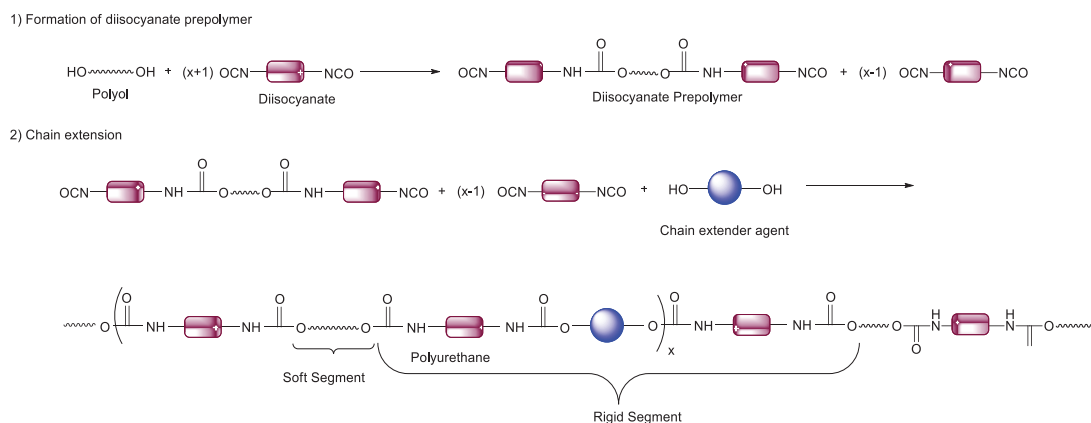
PUs contains the repeating unit of the urethane group derived from the reaction between hydroxyl (-OH) and isocyanate (-NCO) functions. Other groups such as urea, ester, and ether could also be found in PUs. Traditionally, there are two major steps to synthesize PUs. ^[9] Firstly, an excess of diisocyanate is introduced in a polyol. Next, the NCO end-group of the PU prepolymer is reacted with another polyol as chain extender, usually low molecular weight diols (e.g., 1, 4-butanediol) to produce the corresponding PUs (Scheme 1). ^[3] The obtained PUs contains soft segments and rigid segments. Initially, most polyols originate from petroleum, but the urgent environmental concerns and energy crisis make it necessary to search for more sustainable and environment-friendly resources.

¹⁴ Chattopadhyay, D. K.; Raju, K. V. S. N. *Prog. Polym. Sci.* **2007**, *32*, 352–418.

¹⁵ Rafiee, Z.; Keshavarz, V. *Prog. Org. Coat.* **2015**, *86*, 190–193.

¹⁶ Zia, K. M.; Anjum, S.; Zuber, M.; Mujahid, M.; Jamil, T. *Int. J. Biol. Macromol.* **2014**, *66*, 26–32.

¹⁷ Romaskevicius, T.; Budriene, S.; Pielichowski, K.; Pielichowski, J. *Chemija* **2006**, *17*, 74–89.



Scheme 1. Two-step synthesis of PUs ^[3]

Generally, polyols and isocyanates are reacted in the presence of either catalysts or ultraviolet light activation to produce PUs. ^[18] The different types of polyols and isocyanates directly affect the properties of PUs. ^[19] The polyols having long flexible segments and low crosslinking are always used to produce soft elastomeric polymers, whereas the rigid PUs contain shorter chains and more cross linkages. ^[20] Furthermore, modifying the ratio of the long chains and the amount of cross linkages would afford desired foam polymers. Isocyanates and polyols, along with a variety of additives, as well as different processing conditions, would confer various characteristic feature to the polymers and allow achieving a wide range of applications. ^[21]

Polyols incorporating two or more hydroxyl groups used for PU synthesis and various commercially available polyols can be prepared in various ways. For instance, polyether polyols are synthesized from ethylene oxide by reaction with a suitable polyol precursor and copolymerization of propylene oxide (Scheme 2); ^[22] meanwhile, the polyester polyols are prepared using a strategy similar to the strategy used for

¹⁸ Soto, M.; Sebastián, R. M.; Marquet, J. *J. Org. Chem.* **2014**, *79*, 5019–5027.

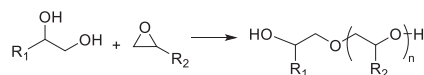
¹⁹ Charlon, M.; Heinrich, B.; Matter, Y.; Couzigné, E.; Donnio, B.; Avérous, L. *Eur. Polym. J.* **2014**, *61*, 197–205.

²⁰ Mihail, L. *Chemistry and Technology of Polyols for Polyurethanes*. iSmithers Rapra Publishing, **2005**.

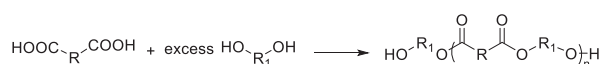
²¹ Nik Pauzi, N. N. P.; A. Majid, R.; Dzulkifli, M. H.; Yahya, M. Y. *Compos. Part B Eng.* **2014**, *67*, 521–526.

²² A, Zoran; S, P. *Polym. Rev.* **2008**, *48*, 109–155.

polyesters synthesis through polyesterification (Scheme 3).^[23] Indeed, the polyether polyols are the main polyols (75%) used for the PUs syntheses. The remaining part mainly concerns the polyesters polyols.^[9, 24]



Scheme 2. Access to polyether polyols



Scheme 3. Access to polyester polyols

At present, using bio-based polyether polyols derived from sorbitol and sucrose to synthesize PUs can increase the renewable content of PUs. Furthermore, propane-1,3-diol derived from glycerol can be used to synthesize polyether polyol by polycondensation. In addition, polyester polyols can originate from bio-based raw material and are generally produced from bio-based diacids (succinic acid and adipic) and glycols (propane-1,3-diol and 1,4-butanediol). Other polyols structures are shown in Figure 2. The synthesis of polyhydroxyurethanes (PHUs) can match some special requirement manufacture of the elastomers, sealants, and adhesives.^[11]

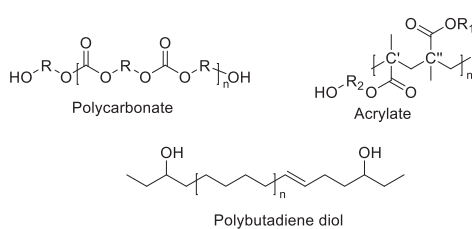


Figure 2. Various types of polyols

Even though a mixture of polyols with different molecular weights are usually used in the industry, the ratio of different polyols is carefully controlled to synthesize PUs with specific properties. Low molecular weight polyols (a few hundred $\text{g}\cdot\text{mol}^{-1}$) are used for

²³ Domanska, A.; Boczkowska, A. *Polym. Degrad. Stab.* **2014**, *108*, 175–181.

²⁴ Desroches, M.; Escouvois, M.; Auvergne, R.; Caillol, S.; Boutevin, B. *Polym. Rev.* **2012**, *52*, 38–79.

producing rigid PUs, whereas high molecular weight polyols (Mw range from 2,000 - 10,000 g·mol⁻¹) are used for producing flexible PUs. [25] On the other hand, the isocyanates have a high reactive activity with hydroxyl in theory. Interestingly, the reaction processes at a slow rate at room temperature. [26] Thus, the use of surfactants for increasing the phase compatibility and catalysts for polarizing the isocyanate or the hydroxyl function are necessary to improve the reaction kinetics. [27-28] So, the electrophilic ability of an isocyanate can be increased by decreasing the electron density of the NCO group from N or O atoms. Aliphatic isocyanates such as isophorone diisocyanate (IPDI) and methylene-bis(4-cyclohexylisocyanate) (HMDI) are generally poorly reactive compared with the aromatic congeners such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). [29] The related structures of the previously mentioned isocyanates are shown in the Figure 3.

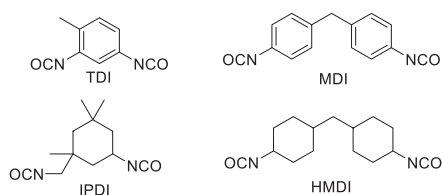


Figure 3. Aromatic vs aliphatic isocyanates

Nevertheless, the application of PUs has resulted in several health and environmental concerns from their birth to their end of life. Firstly, deadly phosgene is necessary for converting amines to the corresponding isocyanates. Secondly, TDI and MDI are classified as CMR (Carcinogenic, Mutagenic, and Reprotoxic), hence labelled as “Substances of Very High Concern” by the European REACH Regulation. [30 - 31]

²⁵ Ionescu, M. *Chemistry and Technology of Polyols for Polyurethanes*. 2nd Edition, Shrewsbury: iSmithers Rapra Publishing, **2016**.

²⁶ Sonnenschein M. F. *Polyurethanes: science, technology, markets, and trends*. John Wiley & Sons, **2021**.

²⁷ Motamedi, M.; Tehrani-Bagha, A. R.; Mahdavian, M. *Prog. Org. Coat.* **2014**, *77*, 712–718.

²⁸ Zheng, J.; Luo, J.; Zhou, D.; Shen, T.; Li, H.; Liang, L.; Lu, M. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *363*, 16–21.

²⁹ Saunders, J. H.; Slocombe, H. J. *Chem. Rev.* **1948**, *43*, 203–218.

³⁰ United Nations. Economic Commission for Europe. Secretariat. *Globally harmonized system of classification and labelling of chemicals (GHS)*. Midland, MI, USA, **2015**.

³¹ Bello, D.; Herrick, C. A.; Smith, T. J.; Woskie, S. R.; Streicher, R. P.; Cullen, M. R.; Liu, Y.; Redlich, C.

Moreover, people are more and more concerned about isocyanates, and government laws and regulations prohibit several isocyanates in particular because the decomposition of PUs might result in the production of toxic HCN or aromatic amines.

[32-33]

2.2 The PUs' application market

The PUs can be synthesized from a wide variety of starting materials. They are classified as rigid, flexible, coating, elastomers, adhesives, sealants, thermoplastic, binders, and waterborne for different purposes. [11] Significant amount of PU foam is used worldwide. In this sense it is one of the most outstanding applications among the various products. The PU market (Figure 4) is shared in volumes between flexible foams (31%), rigid foams (25%), molded foams (11%), adhesives and sealants (6%), and elastomers (6%). [34] The building and fridge-freezer insulation panels mainly contain rigid foams, while the mattresses, seats, sofas, and automotive usually contain flexible foams. [4]

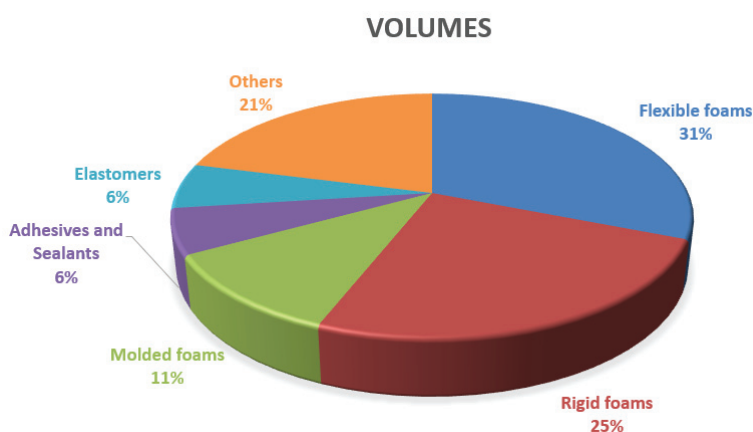


Figure 4. The global PUs market share in 2016

A. *Health Perspect.* **2007**, *115*, 328–335.

³² Levchik, S. V.; Weil, E. D. *Polym. Int.* **2004**, *53*, 1585–1610.

³³ McKenna, S. T.; Hull, T. R. *Fire Sci. Rev.* **2016**, *5*, 1–27.

³⁴ Ecochard, Y.; Caillol, S. *Eur. Polym. J.* **2020**, *137*, 109915.

PU foams could be easily modified according to different strategies by changing the types and quantities of polyol, isocyanate, catalyst, blowing agents, and the extent of exfoliation and intercalation between matrices and fillers to obtain the desired products. ^[31, 35] Generally, flexible PU foams are segmented copolymers. Thus, their properties depend on the phase separation between the soft and the hard segments. ^[36] Adapting the ratio of the two segments affects durability, density, tearing resistivity, firmness, surface elasticity, combustibility, etc. Those properties ensure an excellent flexibility. The rigid PU foams generally have high physical and mechanical properties. The hydroxyl group category (primary or secondary) could profoundly affect the rigid PU foams properties, and the primary hydroxyl are more reactive than the secondary. ^[37] Therefore, the mixture of polyols containing two kinds of hydroxyls can be used for the different applications. ^[20]

Specific PUs have excellent properties such as chemical and corrosion resistance, good abrasion, toughness, high mechanical strength, and low-temperature flexibility, making them a popular coating application. ^[38-39] Another pivotal family of PUs is "polyurethane elastomers" that have been deeply introduced into various engineered products and displayed obviously irreplaceable properties, such as excellent stress recovery properties, lighter than metals, and strong environmental tolerance. ^[40-41]

³⁵ Taheri, N.; Sayyahi, S. *E-Polymers* **2016**, *16*, 65–73.

³⁶ Cinelli, P.; Anguillesi, I.; Lazzeri, A. *Eur. Polym. J.* **2013**, *49*, 1174–1184.

³⁷ Heinen, M.; Gerbase, A. E.; Petzhold, C. L. *Polym. Degrad. Stab.* **2014**, *108*, 76–86.

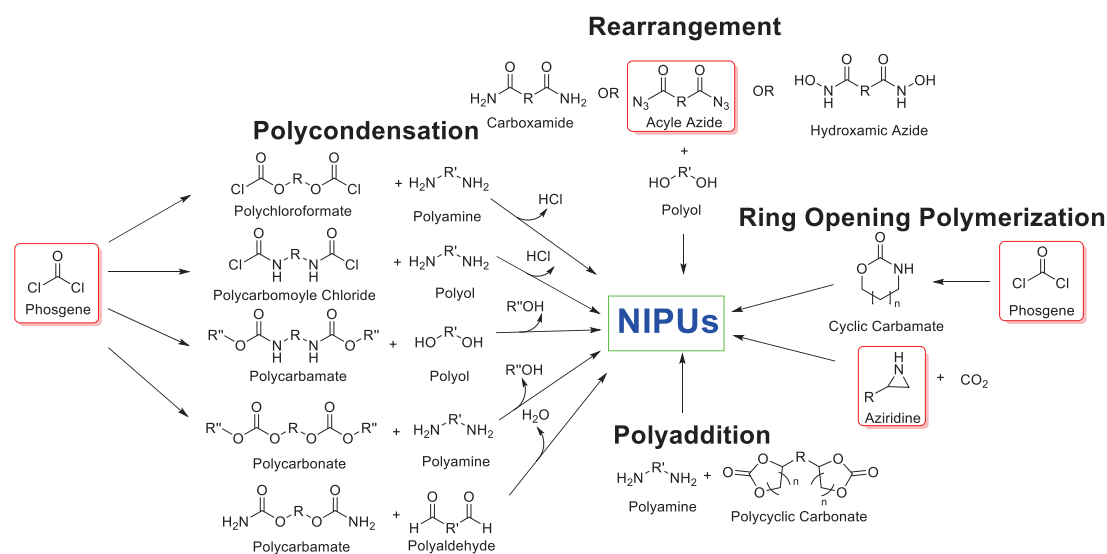
³⁸ Ismail, E. A.; Motawie, A. M.; Sadek, E. M. *Egypt. J. Pet.* **2011**, *20*, 1–8.

³⁹ Xu, Y.; Petrovic, Z.; Das, S.; Wilkes, G. L. *Polymer* **2008**, *49*, 4248–4258.

⁴⁰ Zia, K. M.; Zuber, M.; Saif, M. J.; Jawaid, M.; Mahmood, K.; Shahid, M.; Anjum, M. N.; Ahmad, M. N. *Int. J. Biol. Macromol.* **2013**, *62*, 670–676.

⁴¹ Zia, K. M.; Bhatti, H. N.; Ahmad Bhatti, I. *React. Funct. Polym.* **2007**, *67*, 675–692.

3 Non-Isocyanate PolyUrethanes (NIPUs)



Scheme 4. Overview of NIPUs synthesis routes [2, 42-43]

Given the drawbacks inherent to the use of isocyanates in the synthesis of PUs, the so-called NIPUs (Non-Isocyanate PolyUrethanes) have been developed. Academic and industrial researchers have paid much hard work to explore alternative routes to synthesize isocyanate-free polyurethanes (NIPU, PHU, H-NIPU) over the past decades. The NIPUs (Non-isocyanate PolyUrethanes) correspond to the generic name of isocyanate-free polyurethanes. The NIPUs could be synthesized from the reaction between cyclic carbonates (CCs) and amines that could produce hydroxyurethane repeating units, giving the PHU name (PHU: PolyHydroxyUrethane). Furthermore, another nomenclature, namely H-NIPU for Hybrid Non-Isocyanate PolyUrethane is used to describe respectively monomers and copolymers of NIPU with other polymers. Polyaddition, polycondensation, ring-opening-polymerization, and rearrangement are the major four synthetic routes that are reported in the literature, and they are all shown in Scheme 4. [2, 42-43]

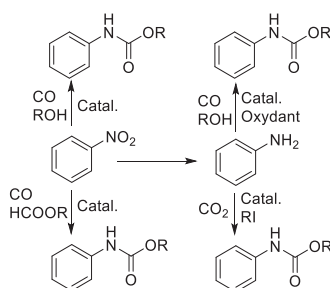
⁴² Blattmann, H.; Fleischer, M.; Bähr, M.; Mülhaupt, R. *Macromol. Rapid Commun.* **2014**, *35*, 1238–1254.

⁴³ Suryawanshi, Y.; Sanap, P.; Wani, V. *Polym. Bull.* **2019**, *76*, 3233–3246.

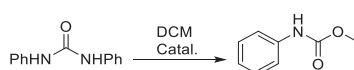
3.1 The different pathways to NIPU synthesis

3.1.1 Polycondensation pathway (Transurethanization)

The polycondensation routes involves different protocols such as the reactions between a polychloroformate and a polyamine, a polycarbamate and a polyol by transurethanization, a polycarbamoyl chloride and a polyol, polycarbonate and a polyamine (Scheme 4). However, the different routes still need the use of phosgene or an isocyanate with an alcohol for the synthesis of polycarbamate, and produces HCl along the reaction, which is a serious limitation for an application in industry. [44] Therefore, the search for a sustainable pathway to the synthesis of polycarbamates was proposed, and some useful methods have been developed starting from nitro compounds, oxidative amines, and urea (Scheme 5 and Scheme 6). [45-46]



Scheme 5. Carbamates from nitro compounds and amines



Scheme 6. Example of a carbamate synthesis from a urea

However, these reactions are generally launched at high temperatures. Another reaction between polycarbamate and polyaldehyde seems to be promising (Scheme 4), but there is a long way to increase the yield. [47] So far, the developed methods need catalysts, long reaction time, extra operation to purify the product, and toxic by-

⁴⁴ Nowick, J. S.; Powell, N. A.; Nguyen, T. M.; Noronha, G. *J. Org. Chem.* **1992**, *57*, 7364–7366.

⁴⁵ Paul, F. *Coord. Chem. Rev.* **2000**, *203*, 269–323.

⁴⁶ Shi, F.; Deng, Y. *J. Catal.* **2002**, *211*, 548–551.

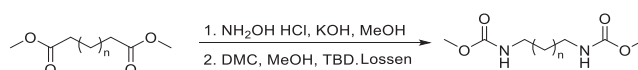
⁴⁷ Argyropoulas, J. N.; Bhattacharjee, D. EP, Patent, 0879946A2, **1998**.

products are produced at times. ^[48] Thus, these drawbacks limit the development of the polycondensation strategy at the industrial scale.

3.1.2 Rearrangement

The rearrangement approach toward the synthesis of NIPUs includes acyl azides (Curtius rearrangement), carboxamides (Hoffman rearrangement), or hydroxamic azides (Lossen rearrangement) (Scheme 4). ^[49 - 50] The Curtius and Hofmann rearrangements involve highly toxic reagents. Among these rearrangement reactions, isocyanates are produced *in situ*. The latter next reacts with the alcohols to afford PUs, and halogens such as chlorine and bromine are necessary. In addition, the starting materials such as acyl azides, carboxamides, and hydroxamic azides are highly toxic chemicals, and the isocyanate is an ineluctable intermediate.

Yet, the Lossen rearrangement reaction gives researchers a chance to explore a toxic-free pathway to synthesize NIPU. Unverferth *et al.* ^[51] developed diols and dimethyl dicarbamates from bio-based castor oil with dimethyl carbonate (DMC) using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst to synthesize carbamate, thus avoiding the isocyanate production reduces the toxicity of the reaction (Scheme 7).



Scheme 7. Synthesis of a carbamate through Lossen rearrangement

⁴⁸ Datta, J.; Włoch, M. *Polym. Bull.* **2016**, *73*, 1459–1496.

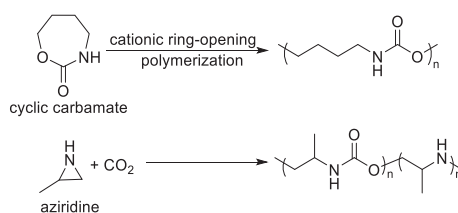
⁴⁹ Guan, J.; Song, Y.; Lin, Y.; Yin, X.; Zuo, M.; Zhao, Y.; Tao, X.; Zheng, Q. *Ind. Eng. Chem. Res.* **2011**, *50*, 6517–6527.

⁵⁰ Turnbull, K.; Scriven, E. F. V. *Chem. Rev.* **1988**, *88*, 298–368.

⁵¹ Unverferth, M.; Kreye, O.; Prohammer, A.; Meier, M. A. R. *Macromol. Rapid Commun.* **2013**, *34*, 1569–1574.

3.1.3 Ring-opening polymerization

The ring-opening polymerization of aliphatic cyclic carbamates or aziridines can also afford NIPUs (Scheme 8).^[52-53] Although these routes do not produce any by-products, these reactions are often launched at relatively high temperatures and the cyclic carbamates generally originate from phosgene, and the harmful aziridines still are a significant issue. Researchers have made many efforts to explore sustainable methods for the synthesis of cyclic carbamates, but as we all know there is not any method that can give a relatively less toxic aziridine ring.



Scheme 8. Ring opening access to NIPUs

3.1.4 The cyclic carbonate pathway (polyaddition)

The last but not the least pathway is the polyaddition of CCs and amines to synthesize NIPU. This route seems to be the best choice since it avoids the use of the toxic phosgene and isocyanates.^[48, 54] Furthermore, the CCs are not harmful, and the aminolysis reaction between cyclic carbonate (CC) and amine generally does not produce side products such as urea and CO₂.

The formation of the CC is the first step of the polyaddition reaction, and the reaction of an epoxide with CO₂ is the most efficient way to synthesize CCs (Scheme 9). However, this reaction needs a special catalyst and often proceeds at relatively high pressure and temperature, thus, limiting the application of the method in industry.^{[55-}

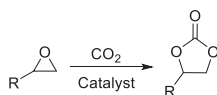
⁵² Neffgen, S.; Keul, H.; Höcker, H. *Macromol. Rapid Commun.* **1996**, *17*, 373–382.

⁵³ Ihata, O.; Kayaki, Y.; Ikariya, T. *Angew. Chem.* **2004**, *116*, 735–737.

⁵⁴ Włoch, M.; Datta, J. *Nonisocyanate Polyurethanes, Polyurethane Polymers*. Chapter II. Elsevier, **2017**.

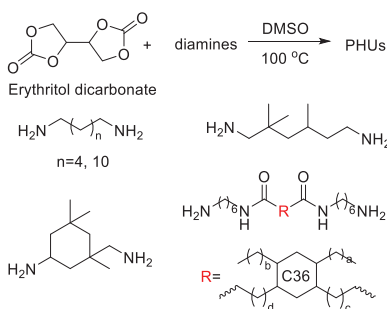
⁵⁵ North, M.; Pasquale, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2946–2948.

^{56]} Given the non-by-product formation and the high yield generally obtained, the polyaddition is better compared with the polycondensation. Goodrich *et al.* ^[57] developed mild reaction conditions to synthesize CC from the epoxide and CO₂ under various azolate ionic liquids (ILs), achieving the metal and halide free synthesis.



Scheme 9. Schematic reaction between epoxide and CO₂

The aminolysis reaction happens when the amine attacks the CC. The temperature of the reaction plays a pivotal role in this transformation, even though it's a simple addition reaction. Thus, the reaction can be achieved at room temperature, and the efficiency of the reaction increases with the temperature. ^[58] Polyaddition as described above is one of the effective methods to synthesize PHUs. Recently, Schmidt *et al.* ^[59] reported the use of bio-based erythritol dicarbonate with typical diamines to produce PHUs in DMSO at 100°C through polyaddition reactions (Scheme 10). However, all the products molecular weights are lower than the isocyanate-based PUs, resulting in almost 10°C lower glass transition temperature.



Scheme 10. PHUs originating from bio-based dicarbonates

⁵⁶ Bhat, G. A.; Darensbourg, D. J. *Green Chem.* **2022**, *24*, 5007–5034.

⁵⁷ Goodrich, P.; Gunaratne, H. Q. N.; Jacquemin, J.; Jin, L.; Lei, Y.; Seddon, K. R. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5635–5641.

⁵⁸ Javni, I.; Hong, D. P.; Petrovič, Z. S. *J. Appl. Polym. Sci.* **2013**, *128*, 566–571.

⁵⁹ Schmidt, S.; Gatti, F. J.; Luitz, M.; Ritter, B. S.; Bruchmann, B.; Mülhaupt, R. *Macromolecules* **2017**, *50*, 2296–2303.

3.2 The non-toxic sustainable approach to the synthesis of CC

Considering all the above methods to synthesize NIPUs and comparing the four different pathways, the other three initial routes explain the very limited literature and industry uses. Conversely, there has been a focus on the polyaddition route to synthesize PHUs.

Even though the synthesis of CC was developed in the industry in the recent 15 years, researchers have studied this transformation more than 60 years ago. ^[60] The five-membered CCs (5CCs) (Figure 5) are the most popular and commercially available CCs.

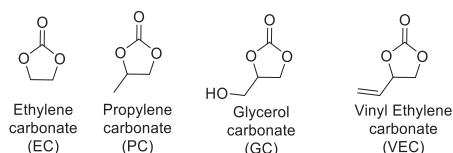


Figure 5. Structure of the most popular 5CCs

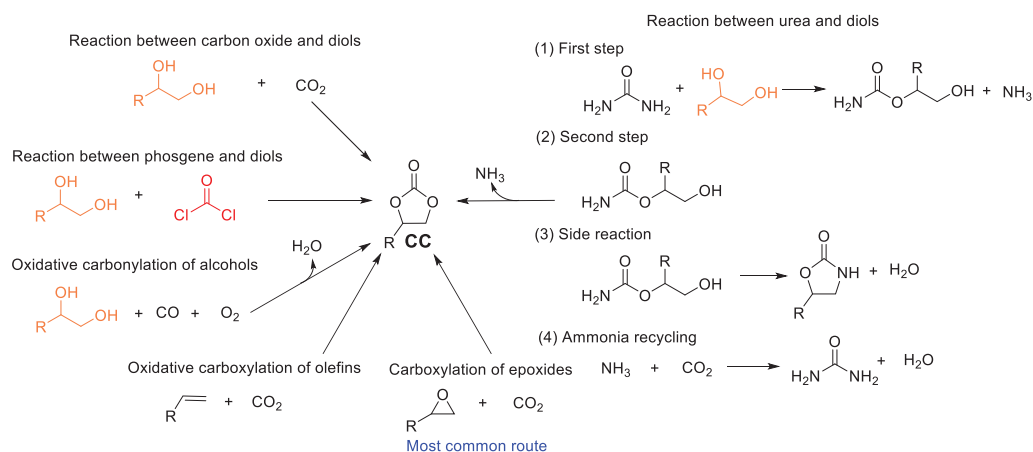
Conventionally, CC are produced by the reaction between a diol and phosgene or its derivatives. ^[61] This method is often considered better than others thanks to the high reactivity of phosgene and the high yield generally obtained. Nevertheless, the phosgene and its derivatives are toxic, so searching for greener alternative pathways has been embraced. Nowadays, the most common approaches involve diols and epoxide, and only the approaches presenting potential renewable resources are discussed because of the healthy and environmental concerns (Scheme 11). ^[62] CO₂ is a sustainable resource obtained from natural and industrial sources. ^[63]

⁶⁰ Clements, J. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 663–674.

⁶¹ Burk, R. M.; Roof, M. B. *Tetrahedron Lett.* **1993**, *34*, 395–398.

⁶² Benyahya, S.; Desroches, M.; Auvergne, R.; Carlotti, S.; Caillol, S.; Boutevin, B. *Polym. Chem.* **2011**, *2*, 2661–2667.

⁶³ Aresta, M.; Dibenedetto, A. *J. Chem. Soc. Dalt. Trans.* **2007**, *28*, 2975–2992.



Scheme 11. Potential renewable routes to synthesize CC

CC can be synthesized from diols and CO_2 through an oxidative carbonylation using O_2 as an oxidant. Many heterogeneous catalysts have been developed allowing an easy separation and catalyst recycling.^[64] The diols can be converted to CC in the presence of urea under high temperatures and reduced pressure.^[65] Although various diols could produce the desired CC through two-step reactions, ammonia and oxazolidone are the ineluctable by-products. Fortunately, formed ammonia could achieve recycling use through a reaction with CO_2 to produce urea and water, and the urea could be reused in the system (Scheme 11). CCs could be synthesized from diols and CO_2 in supercritical conditions, and a variety of catalysts such as organic bases or metal oxides were developed to improve the reaction.^[66] Although the reaction could achieve high catalytic selectivity under different conditions, the main drawback of the reaction is the low desired product yield. Furthermore, removing the water formed during the reaction is necessary in the system.

Oxidative carbonylation of olefins also can also be envisioned for the preparation of CCs from olefin and CO_2 (Scheme 11). Interestingly, this approach avoids the formation and purification of epoxides. Various olefins have been studied since it was first

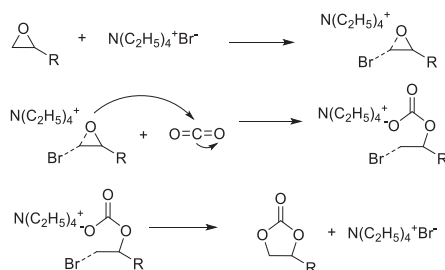
⁶⁴ Chavan, S. P.; Bhanage, B. M. *Tetrahedron Lett.* **2014**, *55*, 1199–1202.

⁶⁵ Doya, M.; Kimizuka, K.; Kanbara, Y. US, Patent, US5489702, **1996**.

⁶⁶ Tamura, M.; Honda, M.; Nakagawa, Y.; Tomishige, K. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 19–33.

reported in 1962. [67] Main researches concentrated on the use of styrene as the starting material and oxygen as the oxidant even though a variety of oxidants were also reported. [68-69]

CO₂ can also react with epoxides to produce CCs. This strategy is the major pathway to synthesize CCs in the industry through bubbling CO₂ into oxiranes under high pressures and temperatures. [70] An alkylammonium halide is a common catalyst to activate the epoxy ring (Scheme 12). CO₂ is generally poorly soluble in the traditional solvents, though CC could be used both as a reagent and a solvent. As a consequence, researchers still explore the development of solvent-free systems. Of note new alternative methods have been developed such as reactions in supercritical CO₂ (scCO₂), ILs playing solvent and catalyst role or a combination of both. [71] Using these conditions, the desired product could be obtained under mild temperature and ambient pressure, thus achieving economic and energy savings. Furthermore, an easy separation between CC and scCO₂ is beneficial to achieving catalyst recovery.



Scheme 12. Mechanism of synthesis of CCs from epoxides

CCs can be synthesized from diols and DMC through transcobonation (Scheme 13), DMC being prepared directly from carbon monoxide and methanol according to a green process. [72-73] Although the transcobonation is a reversible reaction, high

⁶⁷ Verdol, J. A. US, Patent, US3205305, **1962**.

⁶⁸ Bai, D.; Jing, H. *Green Chem.* **2010**, *12*, 39–41.

⁶⁹ Sun, J.; Fujita, S. I.; Zhao, F.; Hasegawa, M.; Arai, M. *J. Catal.* **2005**, *230*, 398–405.

⁷⁰ North, M.; Pasquale, R.; Young, C. *Green Chem.* **2010**, *12*, 1514–1539.

⁷¹ Cheng, W.; Su, Q.; Wang, J.; Sun, J.; Ng, F. T. T. *Catalysts* **2013**, *3*, 878–901.

⁷² Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1993**, *444*, 65–66.

⁷³ Delledonne, D.; Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1995**, *488*, 15–19.

conversion and yield can be achieved with heterogeneous basic catalysts, and a series of catalysts such as CaO, MgO, CaCO₃, and Amberlyst A-26(OH) were screened by Ochoa-Gómez *et al.* [74] Meanwhile, a green method involving molecular sieves as the catalyst to synthesize 5CCs or 6CCs has been reported. [75] Furthermore, Guidi *et al.* [76] developed a catalyst-free system to synthesize CCs under both batch and continuous conditions. Although the DMC is popular for the transcarbonation reaction, other carbonyl source such as diphenyl carbonate can also be used in transcarbonation. [59]



Scheme 13. Pathway synthesis of CCs through transcarbonation

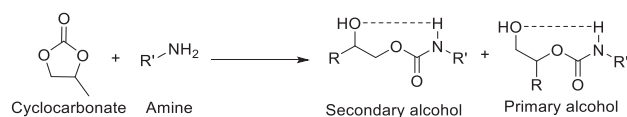
3.3 Generalities about the aminolysis reaction

The reaction of aminolysis between amines and CCs can produce urethane groups with both primary and secondary hydroxyl functional groups hanging out of the main polymer chain, accounting for the terminology PHUs. So, the structure of PHUs is different from that of the NIPUs and classical PUs. Moreover, the hydroxyl groups can interact intramolecularly *via* hydrogen bonds with the H-N of the urethane group. The resulting cyclic structure blocks the carbonyl carbon increasing the stability of the urethane group, hence improving the hydrolytic stability. [49] Hence, polymers containing intramolecular hydrogen bonds present 1.5-2 greater chemical resistance than similar structure polymers without intramolecular hydrogen bonds. [10]

⁷⁴ Ochoa-Gómez, J. R.; Gómez-Jiménez-Aberasturi, O.; Maestro-Madurga, B.; Pesquera-Rodríguez, A.; Ramírez-López, C.; Lorenzo-Ibarreta, L.; Torrecilla-Soria, J.; Villarán-Velasco, M. C. *Appl. Catal. A Gen.* **2009**, *366*, 315–324.

⁷⁵ Pyo, S. H.; Hatti-Kaul, R. *Adv. Synth. Catal.* **2016**, *358*, 834–839.

⁷⁶ Guidi, S.; Calmanti, R.; Noè, M.; Perosa, A.; Selva, M. *ACS Sustain. Chem. Eng.* **2016**, *4*, 6144–6151.

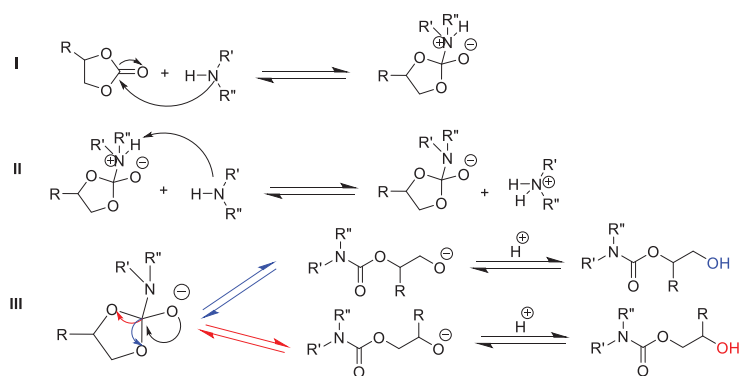


Scheme 14. General aminolysis reaction scheme

To avoid the use of toxic chemicals, NIPUs and classical PUs. Moreover, my thesis focuses on the aminolysis reaction toward the synthesis of PHUs. The reaction involves the ring-opening of a CC with an amine (Scheme 14).

3.2.1 The parameters affect the reactivity of the aminolysis reaction

Garipov *et al.* [77] reported a mechanism dealing with the amine opening of CC involving 3 steps in 2003 (Scheme 15). In the first step, the nucleophilic attack of the amine on the carbonyl of the CC giving a tetrahedral intermediate is considered the determining step of the reaction. In a second step, a second amine deprotonates the tetrahedral intermediate. In the last step, the significant electron density initiates the cleavage of the C-O bond, yielding a hydroxyurethane with the primary or secondary alcohol. Of note, the generation of the secondary alcohol is preferred generally because it is more thermodynamically stable. [78]



Scheme 15. Mechanism of CC/amine reaction

⁷⁷ Garipov, R. M.; Sysoev, V. A.; Mikheev, V. V.; Zagidullin, A. I.; Deberdeev, R. Y.; Irzhak, V. I.; Berlin, A. Al. *Dokl. Phys. Chem.* **2003**, *393*, 289–292.

⁷⁸ Steblyanko, A.; Choi, W.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 2375–2380.

According to the mechanism proposed in Scheme 15, several parameters can affect the aminolysis reaction, including the carbonate structure and substituents, the structure of the amine, the catalyst, the solvent, the temperature, and others (Figure 6).

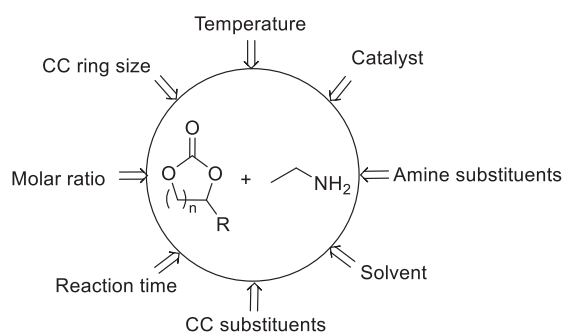


Figure 6. Main reaction parameters affecting the aminolysis reaction

3.2.2 The effect of the carbonate structure and its substituents

3.2.2.1 The effect of the carbonate structure

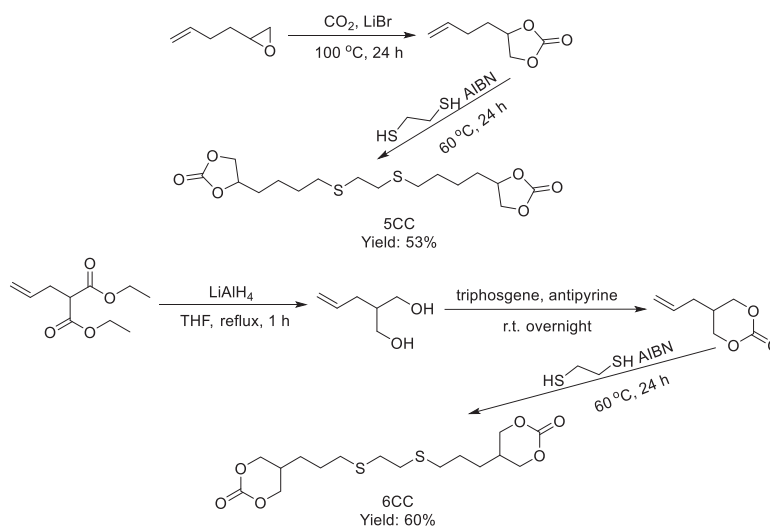
The ring size of the CC plays a pivotal role in the aminolysis reaction. Ochiai *et al.*^[79] indicated that a six-membered CC is more reactive than a 5-membered one and supposed that their different reactivity origins from the ring strain. In 2001, two chemically similar bis CCs of 5-membered ring (5CC) and 6-membered ring (6CC) were synthesized by Tomita *et al.*^[80] (Scheme 16). The bis 6-membered CC was quantitatively converted after 48 h, whereas with the bis 5-membered CC, a conversion of only 67% was observed over the same reaction time. Subsequently, many researchers confirmed the difference in the reactivity of the two different size rings from their respective series.^[81-82]

⁷⁹ Ochiai, B.; Matsuki, M.; Miyagawa, T.; Nagai, D.; Endo, T. *Tetrahedron* **2005**, *61*, 1835–1838.

⁸⁰ Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 860–867.

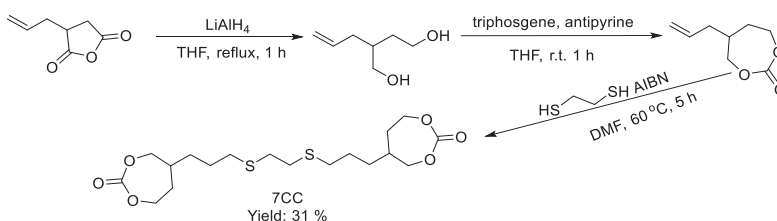
⁸¹ Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 162–168.

⁸² He, Y.; Keul, H.; Möller, M. *React. Funct. Polym.* **2011**, *71*, 175–186.



Scheme 16. The synthetic access to 5CC and 6CC

Furthermore, the Tomita *et al.* ^[83] group synthesized bis 7-membered CCs (7CCs) (Scheme 17) and compared their reactivity with the bis 6- and 5-membered CCs. Their results indicated that the 7-membered CCs are even more reactive than the 6CC congeners.



Scheme 17. The synthetic pathway to 7CC

Going even further, Yuen *et al.* ^[84] prepared 8-membered CCs (8CCs) and observed higher reactivity and molecular weight with the latter compared with the bis 6- and 5-membered CCs. Therefore, the reactivity of the ring-opening reaction increases according to the following order: 5CC < 6CC < 7CC < 8CC. Although 8CCs are more

⁸³ Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 4091–4100.

⁸⁴ Yuen, A.; Bossion, A.; Gómez-Bengoia, E.; Ruipérez, F.; Isik, M.; Hedrick, J. L.; Mecerreyes, D.; Yang, Y. Y.; Sardon, H. *Polym. Chem.* **2016**, *7*, 2105–2111.

reactive, their synthesis involve toxic reagents such as phosgene or its derivatives or carbon disulfide. [4]

5CC is the least reactive, nevertheless, they are most easily synthesized and popularly used. Furthermore, considering the sustainable pathways toward CCs and the vast variety of bio-based diol precursors, the 5CCs are the best choice.

3.2.2.2 The effect of the carbonate substituents

The substituents connected to the CC ring have also a profound influence on its reactivity. Tomita *et al.* [85] explored a large amount of monosubstituted 5-membered CCs. The results of his experiments indicated that the aminolysis reaction rate increased with the substituent electron-withdrawing property. Garipov *et al.* [77] found that an electron releasing group (ERG) substituent connected to the CCs will partially decrease the positive charge of the carbonyl carbon. This results in reducing the electrophilicity of the carbonyl carbon toward the amine. On the contrary, electron-withdrawing group (EWG) promote the electrophilicity of carbonyl and thus nucleophilic attack of the amine (Figure 7).

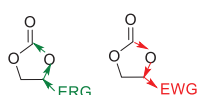


Figure 7. Effect of the ERG and EWG effects of the substituents

As we all know, the electronic inductive effect decreases when the distance between CC and substituents increases. Cornille *et al.* [86] studied the reactivity of a series of CCs with different substituents reacted with amine (EDR-148) and proposed the following sequence: butane < phenyl ether \approx ethyl ether < benzoate ethyl ether < trimethylhexanoate < acetate < ethyl ester (Figure 8).

⁸⁵ Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 3678–3685.

⁸⁶ Cornille, A.; Blain, M.; Auvergne, R.; Andrioletti, B.; Boutevin, B.; Caillol, S. *Polym. Chem.* **2017**, *8*, 592–604.

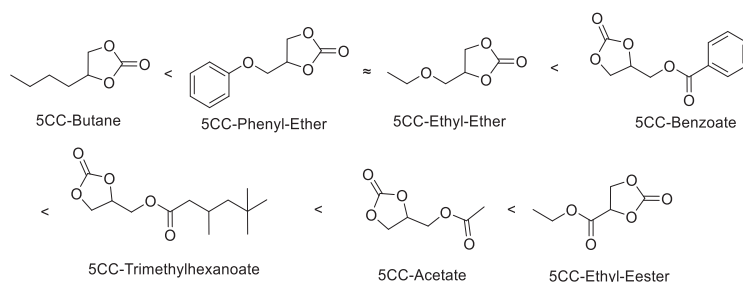


Figure 8. Examples of 5CC bearing different substituents

Their works indicated that ethyl-ether and acetate of 5-CC are more reactive than phenyl-ether and benzoate respectively since the phenyl group exhibits more steric hindrance than alkyl groups.

3.2.3 The effect of the amine

Lots of research indicated that the structure of the amine deeply influences the aminolysis reaction with CC. Generally, the authors reach a consensus that the secondary amines are less reactive than primary ones. Sometimes, secondary amines are even nonreactive toward CCs. The reactivity seems to be governed by nucleophilicity. [77, 81, 87-88] Diakoumakos *et al.* [89] built a model reaction between an ether-5CC and different amines. Their works showed that the structure of the amines has a strong influence on their reactivity, and amines with strong electron donating group (EDG) in the α or β position display a lesser reactivity. Furthermore, their research demonstrated that the lower molecular weight amines were more reactive than the large ones (Figure 9). Subsequently, many other researchers confirmed the conclusion that the amine reactivity relies on their nucleophilicity, chemical structure, and their steric hindrance. [81, 90-91]

⁸⁷ Webster, D. C. *Prog. Org. Coat.* **2003**, *47*, 77–86.

⁸⁸ Rokicki, G.; Łaziński, R. *Die Angew. Makromol. Chem.* **1989**, *170*, 211–225.

⁸⁹ Diakoumakos, C. D.; Kotzev, D. L. *Macromol. Symp.* **2004**, *216*, 37–46.

⁹⁰ Webster, D. C.; Crain, A. L. *Prog. Org. Coat.* **2000**, *40*, 275–282.

⁹¹ Tabushi, I.; Oda, R. *Nippon Kagaku zasshi* **1963**, *84*, 162–167.

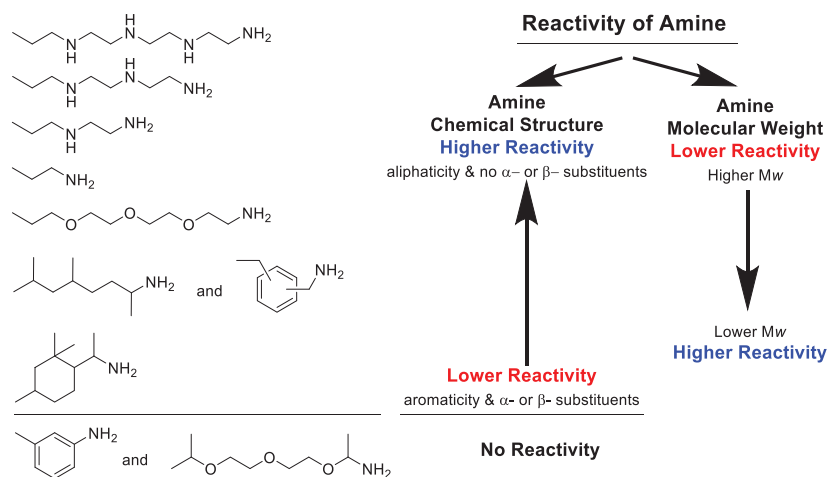


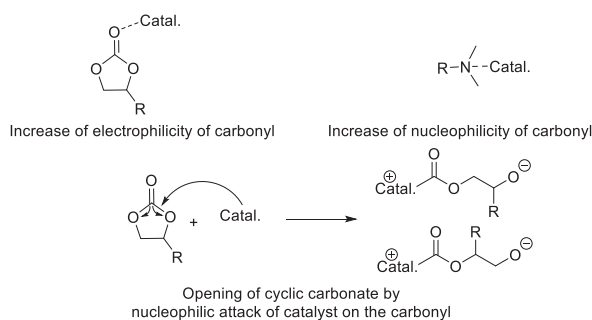
Figure 9. Reactivity between various amines and ether-5CC

The molar ratio of amine and CC also affects the aminolysis reaction, and the research indicated that an equimolar ratio of amine and CC produces the higher yield in property PHUs. However, with either an equimolar ratio or a non-stoichiometric ratio, the presence of side-products is ineluctable, finally, influencing the conversion and the polymer molecular weight. [58, 92]

3.2.4 The effect of the additives and catalyst

The aminolysis reaction between amines and CCs, may be accelerated by the activation of the monomers. For this purpose, there are three means to achieve the catalytic aminolysis of CCs. The electrophilicity of the CC group may be increased by using weakly Lewis acidic and electrophilic additives. In addition, the nucleophilicity of the amines could be increased by using basic additives. Another possibility is opening the CC by using a Lewis base to attack the carbonyl carbon (Scheme 18). [77]

⁹² Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H. *Chem. Rev.* **2015**, *115*, 12407–12439.



Scheme 18. Three mechanisms of aminolysis under the different catalysts

There are many different kinds of catalysts to favor the aminolysis reaction. Various researchers explored the use of organocatalysts (Figure 10) such as: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), piperazine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylamine (TEA), or Bronsted acids such as glacial acid, acetic, and methanesulfonic acid, organometallic catalysts, lithium-based salts, and salts combining an alkali metal or ammonium salt cation and even strong bases. [89, 93-94] Among the salt catalysts, researchers often preferred to use lithium salts, which are often more reactive than CaCl_2 , Bu_4NCl , and Bu_4Sn , and are less harmful to human health and the environment. [95]

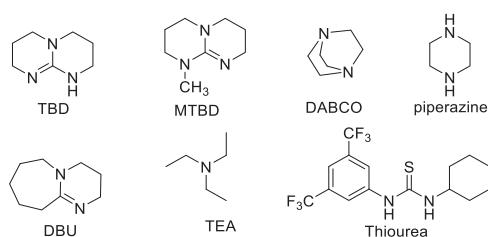


Figure 10. Representative structures of some organocatalysts

Recently, our group reported more available thioureas as a catalyst in aminolysis of propylene carbonate (PC) that could be used in the formation of PHUs (Table 1). [96]

⁹³ Fleischer, M.; Blattmann, H.; Mülhaupt, R. *Green Chem.* **2013**, *15*, 934–942.

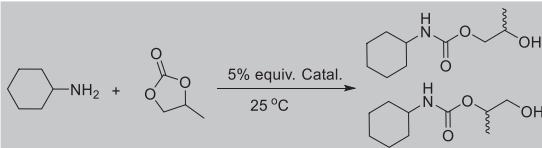
⁹⁴ Honel, M.; Ziegler, P.; Foedde, H. US, Patent, US5132458, **1992**.

⁹⁵ Ochiai, B.; Inoue, S.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 6282–6286.

⁹⁶ Blain, M.; Yau, H.; Jean-Gérard, L.; Auvergne, R.; Benazet, D.; Schreiner, P. R.; Caillol, S.; Andrioletti, B. *ChemSusChem* **2016**, *9*, 2269–2272.

Indeed, the TBD and the thiourea are the most effective among all catalysts tested for CC aminolysis. [97]

Table 1. Thiourea (a) and urea (b) catalyzed aminolysis of PC.

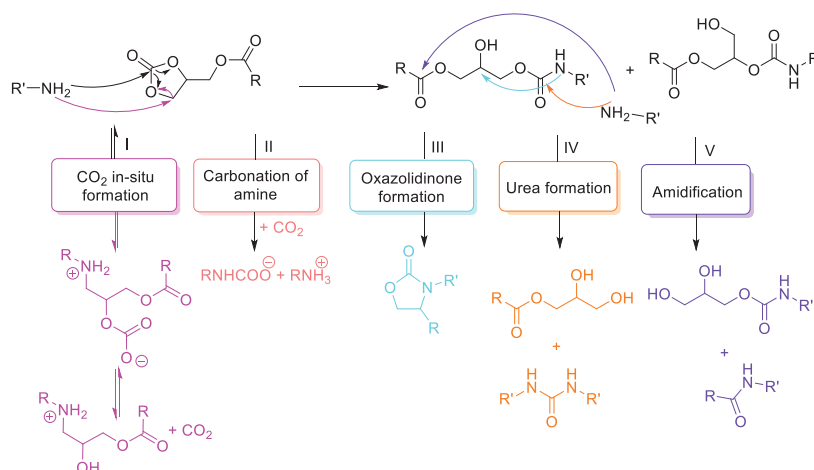


(Thio)urea Substrate	(Thio)urea	Conv. % t=0,5 h	t=1 h
	none	5	9
R ¹ =3,5-(CF ₃) ₂ C ₆ H ₃	1 a	55	66
R ² =cyclohexyl	1 b	42	48
R ¹ =R ² =cyclohexyl	2 a	17	26
	2 b	5	21
R ¹ =R ² =Ph	3 a	44	51
	3 b	47	53
R ¹ =R ² =3-(CF ₃)C ₆ H ₄	4 a	40	52
	4 b	60	67
R ¹ =R ² =3,5-(CF ₃) ₂ C ₆ H ₃	5 a	28	41
	5 b	65	70
R ¹ =3,5-(CF ₃) ₂ C ₆ H ₃	6 a	55	64
R ² =Ph	6 b	65	71

3.2.5 The effect of the temperature, solvent, and other reaction conditions

To avoid the side reactions and synthesize PHUs more efficiently, much work has been dedicated to avoid the side reaction such as the production of CO₂ *in situ*, amine carbonation, urea, and amidation reaction (Scheme 19). [34]

⁹⁷ Blain, M.; Jean-Gérard, L.; Auvergne, R.; Benazet, D.; Caillol, S.; Andrioletti, B. *Green Chem.* **2014**, *16*, 4286–4291.



Scheme 19. Major by-products found in the CC aminolysis reaction

Clements *et al.* ^[60] proposed that the nucleophilic attack of the amine on the α carbon atom may produce CO_2 *in situ* (Scheme 19, I). It is also worth noting that carbonate anions and ammonium salts can also be produced if the reaction is exposed to atmospheric CO_2 (Scheme 19, II). ^[98-99] Some authors reported the oxazolidinone formation by rearrangement and dehydration. This observation was next confirmed by Cornille *et al.* ^[100] (Scheme 19, III), and the authors also showed that ureas could be produced in the transurethane reaction without a catalyst (Scheme 19, IV). In general, it is acknowledged that nucleophilic amine can react on hydroxyurethane function to produce ureas under temperature $> 100^\circ\text{C}$. ^[101] However, at a relatively low temperature (80°C), CCs can be functionalized and connected to different compounds through ether or ester function groups. The nature of the functionalization is of prime importance as the amines can react with the carbonyl of an ester instead of the carbonate to form an amide (Scheme 19, V). ^[102-103] Ester groups are found commonly in the synthesis of bio-based CC monomers; thus, in this case, researchers should take

⁹⁸ Astarita, G.; Marrucci, G.; Gioia, F. *Chem. Eng. Sci.* **1964**, *19*, 95–103.

⁹⁹ Blain, M.; Jean-Gérard, L.; Benazet, D.; Boutevin, B.; Andrioletti, B.; Caillol, S. *Macromol. Mater. Eng.* **2016**, *301*, 682–693.

¹⁰⁰ Cornille, A.; Michaud, G.; Simon, F.; Fouquay, S.; Auvergne, R.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2016**, *84*, 404–420.

¹⁰¹ Bürgel, T.; Fedtke, M. *Polym. Bull.* **1991**, *27*, 171–177.

¹⁰² Lamarzelle, O.; Durand, P. L.; Wirotius, A. L.; Chollet, G.; Grau, E.; Cramail, H. *Synthesis. Polym. Chem.* **2016**, *7*, 1439–1451.

¹⁰³ Doley, S.; Dolui, S. K. *Eur. Polym. J.* **2018**, *102*, 161–168.

care of the potential formation of the amide by-product in the bio-based PHUs synthesis. This is particularly the case with Bis-CC originating from glycerol carbonate (GC) bearing carboxylic acid or its derivatives. Indeed, the amine can react with the ester to produce an amide. Nevertheless, the amidification reaction is affected by the temperature. Thus, Tamami *et al.*'s ^[104] works indicated that amide groups were not detected at room temperature through FT-IR and ¹³C NMR spectroscopy.

Javni *et al.* ^[105] used the carbonated soybean oil to study the competition between the aminolysis and the amidification reaction. Their research results indicated that an excess of amine favors the side reaction. Indeed, using these conditions, even if the aminolysis reaction is launched in the traditional temperature range from 70 to 100°C, the amide stretching band located around 1636 to 1643 cm⁻¹ could be found in the FT-IR spectrum.

Many different research groups have explored the kinetics of the CC aminolysis reaction. Some authors pointed out the influence of temperature, solvent, and starting material concentration. Higher reaction rates were found at relatively higher reaction temperature. Nevertheless, Bürgel *et al.* ^[106] demonstrated that temperatures above 100°C could induce the formation of by-products. Hence, it is necessary to find a compromise between kinetics and control of the reaction.

In summary, various side reactions competitive with the PHU synthesis have been reported in the past. Although all of these side reactions generally happen above 100°C or involve the use of a catalyst, many side reactions decrease the amine content and result in breaking the equimolar stoichiometry, thus ending the polymer chain growth, finally giving low molecular weight products.

Besides, the reaction rates are variable, strongly depending on the nature of the solvents used. DMF or DMSO are among the most popular solvents in this reaction.

¹⁰⁴ Tamami, B.; Sohn, S.; Wilkes, G. L. *J. Appl. Polym. Sci.* **2004**, *92*, 883–891.

¹⁰⁵ Javni, I.; Doo, P. H.; Petrović, Z. S. *J. Appl. Polym. Sci.* **2008**, *108*, 3867–3875.

¹⁰⁶ Bürgel, T.; Fedtke, M. *Polym. Bull.* **1993**, *30*, 61–68.

Noticeably, Tomita *et al.* ^[85, 107] achieved higher conversions in toluene than in DMSO. Scheme 15 indicated that the aminolysis reaction limiting step is the first step in an aprotic solvent. However, a protic solvent can also interact with the oxygen of a carbonyl group *via* hydrogen bonding hence favoring the nucleophilic attack of the amine. In this case the deprotonation will be the limiting step. ^[77] Nowadays, the current trend is the search for a green solvent to perform synthetic reactions.

There are many hydroxyl groups in PHUs. This hydroxyl group promotes the density of hydrogen bonds by inter- or intra-molecular interactions. Using NMR spectroscopy and differential scanning calorimetry (DSC), Blain *et al.* ^[108] demonstrated that the hydroxyl groups play a major negative role in the aminolysis reaction, limiting conversion and molar weight more than the side reactions. The NMR and DSC results showed that there is a second enthalpy in the reaction system, owing to the hydrogen-bonding network, except for the major enthalpy of the reaction between CC and amine, thus explaining why a full conversion could not be achieved. Nevertheless, protic solvent such as MeOH, EtOH as additives (plasticizers) can be used in the reaction to reduce the inter- or intra- molecular hydrogen bonds, increasing the chain mobility and promoting the of the starting material to produce longer polymer chains (Figure 11). ^[86, 108] Overall, protic solvents are recommended to obtain high conversion and molar mass.

¹⁰⁷ Tomita, H.; Sanda, F.; Endo, T. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 851–859.

¹⁰⁸ Blain, M.; Cornille, A.; Boutevin, B.; Auvergne, R.; Benazet, D.; Andrioletti, B.; Caillol, S. *J. Appl. Polym. Sci.* **2017**, *134*, 44958.

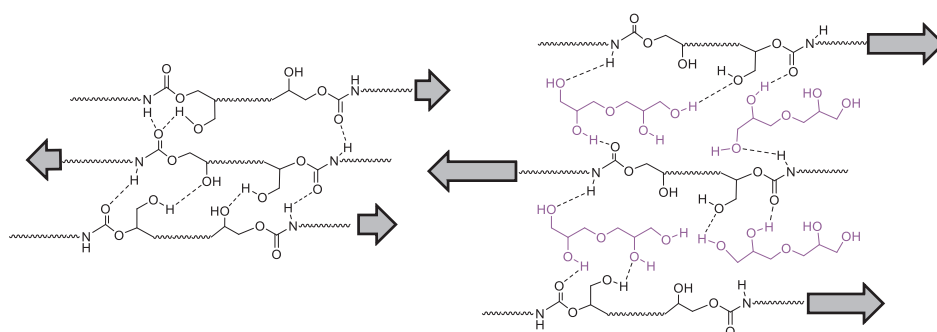


Figure 11. Example of a protic solvent affecting the mobility of the PHUs chains

3.4 Major advantages and disadvantages of the aminolysis reaction

The innovative pathways to NIPUs presented above give a perspective route to replace conventional PUs. Nevertheless, all present either advantages or drawbacks. [107, 109] In general, although the aminolysis reaction requires a long reaction time (often several days), this approach is the most widely adopted to elaborate PHUs. Indeed, polyaddition is less restrictive and could possibly be implemented in industry, compared with the other three routes such as ring-opening polymerization, rearrangement, and transurethanization.

Unfortunately, although various monomers and catalysts have been developed, the starting material conversion generally does not exceed 80% and low molecular weight and low degree of polymerization are often observed. In summary, given that noxious solvent and several days of reaction time impede the widespread application of the aminolysis reaction, there is a much room for improving this reaction at temperatures below 100°C.

3.5 Promising applications of PHUs

Recently, a variety of PHUs materials have been explored for industrial applications, especially, since they are mainly used in low molar weight and do not influence practical properties. Similar to the traditional PUs, PHUs can be generally used as thermosets and thermoplastics, also be applied in foams, hydrogels, or latexes. [4]

¹⁰⁹ Deepa, P.; Jayakannan, M. *J. Polym. Sci. Part A Polym. Chem.* **2008**, *46*, 2445–2458.

Interestingly, while carried out in the presence of a blowing agent, the aminolysis reaction can proceed with a full conversion at low temperature as reported by Cornille *et al.* ^[110] In addition, in the same study, the authors indicated that the PHUs-based foams are excellent with increased adhesion properties compared to the PU analogues. These observations open new doors considering that 66% of the PUs are actually used as foams.

4 Sustainable syntheses of polymers

The conventional non-biodegradable plastics based on fossil sources have resulted in serious troubles in natural ecosystems. In principle, bio-based polymers are expected to be less deleterious for the environment than their oil-based counter parts. Different types of bio-based monomers such as lactic acid, hydroxyalkanoates, starch, cellulose, amino-acids, ethylene glycol, furan-2,5-dicarboxylic acid (FDCA) and many other have been developed to synthesize bio-based polymer in the past. ^[111-112]

In the utilization and transformation of biomass, some small molecules come from the biomass feedstock and have become high value-added molecules downstream. These key molecules are called biomass platform molecules. Originally, the United States Department of Energy (USDoE) listed 12 most relevant bio-mass platform molecules in 2004. ^[113] These molecules were considered as promising starting materials. In 2010, Petersen and Bozell considered the preparation route, theoretical feasibility, application prospects, and other factors to complete the list and adding novel molecules (Figure 12). ^[114] These small molecules play an important role in replacing

¹¹⁰ Cornille, A.; Michaud, G.; Simon, F.; Fouquay, S.; Auvergne, R.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2016**, *84*, 404–420.

¹¹¹ Meyer, H. P. *Org. Process Res. Dev.* **2011**, *15*, 180–188.

¹¹² Cherubini, F. *Energ. Convers. Manag.* **2010**, *51*, 1412–1421.

¹¹³ Werpy, T.; Petersen, G.; Aden A.; Bozell J.; Holladay J.; White J.; Manheim Amy. Top Value Added Chemicals from Biomass Volume I-Results of Screening for Potential Candidates from Sugars and Synthesis Gas. **2001**, 10–70.

¹¹⁴ Bozell, J. J.; Petersen, G. R. *Green Chem.* **2010**, *12*, 539–555.

traditional products to generate high value-added chemicals and have broad application prospects.

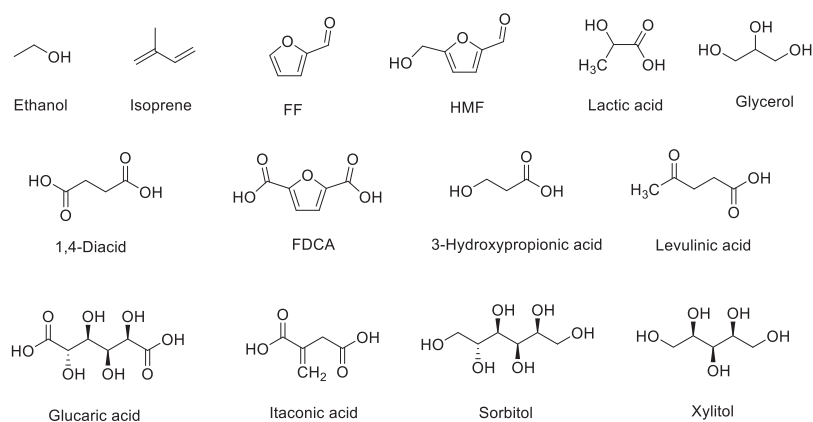


Figure 12. TOP 10+4 most relevant bio-mass platform molecules

4.1 Bio-based cyclic carbonate from glycerol

Over the last decades, among the Top 10+4 platform molecules, glycerol is the fastest growing in the industry due to the biodiesel rapid expansion and development in the transportation sector. Indeed, glycerol is produced as a by-product from the diesel production processes in many countries. ^[115-116] Therefore, the crude glycerol is produced in large quantities at lost cost. Glycerol is an odorless, colorless, non-toxic, water-soluble viscous polyol. Glycerol is particularly interesting as a building block to produce bio-based molecules with added value, including CC. ^[69, 70]

Various routes to Glycerol carbonate (GC) from glycerol have been developed concurrently with investigations and developments in NIPUs. GC is a cheap, biodegradable, non-toxic, and renewable compound. It has aroused wide interest in research and industry in the past decades because of its versatile reactivity and

¹¹⁵ Algoufi, Y. T.; Akpan, U. G.; Kabir, G.; Asif, M.; Hameed, B. H. *Manag.* **2017**, *138*, 183–189.

¹¹⁶ de Caro, P.; Bandres, M.; Urrutigoity, M.; Cecutti, C.; Thiebaud-Roux, S. *Front. Chem.* **2019**, *7*, 308.

applications thanks to its two different functions (hydroxyl and CC).^[10, 117-118] It is currently considered a promising bio-based platform molecule to produce other value-added chemicals, which can be widely applied in various fields such as cosmetics, detergents, and intermediates.^[115, 118]

In addition, as illustrated in recent reviews, GC can be synthesized from multiple, rather simple, synthetic routes. However, some of the synthetic protocols do not match the green chemistry concepts because they involve toxic reagents such as phosgene and carbon monoxide (Figure 13). Using CO₂ as C1 building block to prepare the GC is environmentally interesting, but the reaction system generally needs an organic solvent and catalyst under harsh temperature (180°C) and pressure (150 bar) conditions, so it is unsuitable for large-scale production.^[119-120] Syntheses of GC from urea in the presence of an appropriate catalyst is an attractive method for the production of GC. Noteworthy, the reaction will lead to the production of a large quantity of ammonia as a by-product, limiting the industrial implementation.^[121] GC can also be synthesized by transesterification of CCs or aliphatic carbonates in the presence of a basic catalyst.^[116, 118, 122] A solvent is not necessary since the excess reactant of carbonates (carbonate: glycerol ratio range from 2:1 to 5:1) can play the role of a solvent. Furthermore, the excess carbonate could shift the reaction equilibrium toward GC production.^[123-124]

¹¹⁷ Ochoa-Gómez, J. R.; Gómez-Jiménez-Aberasturi, O.; Ramírez-López, C.; Belsué, M. *Org. Process Res. Dev.* **2012**, *16*, 389–399.

¹¹⁸ Sonnati, M. O.; Amigoni, S.; Taffin De Givenchy, E. P.; Darmanin, T.; Choulet, O.; Guittard, F. *Green Chem.* **2013**, *15*, 283–306.

¹¹⁹ Ozorio, L. P.; Mota, C. J. A. *ChemPhysChem* **2017**, *18*, 3260–3265.

¹²⁰ Dabral, S.; Schaub, T. *Adv. Synth. Catal.* **2019**, *361*, 223–246.

¹²¹ Nguyen, N.; Demirel, Y. *J. Sustain. Bioenergy Syst.* **2013**, *03*, 209–216.

¹²² Li, J.; Wang, T. *J. Chem. Thermodyn.* **2011**, *43*, 731–736.

¹²³ Teng, W. K.; Ngoh, G. C.; Yusoff, R.; Aroua, M. K. *Chem. Eng. J.* **2016**, *284*, 469–477.

¹²⁴ Simanjuntak, F. S. H.; Kim, T. K.; Lee, S. D.; Ahn, B. S.; Kim, H. S.; Lee, H. *Appl. Catal. A Gen.* **2011**, *401*, 220–225.

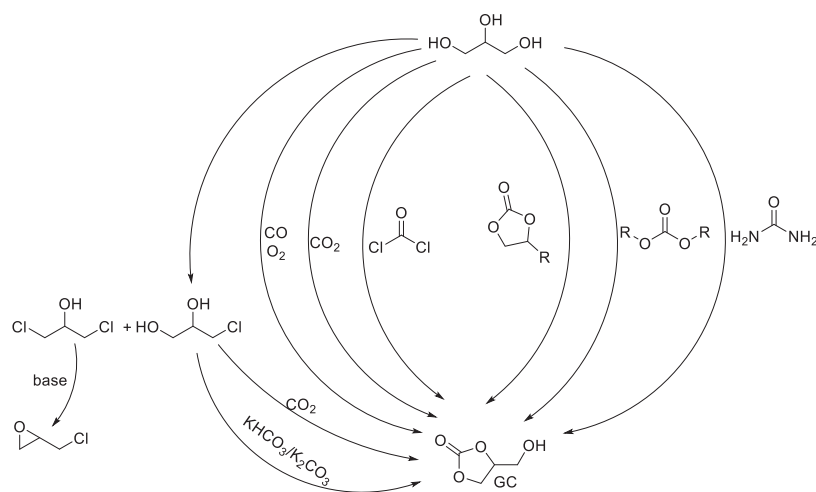
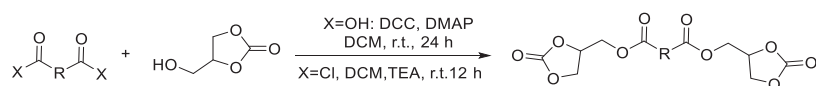


Figure 13. Major routes for the synthesis of GC

Interestingly, the GC can be reacted with diacids through a coupling reaction to obtain Bis-CC (Scheme 20).^[125]



Scheme 20. Connection between GC and a dicarboxylic acid

On the other hand, diglycerol, a dimer of glycerol, could give a bifunctional CC compound through transesterification with DMC, using the monomer with different diamines to produce fully bio-based PHUs.^[126-127]

4.2 Aromatic bio-based platform molecules

FDCA is a very attractive bio-based aromatic platform molecule because it is considered as a possible alternative to fossil-based monomers like terephthalic acid. As a consequence, it has a bright perspective for renewable polyesters and other polymers applications.^[128-129] There are several synthetic routes to produce the FDCA,

¹²⁵ Benyahya, S.; Habas, J. P.; Auvergne, R.; Lapinte, V.; Caillol, S. *Polym. Int.* **2012**, *61*, 1666–1674.

¹²⁶ Van Velthoven, J. L. J.; Gootjes, L.; Van Es, D. S.; Noordover, B. A. J.; Meuldijk, J. *Eur. Polym. J.* **2015**, *70*, 125–135.

¹²⁷ Tryznowski, M.; Świdarska, A.; Gołofit, T.; Zolek-Tryznowska, Z. *RSC Adv.* **2017**, *7*, 30385–30391.

¹²⁸ Maity, S. K. *Renew. Sustain. Energy Rev.* **2015**, *43*, 1427–1445.

¹²⁹ Marshall, A.; Jiang, B.; Gauvin, R. M.; Thomas, C. M. *Molecules* **2022**, *27*, 4071.

but the oxidation of 5-hydroxymethyl furfural (HMF) certainly is the major process.^[130] However, the HMF currently originates from mono- and poly-saccharides such as glucose and fructose which are competitive with the human food. In addition, as its oxidation uses noble metal catalysts and a high concentration of base, the oxidation reaction process is not sustainable enough. Recently, Yin *et al.*^[131] reported the synthesis of FDCA through the oxidative carbonylation of furfural (FF). Subsequently, they developed a series of approaches involving homogeneous, biphasic, and/or heterogeneous systems to convert C5 FF derivatives to FDCA efficiently.^[103-104]

Poly(ethylene 2,5-furandicarboxylate) (PEF) based on the FDCA has aroused great attention, which can lead to an obvious reduction in energy use and greenhouse gas emissions as reported in several papers.^[132-133] Furthermore, some researchers' studies indicated that the polymers containing aromatic furan rings display a high potential of biodegradability.^[134-135]

Boufi *et al.*^[136] introduced the renewable furan heterocycles in PU structures applied in thermoplastic elastomers through the diisocyanate, chain extender, or both methodologies. The renewable furanic homologues are prone to exhibit lower thermal transition and modulus, thus could fulfil specific application based on their properties. Mou *et al.*^[137] used the 5,5'-bihydroxymethyl furyl (BHMF) (Figure 14) and various diisocyanates under catalysis through polyaddition to produce linear PUs and used triol 5,5'-dihydroxymethyl furoin (DHMF) and tetraol 5,5'-bihydroxymethyl hydrofluoric (BHMH) (Figure 14) monomer to obtain cross-linked PUs. Wilson *et al.*^[138] used the difuranic diols (diol A and diol B) (Figure 14) with highly reactive and rigid

¹³⁰ Shen, G.; Andrioletti, B.; Queneau, Y. *Curr. Opin. Green Sustain. Chem.* **2020**, *26*, 100384.

¹³¹ Zhang, S.; Shen, G.; Chen, Z.; Yin, G. *ChemistrySelect* **2017**, *2*, 7096–7099.

¹³² Ma, J.; Pang, Y.; Wang, M.; Xu, J.; Ma, H.; Nie, X. *J. Mater. Chem.* **2012**, *22*, 3457–3461.

¹³³ Sousa, A. F.; Matos, M.; Freire, C. S. R.; Silvestre, A. J. D.; Coelho, J. F. J. *Polymer* **2013**, *54*, 513–519.

¹³⁴ Wu, B.; Xu, Y.; Bu, Z.; Wu, L.; Li, B. G.; Dubois, P. *Polymer* **2014**, *55*, 3648–3655.

¹³⁵ Maniar, D.; Silvianti, F.; Ospina, V. M.; Woortman, A. J. J.; van Dijken, J.; Loos, K. *Polymer* **2020**, *205*, 122662

¹³⁶ Boufi, S.; Gandini, A.; Belgacem, M. N. *Polymer* **1995**, *36*, 1689–1696.

¹³⁷ Mou, Z.; Feng, S.; Chen, E. Y. X. *Polym. Chem.* **2016**, *7*, 1593–1602.

¹³⁸ Wilson, J. F.; Chen, E. Y. X. *ACS Sustain. Chem. Eng.* **2019**, *7*, 7035–7046.

MDI or low reactivity and flexible hexamethylene diisocyanate (HDI) to synthesize a series of PUs. The studies indicated that PUs exhibited a wide range of glass transition temperature (T_g) values and storage moduli owing to the presence of the furan C=C double bonds.

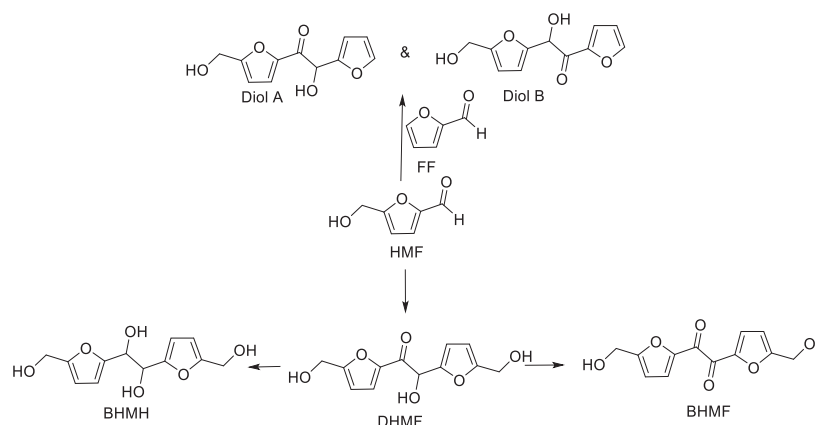
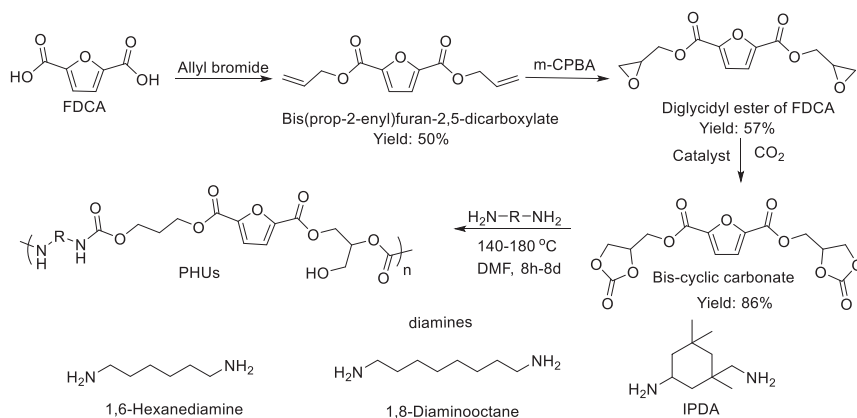


Figure 14. Structure of bio-based furanic polyol

Zhang *et al.* ^[139] reported a novel procedure to synthesize bio-based PHUs from renewable resources. Firstly, FDCA was reacted with allyl bromide. Next the epoxidation with *m*-CPBA followed, and finally, CO₂ as a carbonyl source reacted with the diglycidyl ester of FDCA to yield FDCA-derived Bis-CC (Scheme 21). Nevertheless, a high reaction temperature and long reaction time are necessary to activate the little reactive 2,5-furanic-Bis-CC. Finally, the polymers M_n ranges from 3900 to 7000 g·mol⁻¹ and the polydispersity (PDI) values range from 2.3 to 4.3.

¹³⁹ Zhang, L.; Luo, X.; Qin, Y.; Li, Y. *RSC Adv.* **2017**, *7*, 37–46.



Scheme 21. Synthetic pathway towards FDCA based PHUs

4.3 Bio-based furanic diamines

Amines are popularly used in the polymer industry, but they originate mainly from fossil resources. In general, primary amines derive from the corresponding carbonyl or alcohol compounds through a reductive amination reaction. There are some papers about the synthesis of bio-based diamines, among which the bio-based furanic diamines are shown in the Scheme 22. ^[140] Recently, Komanoya *et al.* ^[141] prepared the 2,5-bis(aminomethyl)furan (BAMF) from the HMF in a high yield under the Ru complex catalytic system. Zhou *et al.* ^[142] using the Raney Ni as catalyst achieved HMF to BAMF under benign conditions. Using NH₃·H₂O as the reductant, Chatterjee *et al.* ^[143] synthesized the furfuryl amine (FAM) from FF with a high yield under Rh/Al₂O₃ catalytic system. Skouta *et al.* ^[144] developed a simple method, using the acetone as a cross-linker and the concentrated HCl as the catalyst, to synthesize a high yield of difuranic amines (PBFA) from FAM (Scheme 22).

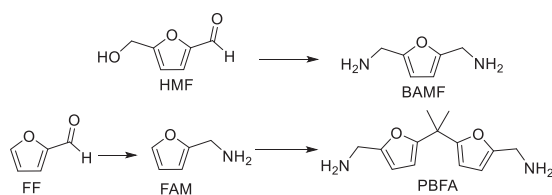
¹⁴⁰ Pelckmans, M.; Renders, T.; Van De Vyver, S.; Sels, B. F. *Green Chem.* **2017**, *19*, 5303–5331.

¹⁴¹ Komanoya, T.; Kinemura, T.; Kita, Y.; Kamata, K.; Hara, M. *J. Am. Chem. Soc.* **2017**, *139*, 11493–11499.

¹⁴² Zhou, K.; Liu, H.; Shu, H.; Xiao, S.; Guo, D.; Liu, Y.; Wei, Z.; Li, X. *ChemCatChem* **2019**, *11*, 2649–2656.

¹⁴³ Chatterjee, M.; Ishizaka, T.; Kawanami, H. *Green Chem.* **2016**, *18*, 487–496.

¹⁴⁴ Skouta, M.; Lesimple, A.; Le Bigot, Y.; Delmas, M. *Synth. Commun.* **1994**, *24*, 2571–2576.



Scheme 22. Structure of some bio-based furanic diamines

4.4 The eco-friendly solvents in the aminolysis reaction

In a chemical process, solvents are generally used for dissolving starting material, affecting chemical reactivity, extracting or washing the target products from the mixtures. Many traditional organic solvents are flammable, explosive, volatile, toxic for human beings and the environment, and non-biodegradable. ^[145-146] The search for a sustainable green solvent to replace petroleum-based reaction media commonly used in the chemical system is advantageous for the human health and the environment. ^[147-148] Conventionally, it is acknowledged that there are 5 categories of “green solvents”: water, ionic liquids (ILs), fluoruous solvents, supercritical fluids (SCFs), and renewable sources of organic solvents. ^[8, 149-150]

Water is better than any other green solvents, for the following reasons: it is non-flammable, non-toxic, colorless and odourless, cheap, and widely available. ^[151] Its polarity facilitates the dissolution of polar molecules and is immiscible with many organic solvents. Thus, it is beneficial for the production separation and very suitable for biphasic catalytic systems. However, on the one hand, many organic chemicals are not miscible with water and on the other hand, many reactants, products, catalysts or

¹⁴⁵ Gu, Y. *Green Chem.* **2012**, *14*, 2091–2128.

¹⁴⁶ Shanab, K.; Neudorfer, C.; Schirmer, E.; Spreitzer, H. *Curr. Org. Chem.* **2013**, *17*, 1179–1187.

¹⁴⁷ Gu, Y.; Jérôme, F. *Chem. Soc. Rev.* **2013**, *42*, 9550–9570.

¹⁴⁸ Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. *J. Am. Chem. Soc.* **2004**, *126*, 9142–9147.

¹⁴⁹ Jessop, P. G. *Green Chem.* **2011**, *13*, 1391–1398.

¹⁵⁰ Sheldon, R. A. *Green Chem.* **2005**, *7*, 267–278.

¹⁵¹ Li, C. J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68–82.

intermediates are sensitive to water or may be destroyed, thus limiting the scope of the application. ^[152]

Highly fluorinated alkanes, ethers, and tertiary amines were described as fluoruous solvents, whose special features make them suitable for application in biphasic catalysis. ^[153] Nevertheless, there is a huge debate on the greenness of their synthesis and fate, because they have been found in a large proportion of wildlife and almost all humans, and their expensive price limit their use. ^[154]

A Super Critical Fluid (SCF) is defined as a compound above its critical pressure and temperature but below the pressure to be condensed into a solid. ^[155] SCFs have liquid and gas properties. Their density is comparable to a liquid and their viscosity is comparable to that of gases. ^[156] Many studies indicate that low molecular weight, low polarity and high vapor pressure of the compound are beneficial for the solubility in SCFs. ^[157] Of note, for the supercritical carbon dioxide (scCO₂), the critical temperature and pressure are moderate: 31°C and 74 bar, respectively. Furthermore, carbon dioxide is inert to many chemicals, non-toxic, non-flammable, and easily separated from the reaction system, and the excess of reactant and catalysts that are easily removed from the reaction medium. ^[158] However, special necessary equipment is necessary for handling the scCO₂, thus increasing the difficulty and price.

Organic solvents originating from renewable sources are called “bio-solvent”. Compared with petrol-based solvents, many of them give excellent advantages such as lower toxicity, better biodegradability, and sustainable production. ^[147] At the same

¹⁵² Li, C. J. *Chem. Rev.* **2005**, *105*, 3095–3165.

¹⁵³ Liao, Y. W.; Chen, W. P. *Fluorous Biphasic Catalysis. Catalyst Separation, Recovery and Recycling.* Springer, Dordrech, **2006**.

¹⁵⁴ Sekharan, T. R.; Chandira, R. M.; Tamilvanan, S.; Rajesh, S. C.; Venkateswarlu, B. S. *Biointerface Res. Appl. Chem.* **2022**, *12*, 847–860.

¹⁵⁵ Hyde, J. R.; Licence, P.; Carter, D.; Poliakoff, M. *Appl. Catal. A Gen.* **2001**, *222*, 119–131.

¹⁵⁶ Cantone, S.; Hanefeld, U.; Basso, A. *Green Chem.* **2007**, *9*, 954–997.

¹⁵⁷ Instructors, C. *Supercritical fluids: molecular interactions, physical properties, and new applications.* Springer science & business media, **2002**.

¹⁵⁸ Leitner, W. *Acc. Chem. Res.* **2002**, *35*, 746–756.

time, they display many of the traditional organic solvent properties. Some popular bio-based solvents from FF are shown in Figure 15. [130]

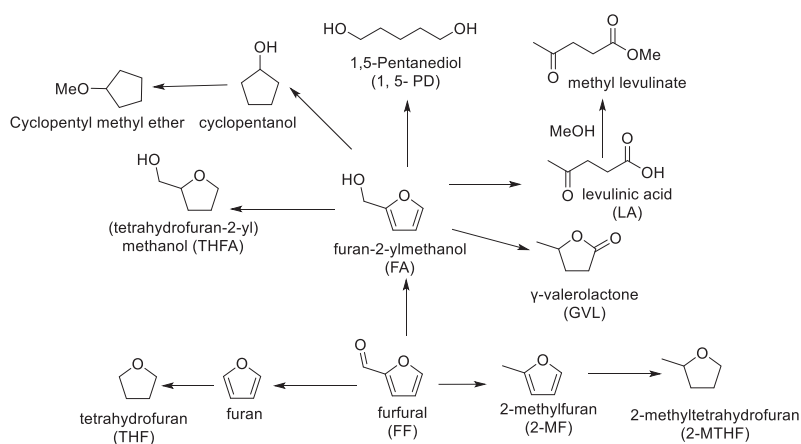


Figure 15. Bio-based solvent from FF

In general, ILs are liquid at relatively low temperature or at room temperature and are believed as environmentally friendly. They display several advantages compared with the traditional organic solvents, but along with the development, researchers gradually realized that many ILs seem to be as harmful as the organic solvents. In addition, they are often costly, difficult to purify, and display toxicity issues such as antibacterial activity and cytotoxicity. [159]

Conversely, deep eutectic solvents (DESs) are one of the green alternative solvents to ILs. Consequently, they have aroused wide attention in the past decades after the first report by Andrew *et al.* [160] DESs are formed by mixing a hydrogen bond acceptor (HBA) and donor (HBD) according to special ratios (Figure 16). [161] DESs are comparable with ILs because they share some common properties such as low volatility, tunable polarity, low vapor pressures, and high thermal stability, giving a potential opportunity to replace volatile organic compounds (VOCs). These properties are responsible for a wide applicability in research and industry. Furthermore, most

¹⁵⁹ Ke, M.; Zhou, A.; Song, Z.; Jiang, Q. *Prog. Chem.* **2007**, *19*, 671–679.

¹⁶⁰ Andrew, P. A.; Glen, C.; David, L. D.; Raymond, K. R.; Vasuki, T. *Chem. Commun.* **2003**, 2003, 70-71.

¹⁶¹ Wang, J.; Han, J.; Khan, M. Y.; He, D.; Peng, H.; Chen, D.; Xie, X.; Xue, Z. *Polym. Chem.* **2017**, *8*, 1616–1627.

DESs are non-toxic, bio-degradable, typically inexpensive, and much easily prepared than ILs. [162] The common HBA is choline that is not harmful to humans and could be produced in industry. At the same time, the urea, a popular HBD, is usually used as fertilizer. [163] Therefore, the DESs have been widely applied in various fields such as organic reactions, bulk processing of metals, polymer synthesis, industrial applications, etc. [164]

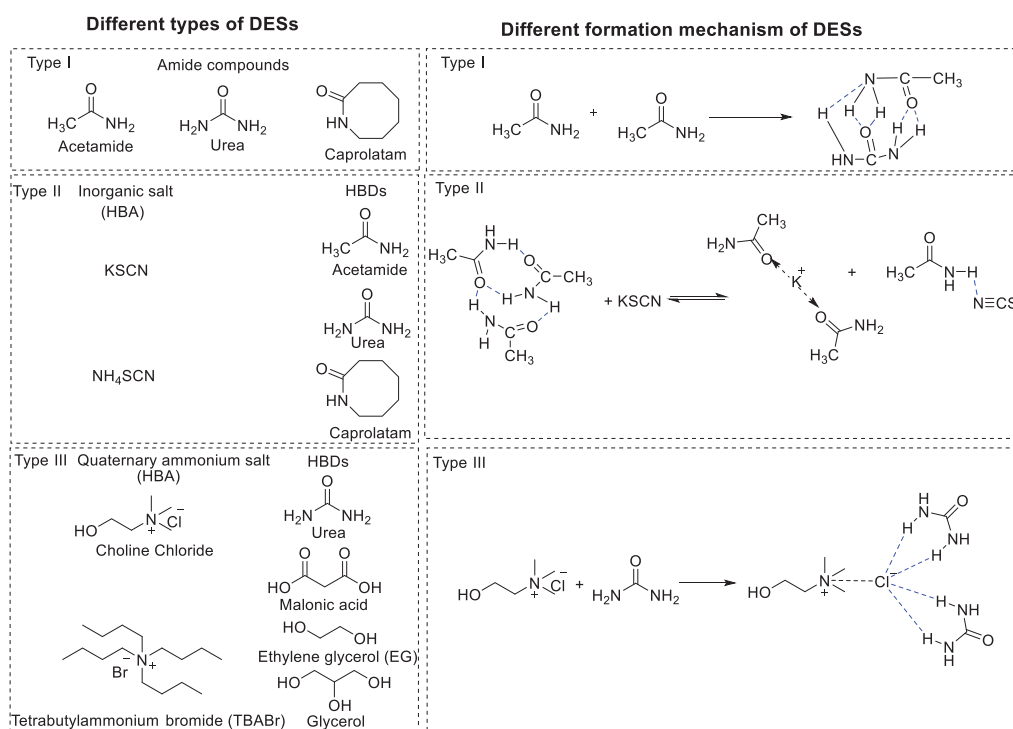


Figure 16. Structure and formation mechanism of different DESs [161]

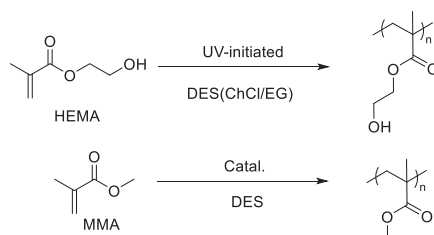
Although DESs display superior performance in solubility compared with the traditional organic solvent, they have been scarcely used for performing polymerization reactions. An exception concerns the use of DESs in a free-radical

¹⁶² Radošević, K.; Cvjetko Bubalo, M.; Gaurina Srček, V.; Grgas, D.; Landeka Dragičević, T.; Redovniković, R. I. *Ecotoxicol. Environ. Saf.* **2015**, *112*, 46–53.

¹⁶³ Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; Gurkan, B.; Maginn, E. J.; Ragauskas, A.; Dadmun, M.; Zawodzinski, T. A.; Baker, G. A.; Tuckerman, M. E.; Savinell, R. F.; Sangoro, J. R. *Chem. Rev.* **2021**, *121*, 1232–1285.

¹⁶⁴ Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146.

polymerization (Scheme 23).^[165] Recently, Xue *et al.*^[166] reported the use of ChCl as HBA with glycerol/PEG-400 as HBD to synthesize ternary DESs, and dissolve lignin under benign conditions to synthesize a rigid foam containing lignin polyurethane. Their studies indicated that the hydrogen bonds between the lignin and the ternary DESs is helpful for lignin dissolution.



Scheme 23. Radical polymerization in DES^[167]

DESs originating from bio-based materials such as alcohols, organic acids, sugars and amino acids (Figure 17), are called natural deep eutectic solvents NaDESs.^[168] They require the same synthesis approach as the one used for “classical” DESs, but are more sustainable, nontoxic, and environmentally benign.^[169-170] Subsequently, sub-DESs families were developed over the very recent years, such as hydrophobic DESs (HDESs), therapeutic DESs (THEDESs), and supramolecular deep eutectic solvents (SUPRADESs).^[171, 172-173] The HDESs overcome conventional hydrophilic DESs limitations; THEDESs

¹⁶⁵ Jablonský, M.; Škulcová, A.; Šima, J. Use of Deep Eutectic Solvents in Polymer Chemistry—a Review. *Molecules* **2019**, *24*, 3978.

¹⁶⁶ Xue, B.; Yang, Y.; Tang, R.; Xue, D.; Sun, Y.; Li, X. *Int. J. Biol. Macromol.* **2020**, *164*, 480–488.

¹⁶⁷ Qin, H.; Panzer, M. J. *ChemElectroChem* **2017**, *4*, 2556–2562.

¹⁶⁸ Choi, Y. H.; van Spronsen, J.; Dai, Y.; Verberne, M.; Hollmann, F.; Arends, I. W. C. E.; Witkamp, G. J.; Verpoorte, R. *Plant Physiol.* **2011**, *156*, 1701–1705.

¹⁶⁹ Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R. L.; Duarte, A. R. C. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1063–1071.

¹⁷⁰ Zuo, J.; Geng, S.; Kong, Y.; Ma, P.; Fan, Z.; Zhang, Y.; Dong, A. *Crit. Rev. Anal. Chem.* **2021**, *12*, 1–22.

¹⁷¹ Lalikoglu, M.; Aşçı, Y. S.; Sırma Tarım, B.; Yıldız, M.; Arat, R. *Sep. Sci. Technol.* **2022**, *57*, 1563–1574.

¹⁷² Rahman, M. S.; Roy, R.; Jadhav, B.; Hossain, M. N.; Halim, M. A.; Raynie, D. E. *J. Mol. Liq.* **2021**, *321*, 114745.

¹⁷³ Janicka, P.; Kaykhaii, M.; Płotka-Wasyłka, J.; Gećbicki, J. *Green Chem.* **2022**, *24*, 5035–5045.

can be used to enhance the efficiency of drugs, and SUPRADESs are more powerful solvents than the traditional solvents.

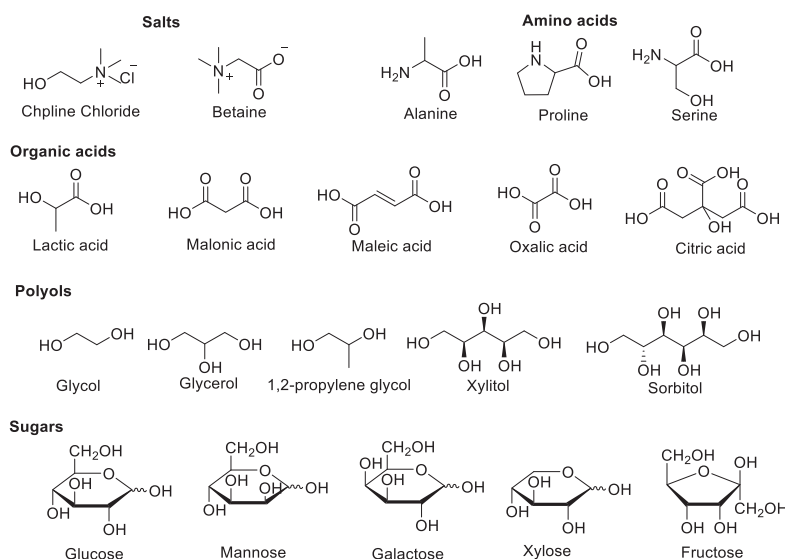


Figure 17. Typical natural deep eutectic solvents (NaDESs)

Although there is still a large space to explore the use of DESs in polymer synthesis, the use of the DESs in the synthesis of the bio-based and degradable plastics will open an innovative breakthrough towards a greener polymer industry.

4.5 Sustainable synthesis of bio-based PHUs

Developing renewable polymers to reduce the consumption of crude oil is very important for the preservation of the environment and the implementation of a more sustainable chemistry. As shown in the Figure 12, many bio-based chemicals are emerging to replace fossil resources. Although several synthetic pathways to the CCs have been developed, there are only a few papers dealing with the synthesis of PHUs from bio-based amines through the aminolysis reaction. Bio-based PHUs become more and more appealing for the researchers in academia and in industry, owing to more and more healthy and environmental questions. Innovation in the development of bio-based NIPUs could be implemented, for instance, in construction or adhesives and automotive materials.

Most research in the field of bio-based PHUs focused on vegetable oils and their derivatives. In addition, only a few patents and publications dealing with the sustainable synthesis of PHUs from bio-based molecules were released. Thus, there is little data on their structure, thermal and mechanical properties. Furthermore, the drawbacks discussed earlier related to the slow kinetics, the low molar mass, and the use of toxic additives or solvent seriously restrict their wide development.

In summary, the past investigations will help us to open a new fire-window to design safer, eco-friendly, healthier, and greener chemical pathway to produce the bio-based PHUs. Given the drawbacks previously identified, exploring more sustainable and efficient routes, such as non-metal-catalyzed strategies and the use of green solvents to prepare bio-based and more biodegradable PHUs will constitute the core of this manuscript.

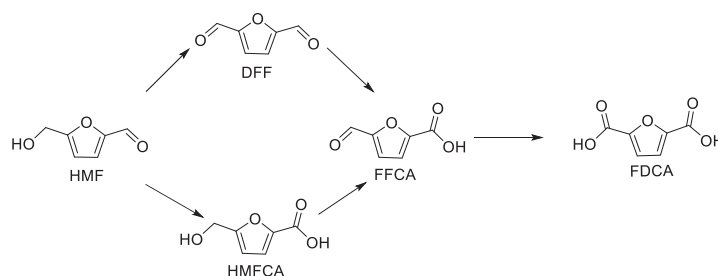
Chapter 2

Introduction

1.1 Bio-based platform molecules

Owing to the three reactive hydroxyl groups, glycerol is an important C3-bio-based building block to produce highly added-value molecules such as the bifunctional glycerol carbonate (GC). [118, 174] GC exhibits some special physical properties such as high flash point, high boiling point, low toxicity and low flammability particularly pertinent for industrial applications, and the two different hydroxyl and cyclic carbonate functions confer GC interesting chemical reactivities. [116, 175]

2,5-Furandicarboxylic acid (FDCA) derived from renewable sources is a high-value bio-based platform molecule. At present, FDCA is produced in more than 15,000 metric tons in the polymer industry per year generally by oxidation of HMF (Scheme 24) [113, 176-177]



Scheme 24. Oxidative pathways to synthesize FDCA from HMF

The synthesis of FDCA through the oxidation of HMF includes the following steps: the formyl or the hydroxymethyl groups are oxidized to generate the 2,5-diformylfuran

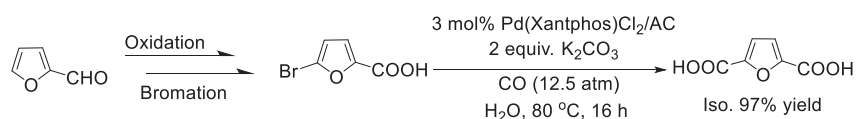
¹⁷⁴ Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, *10*, 13–30.

¹⁷⁵ Besse, V.; Camara, F.; Voirin, C.; Auvergne, R.; Caillol, S.; Boutevin, B. *Polym. Chem.* **2013**, *4*, 4545–4561.

¹⁷⁶ Triebel, C.; Nikolakis, V.; Ierapetritou, M. *Comput. Chem. Eng.* **2013**, *52*, 26–34.

¹⁷⁷ Teong, S. P.; Yi, G.; Zhang, Y. *Green Chem.* **2014**, *16*, 2015–2026.

(DFF) and 5-hydroxymethyl-2 furandicarboxylic acid (HMFCFA) intermediates, which are further oxidized to afford the 5-formyl- 2-furancarboxylic acid (FFCA) and eventually produce FDCA. ^[178] During my master degree, we developed a carbonation method to synthesize the FDCA from furfural (Scheme 25). ^[179]



Scheme 25. The pathway synthesis of FDCA from furfural

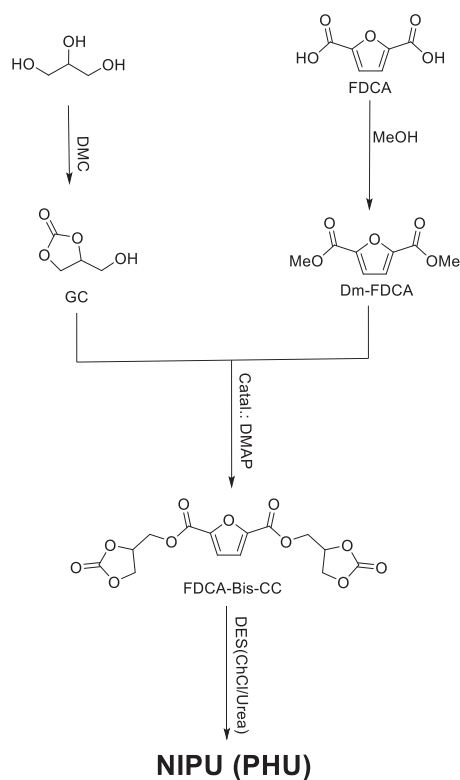
1.2 Purposes and aims

Hence, the synthesis of PHUs containing GC and FDCA is very appealing. Nevertheless, the aminolysis of SCCs to synthesize PHUs generally requires relatively long reaction times and high temperature, which mismatch with the “green” principles of the transformation. Last but not least, the use of catalysts is usually required to permit the use of sterically hindered amines (e.g. -methyl primary amines) and to afford decent molecular weights. ^[4, 34]

During my PhD work, we designed and optimized the reaction of the furan-2,5-dicarboxylate bis cyclic carbonate (FDCA-Bis-CC) with a series of diversely substituted amines in the choline chloride/urea (ChCl/Urea) deep eutectic solvent (DES) that plays both the role of a green solvent and a catalyst during the aminolysis reaction. To the best of our knowledge, this additive-free synthetic pathway of PHUs is unprecedented in the literature (Scheme 26).

¹⁷⁸ Gómez Millán, G.; Hellsten, S.; Llorca, J.; Luque, R.; Sixta, H.; Balu, A. M. *ChemCatChem* **2019**, *11*, 2022–2042.

¹⁷⁹ Shen, G.; Shi, J.; Lei, Y.; Fu, C.; Chen, Z.; Andrioletti, B.; Yin, G. *Catalyst. Ind. Eng. Chem. Res.* **2019**, *58*, 22951–22957.



Scheme 26. Synthetic strategy towards PHUs based on FDCA and glycerol

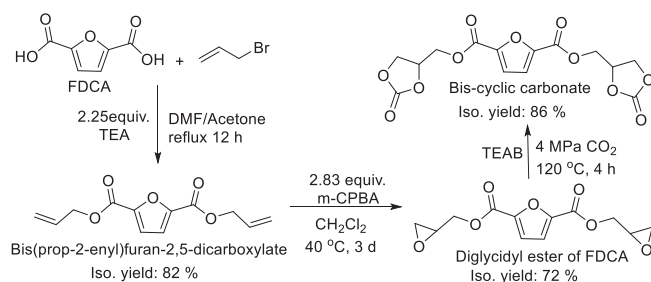
2 Synthesis of FDCA-Bis-CC

2.1 Background

In general, the conventional methods used to synthesize the FDCA-Bis-CC involve the use of large quantities of toxic chemicals such as DMF or *m*-chloroperoxybenzoic acid (*m*-CPBA) (Scheme 27).^[139, 180-181]

¹⁸⁰ Deng, J.; Liu, X.; Li, C.; Jiang, Y.; Zhu, J. *RSC Adv.* **2015**, *5*, 15930–15939.

¹⁸¹ Marotta, A.; Ambrogi, V.; Cerruti, P.; Mija, A. *RSC Adv.* **2018**, *8*, 16330–16335.



Scheme 27. Classical synthesis of FDCA-Bis-CC from FDCA

Conversely, the transesterification of dimethyl furan-2,5-dicarboxylate (Dm-FDCA) (**1**) could avoid the use of toxic chemicals to obtain the desired ester. Many catalysts have been developed in the past, especially for the transesterification of vegetable oils. ^[182] Alkali or acid agents (NaOH, KOH, CH₃ONa and CH₃OK; H₂SO₄, HCl, R-SO₃H) are generally used in homogeneous conditions, knowing that hydroxides are less active than alkali metal alkoxides. ^[183] Solid acid or solid alkali catalysts (Nafion and Amberlyst, CaO, MgO, KNO₃/Al₂O₃, and K₂CO₃/Al₂O₃) are used in heterogeneous system, and the solid base catalysts have been proven more active than the solid acid catalysts. ^[184] Furthermore, the heterogeneous catalysts could be recycled, increasing the economic efficiency, and reducing the pollutants. ^[185] Among all the catalysts, inorganic or organic Brønsted bases or Lewis acids such as distannoxanes have also been reported as efficient catalysts for the transesterification reaction. ^[186-187]

¹⁸² Thangaraj, B.; Solomon, P. R.; Muniyandi, B.; Ranganathan, S.; Lin, L. *Clean Energy* **2019**, *3*, 2–23.

¹⁸³ Saydut, A.; Kafadar, A. B.; Aydin, F.; Erdogan, S.; Kaya, C.; Hamamci, C. *Indian J. Biotechnol.* **2016**, *15*, 596–600.

¹⁸⁴ Ranganathan, S. V.; Narasimhan, S. L.; Muthukumar, K. *Bioresour. Technol.* **2008**, *99*, 3975–3981.

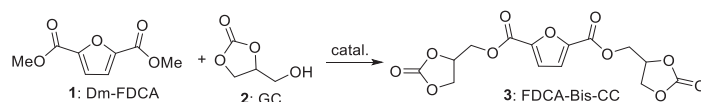
¹⁸⁵ Xie, W.; Huang, X.; Li, H. *Bioresour. Technol.* **2007**, *98*, 936–939.

¹⁸⁶ Christoffers, J.; Önal, N. *European J. Org. Chem.* **2000**, *8*, 1633–1635.

¹⁸⁷ Otera, J.; Yano, T.; Kawabata, A.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2383–2386.

2.2 Scope of the catalysts

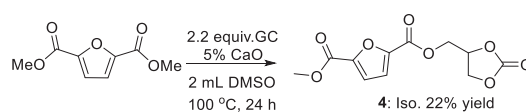
Table 2. Catalysts screening for the transesterification reaction.



Entry	Catal.	PKa	Yield (%)
1	CaO	12.8	Traces
2	NaOCH ₃	15-16	Traces
3	KOH	13.5	Not detected
4	Ti(OBu) ₄	--	Not detected
5	DMAP	9.7	52

Dimethyl furan-2,5-dicarboxylate (1 mmol, 184 mg), GC (2.2 equiv., 259 mg), 10 % Catal. (XX mg) and 2 mL dry Tol. were introduced to flask. The flask was kept open, and the reaction mixture was stirred at 90°C 24 h.

Within the frame of our research towards the development of the greenest process, we first decided to use CaO as the catalyst to promote the transesterification reaction. The heterogeneous catalyst could be easily recovered and reused after the reaction affording a cost-effective green process. Toluene was picked as the solvent and the temperature was set to 90°C. However, under these conditions, only traces of the FDCA-Bis-CC (**3**) desired product (Table 2, entry 1) was isolated. Meanwhile, we also explored the use of CaO at 100°C using DMSO as the solvent. However, we only isolated the desired Me-FDCA-cyclic carbonate (Me-FDCA-CC) (**4**) in 22% yield (Scheme 28). We also found that the presence of the MeOH by-product profoundly influences the reaction. Accordingly, we had to release the MeOH from the system throughout the reaction, otherwise, it could destroy the reaction product, resulting in a yellow oil, which structure is still unknown.



Scheme 28. Uncomplete transesterification of Dm-FDCA and GC

Other alkoxide, inorganic bases such as NaOCH₃ or KOH did not provide the target product in substantial amounts. NaOCH₃ (Table 2, entry 2) only produced traces of the transesterified product and KOH (Table 2, entry 3) induced the degradation of the substrate. Molodtsova *et al.* ^[188] explored the use of Ti(OBu)₄ as the catalyst to synthesize poly(ethylene 2,5-furanoate) from 2,5-dimethyl ester of furandicarboxylic acid through transesterification. Thus, we also tested Ti(OBu)₄ as the catalyst to synthesize the FDCA-Bis-CC at 90°C in toluene (Table 2, entry 4) and at 150°C in DMSO. Unfortunately, in any of these conditions, we did not observe the formation of the target product. To our delight, in the presence of 4-dimethylaminopyridine (DMAP) as the catalyst, we could isolate the desired FDCA-Bis-CC at 90°C in toluene with 52% yield after a simple filtration. (Table 2, entry 5).

2.3 Modification of the conditions

Therefore, we decided to use the DMAP as the catalyst for the synthesis of FDCA-Bis-CC (Scheme 29).

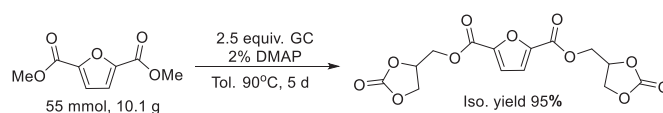


Scheme 29. Synthesis of FDCA-Bis-CC from Dm-FDCA and GC

Transesterification is an equilibrated reaction. So a slight excess of GC (2.2 equiv.) was used first to make sure to obtain the best conversion of Dm-FDCA in toluene. Subsequently, the impact of the temperature on the yield of the transesterification reaction was studied. Using 10 mol% DMAP, at 80°C, the desired FDCA-Bis-CC was isolated as a white powder in 45% yield by simple precipitation, because FDCA-Bis-CC is poorly soluble in toluene at room temperature (Table 3, entry 1). By increasing the temperature to 90°C (Table 3, entry 2), the desired product was isolated in 52% yield by simple filtration. Increasing further the temperature to 100°C (Table 3, entry 3)

¹⁸⁸ Molodtsova, T. A.; Boldyreva, E. V.; Klushin, V. A. *Mater. Sci. Forum* **2020**, *992*, 311–316.

allowed us to isolate the FDCA-Bis-CC in 65% yield. A higher yield was hoped at this temperature but as Dm-FDCA is very easily sublimated, part of the substrate was lost at relatively higher temperature and resulted in reproducibility issues. Thus, the optimal compromise between temperature and yield appeared to be 90°C. In order to increase further the sustainability of the reaction, we explored the effect of the catalytic charge. In the presence of 5 mol% DMAP at 90°C (Table 3, entry 4), we were pleased to find that the reaction yield was not influenced (50% yield vs. 52% yield). However, reducing the catalyst charge to 2.5 mol% load was harmful as only 17% yield of the desired FDCA-Bis-CC was isolated (Table 3, entry 5). Another parameter was studied next: the amount of GC. Interestingly, an insignificant increase of the excess of GC from 2.2 equiv. to 2.5 equiv. allowed isolating the desired dicarbonate in 67% yield (Table 3, entry 6) but a plateau seemed to be reached as the isolated yield remained pretty much the same even though a larger quantity of GC was used (Table 3, entry 7). Accordingly, our results indicated that the best conditions were 2.5 equiv. GC, 90°C, and 5 mol% catalyst. With these optimal conditions in hands, we explored the effect of the reaction time on the yield of the transesterification reaction. After 48 hours, we could further improve the efficiency of the reaction and isolate the FDCA-Bis-CC desired product in 58% yield (Table 3, entry 8). Interestingly, when the reaction was launched in 10g scale (55 mmol Dm-FDCA), after gradually enlarging the experiment, FDCA-Bis-CC was received in 95% yield after a simple filtration and washing with acetone (Scheme 30). This very high yield is explained by a better stirring and a better control of the experimental conditions (limited solvent and catalyst and evaporation).



Scheme 30. Synthesis of FDCA-Bis-CC in large scale

Table 3. Conditions screening for the synthesis of FDCA-Bis-CC through transesterification.

Entry	Temp. (°C)	Catal. (%)	Yield (%)
1	80	10	45
2	90	10	52
3	100	10	65
4	90	5	50
5	90	2.5	17
6 ^a	90	5	67
7 ^b	90	5	69
8 ^c	90	5	58

DM-FDCA (1 mmol, 184 mg), 2 GC (.2 equiv. 259 mg), XX% DMAP were dissolved in 2 mL dry Tol. and the reaction mixture was stirred at the indicated temperature for 24 h. n.r.: no reaction ^a: 2.5 equiv. GC, ^b: 3 equiv. GC. ^c: 48 h.

3 Conditions for the aminolysis reaction

3.1 Background

Having developed an efficient method to produce the FDCA-Bis-CC in large scale (Scheme 30) in the absence of highly toxic reagents and lengthy column chromatographies, we went further on and investigated different diamines (Figure 18) for the aminolysis of FDCA-Bis-CC to synthesize the corresponding PHUs. As it has been recalled in the introduction chapter, it is well acknowledged that many factors can impact the reaction and the recent efforts immersed in optimizing the PHU synthesis were proven fruitful.

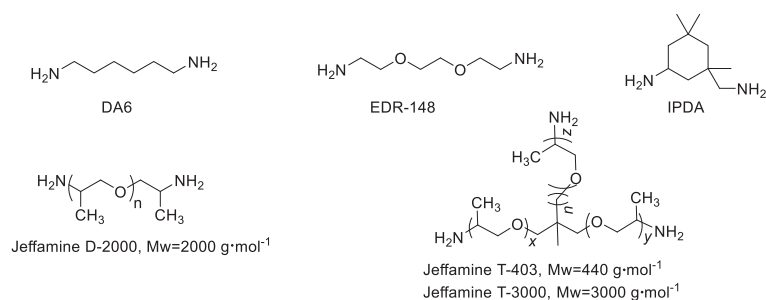
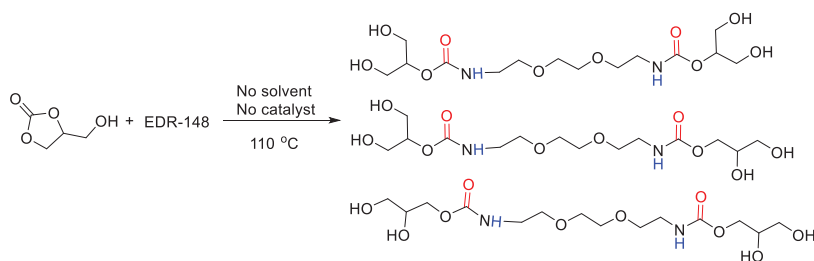


Figure 18. Different types of diamines chemical structure

3.2 The characteristic of urethane

We firstly used the GC and EDR-148 to evaluate the aminolysis reaction without additives and solvent (Scheme 31). After the reaction, the NMR results indicated that the GC carbonyl peak disappeared and the urethane carbonyl peaks located ranged from 156.3 to 156.5 ppm (Figure 19). As aromatic or sterically hindered amines are less reactive than the EDR-148, the use of additives or long reaction time are generally necessary for them.



Scheme 31. Reaction between EDR-148 and GC

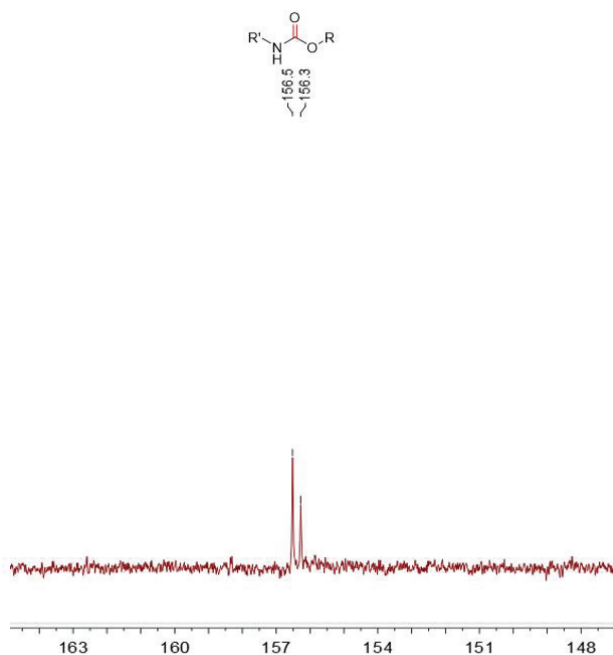


Figure 19. The urethane carbonyl chemical shifts in ^{13}C NMR

3.3 Solvent screening for the aminolysis reaction

In the recent decades, organocatalysts have demonstrated their importance in the catalytic aminolysis reaction, among which the thiourea derivatives and TBD exhibit outstanding activities (Figure 10).^[96, 189] Parallely, a series of investigations on the role of the solvent used in the aminolysis reaction indicated that generally, protic solvents have positive effect on the reactivity and conversion of the cyclic carbonate by improving the carbonyl positive charge and also by interrupting the intra- and inter-molecular hydrogen bonds network present in the PHU chains.^[77, 86, 190]

However, traditional organic solvents (DMF, DMSO) used in the aminolysis reaction are hazardous to the environment and/or present fearful and chronic toxicity to human and a low biodegradability.^[191] For the sake of solving the previously mentioned problems, the deep eutectic solvents (DESS) have been proposed as green,

¹⁸⁹ Lambeth, R. H.; Henderson, T. J. *Polymer* **2013**, *54*, 5568–5573.

¹⁹⁰ Prömpers, G.; Keul, H.; Höcker, H. *Green Chem.* **2006**, *8*, 467–478.

¹⁹¹ Andrioletti, B. *Techniques de l'Ingénieur*, **2016**, CHV4000, 1–7.

alternative to replace toxic solvents over the past two decades. Especially, natural deep eutectic solvents (NaDESs) are most attractive as they are easily prepared from natural or bio-based compounds. ^[161, 192] NaDESs present some excellent properties such as an remarkable dissolution power even for metal oxides compared with the traditional solvents and they can also act as catalysts and could be applied in material chemistry. ^[162, 193]

Recently, Zhu *et al.* ^[194] developed a DES (ChCl/Urea) supported on molecular sieves as the catalyst for the synthesis of cyclic carbonate from epoxides and CO₂. As it has been described in the introduction chapter, Xue *et al.* ^[167] synthesized a lignin-containing rigid polyurethane foam in a DES. Based on those previous results, we explored the use of Jeffamine D-2000 as nucleophile in the aminolysis of FDCA-Bis-CC in a series of green solvents. DMF was used as a reference solvent and as a benchmark in the reaction (Table 4).

Table 4. Screening of the solvents used for the aminolysis of FDCA-Bis-CC with the Jeffamine D-2000.

Entry	Solvent	Results
1	DMF	Many by-products
2	Glycerol	n.r.
3	ChCl/Urea=1:2	Yes
4 ^a	ChCl/Urea=1:2	n.r.
5	ChCl/AcNH ₂ =1:2	n.r.
6	ChCl/Glycerol=1:2	n.r.
7	AcNH ₂ /Urea=1:2	Yes*

Jeffamine D-2000 (0.5 mmol, 1 g), FDCA-CC (0.5 mmol, 178 mg), and 1 mL solvent were introduced into a glass reactor and heated for 24 h at 110°C under an Ar atmosphere. n.r.: no reaction. ^a temperature was set to 100°C. * The AcNH₂/Urea DES is unstable at 110°C.

¹⁹² Xu, P.; Zheng, G. W.; Zong, M. H.; Li, N.; Lou, W. Y. *Bioresour. Bioprocess.* **2017**, *4*, 1–28.

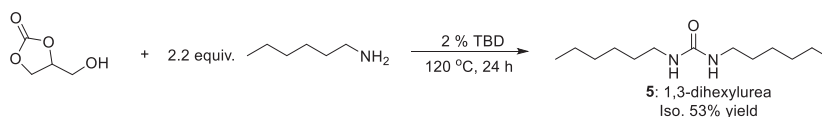
¹⁹³ Taghizadeh, M.; Taghizadeh, A.; Vatanpour, V.; Ganjali, M. R.; Saeb, M. R. *Sep. Purif. Technol.* **2021**, *258*, 118015.

¹⁹⁴ Zhu, A.; Jiang, T.; Han, B.; Zhang, J.; Xie, Y.; Ma, X. *Green Chem.* **2007**, *9*, 169–17.

Under classical conditions (equimolar amounts of bis-carbonate and diamine at 110°C in DMF), the aminolysis reaction did not proceed as expected as many different products were produced during the reaction (Table 4, entry 1). Switching from DMF to glycerol (a bio-based, protic solvent; Table 4 entry 2) was not effective either, because the substrate remained untransformed after 24h at 110°C. The traditional conditions being unsuccessful, we envisioned the use of DES. Among the almost infinite possibilities for combining a hydrogen bond acceptor and a hydrogen bond donor, we concentrated our efforts on DESs originating from choline chloride (ChCl) that provides the advantage of being a potential actor for assisting the aminolysis reaction and on urea that could activate the carbonyl group of the cyclic carbonate function. Other combinations (ChCl/AcNH₂, ChCl/glycerol, ...) were used for assessing the role of the various partners. At the exception of the DES constituted of AcNH₂/urea that was proven to decompose at 110°C, the ChCl/Urea combination was proven effective for increasing the aminolysis reaction (Table 4, entry 3). Notoriously, lowering the temperature to 100°C limited the reaction (Table 4, entry 4). When other hydrogen bond donors were used to replace urea, the reaction did not proceed (Table 4, entries 5 and 6). Hence, the optimal conditions for improving the aminolysis reaction involved the use of ChCl/Urea (1: 2) as the solvent at 110°C.

3.4 By-products identified in the aminolysis reaction

During the ¹³C NMR analysis of the reaction mixture obtained during the aminolysis reaction in ChCl/Urea, we found an interesting peak located at 159 ppm in ¹³C NMR. In order to unambiguously assign this signal, firstly, we launched test reactions involving GC, hexylamine and 2% TBD as the catalyst to synthesize the model 1,3-dihexylurea. The latter could be isolated in 53% yield after purification (Scheme 32). The carbonyl function of the 1,3-dihexylurea (**5**) was found at 158 ppm (Figure 20) vs 160 ppm for the non-alkylated urea.



Scheme 32. Synthesis of 1,3-dihexylurea from hexylamine and GC

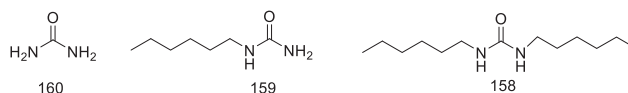
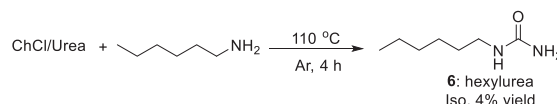


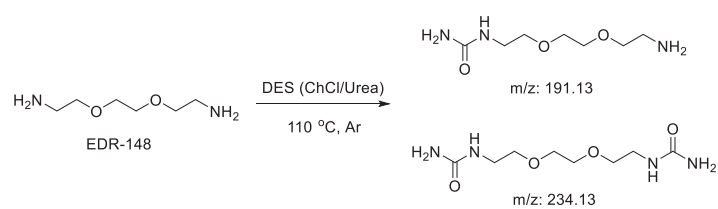
Figure 20. Typical ^{13}C chemical shifts for common symmetrical or unsymmetrical ureas

Next, when heating at 110°C for 4 hours under Ar, a mixture of ChCl/Urea DES (ChCl/Urea = 1:2) and hexylamine, we could isolate hexylurea (**6**) as a by-product in 4% yield (Scheme 33) with its characteristic resonance of the carbonyl signal at 159 ppm. Hence, this reaction demonstrated that the nucleophilic hexylamine could react with the urea of DES under the experimental conditions. This test reaction allowed us to fully assign the different types of carbonyl signals in ^{13}C NMR (Figure 20). The effect of alkyl donating group induces a slight shielding of the signal from 160 ppm to 158 ppm.



Scheme 33. Reaction between hexylamine and urea

EDR-148 displayed a high reactivity during the aminolysis reaction as it could react with FDCA-Bis-CC in the ChCl/Urea DES at 65°C to produce the expected PHU. After the reaction, the NMR and GPC analyses indicated that we obtained the PHU polymer. Of note, we didn't find the signal at 159 ppm in the ^{13}C NMR. Interestingly, in the absence of the FDCA-Bis-CC electrophile, when heating EDR-148 in the DES (ChCl/urea) at 110°C under inert atmosphere (Scheme 34), the signal at 159 ppm could be detected in the ^{13}C NMR spectrum (Figure 21). In addition, we could find the corresponding signals ($[\text{M}+\text{H}]^+$ 192.1 and $[\text{M}+\text{H}]^+$ 235.1) in the MS analysis (Scheme 34).



Scheme 34. Reaction between EDR-148 and urea

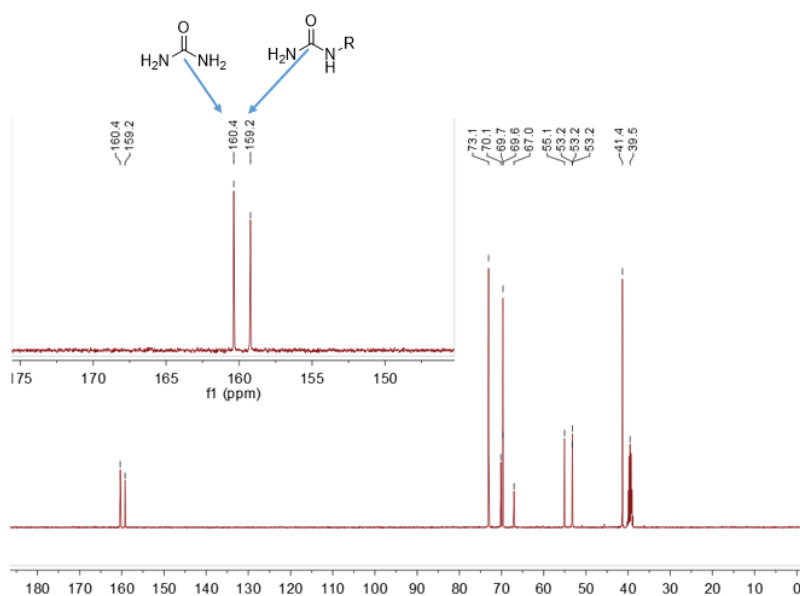
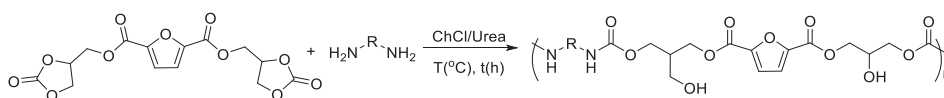


Figure 21. The EDR-148 urethane carbonyl signals in ^{13}C NMR

4 Properties of PHUs

Several substituted amines (Figure 18) were reacted with FDCA-Bis-CC using the previously mentioned optimal conditions (Scheme 35).



Scheme 35. Synthesis of PHUs based on FDCA-Bis-CC and several diamines

Table 5. Properties of PHUs.

Entry	Diamines	T (°C)	t (h)	<i>Mn</i> (g·mol ⁻¹)	PDI
1	EDR-148	110	24	24,578	1.00
2	DA6	110	40	18,137	1.08
3	EDR-148	65	48	25,320	1.03
4	IPDA	110	40	27,374	1.08
5	Jeffamine D-2000	110	40	6,784	1.01
6	Jeffamine T-403	110	40	32,113	1.04
7	Jeffamine T-3000	110	40	7,386	1.01

As expected, the rather nucleophilic amines produced the desired PHUs with *Mn* > 20,000 g·mol⁻¹ (Table 5, entries 1, 3) in relatively benign conditions. To our delight, the reactivity could be preserved for the use of short polyamines displaying high nucleophilicity and low boiling points even at low temperature (65°C instead of 110°C) opening promises for the future. Furthermore, less nucleophilic amines such as IPDA and the α -methylated Jeffamines were reactive enough to offer the corresponding PHUs (Table 5, entries 4-7), whilst generally with lower *Mn*.

5 Conclusion

In this chapter, we disclosed a green, novel and additives free process to prepare PHUs even with sterically hindered α -methyl primary amines that generally display a poor reactivity during the aminolysis reaction. This was given possible by the use of the DES (ChCl/Urea) that was used both as a green solvent and a catalyst. Furthermore, the highly solvent power of the DES allows for the synthesis of PHUs giving a rather high *Mn*. In addition, owing to the bis-carbonate used as the key reagent that contains a FDCA moiety which is known to favor the biodegradability,^[134, 195] it is expected that our strategy will enable the sustainable development of bio-degradable PHUs. Chemical products should be designed so that they could break down into harmless

¹⁹⁵ Iwata, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 3210–3215.

degradation products and cannot persist in the environment at the end of their function. Indeed, the bio-based-character of a polymer may not be sufficient for matching the green chemistry principles if, ultimately, it is not easily degraded.

Chapter 3

Introduction

1.1 Bifunctionalized monomers originated from furfural (FF)

Presently, furfural (FF) is industrially produced from the raw agricultural materials (corn cobs, oat, wheat bran, sawdust, and so on) without any limit. ^[113] However, its estimated market volume production (250 kT per year) is still limited due to the monofunctionalized furan structure. ^[196] Its renewable character combined with an appropriate functionality explains why many researchers, both in academia and industry, consider this molecule promising to produce highly added value bio-based molecules. ^[197]

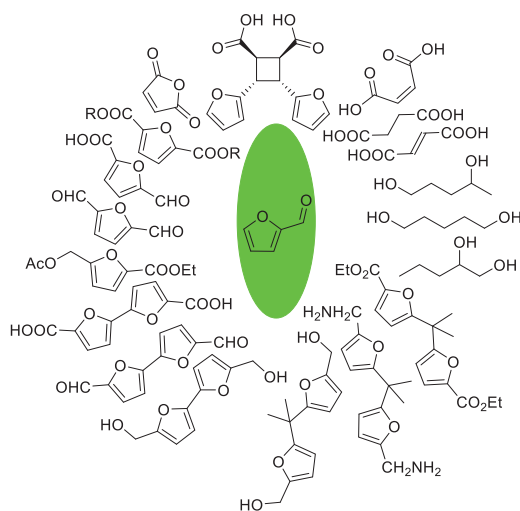


Figure 22. Bifunctionalized monomers originating from FF

For developing the FF application in polymer chemistry, many excellent catalytic pathways have been developed to produce bifunctionalized monomers originating

¹⁹⁶ Delidovich, I.; Hausoul, P. J. C.; Deng, L.; Pfützenreuter, R.; Rose, M.; Palkovits, R. *Chem. Rev.* **2016**, *116*, 1540–1599.

¹⁹⁷ Thoma, C.; Konnerth, J.; Sailer-Kronlachner, W.; Solt, P.; Rosenau, T.; van Herwijnen, H. W. G. *ChemSusChem* **2020**, *13*, 3544–3564.

from FF and its derivatives (Figure 22).^[198-199] 2,2-bifuryl-5,5-dicarboxylic acid (BFDCA) can be synthesized from 5-bromofuroic acid on large scale.^[200] It was recently investigated in the synthesis of several polyesters and polyamides and it was demonstrated that BFDCA presents some superior properties compared with the corresponding polymers obtained from 2,5-furandicarboxylic acid and poly(ethylene terephthalate), which give promising perspectives in other polymer applications.^[201-202]

1.2 Purposes and aims

Herein, we report the synthesis of a fully bio-based bis-cyclocarbonate originating from BFDCA that was involved in aminolysis reactions with a series of variously substituted amines diamines in DES (ChCl/Urea) to obtain PHUs, even the sterically hindered α -methyl primary amines (Scheme 36).

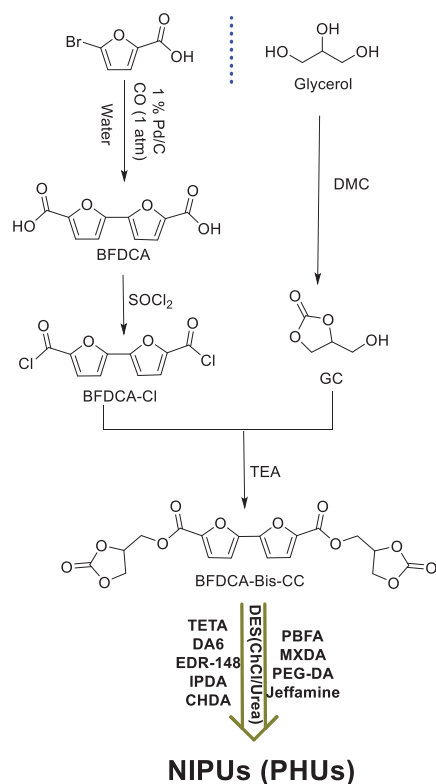
¹⁹⁸ Li, X.; Jia, P.; Wang, T. *ACS Catal.* **2016**, *6*, 7621–7640.

¹⁹⁹ Zhu J.; Yin G. *ACS Catal.* **2021**, *11*, 10058–10083.

²⁰⁰ Lei, Y.; Zhang, S.; Shen, G.; Zhu, J.; Xue, J. W.; Chen, Z.; Yin, G. *Ind. Eng. Chem. Res.* **2020**, *59*, 19876–19883.

²⁰¹ Miyagawa, N.; Suzuki, T.; Okano, K.; Matsumoto, T.; Nishino, T.; Mori, A. *J. Polym. Sci. Part A Polym. Chem.* **2018**, *56*, 1516–1519.

²⁰² Kainulainen, T. P.; Hukka, T. I.; Özeren, H. D.; Sirviö, J. A.; Hedenqvist, M. S.; Heiskanen, J. P. *Biomacromolecules* **2020**, *21*, 743–752.

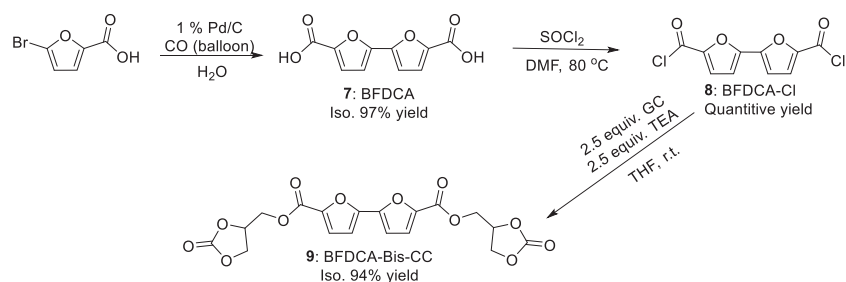


Scheme 36. Synthetic strategy towards PHUs from bio-based BFDCA and glycerol

2 Preparation of PHUs

2.1 Synthesis BFDCA-Bis-CC

Zhu *et al.* ^[198] developed a series of strategies to produce bifunctionalized monomers from furfural. Among all monomers, the authors used Pd/C as the catalyst, CO (air pressure) as the reductant, 2 equivalents of NaOH as the base to achieve the efficient production of BFDCA (**7**) in a large scale. During my Master degree, I also contributed to this work. ^[199] Subsequently, the corresponding diacyl chloride was prepared by reacting BFDCA with SOCl₂ in the presence of a catalytic amount of DMF to afford the 2,2-bifuryl-5,5-dicarboxyl chloride (BFDCA-Cl) (**8**) in quantitative yield. Next, the latter was reacted with an excess of GC in the presence of TEA as the base to neutralize the HCl to produce BFDCA-Bis-CC (**9**) in 94% yield (Scheme 37).



Scheme 37. Pathway to synthesize BFDCA-Bis-CC

2.2 Preparation of PHUs in DES

In the previous chapter, we have reported that the use of the ChCl/Urea DES solvent in aminolysis reactions to synthesize PHUs could display better performances than more conventional solvents. ^[203] Therefore, we have launched a series of aminolysis reactions between BFDCA-Bis-CC and different diamines in DES (ChCl/Urea) under inert atmosphere. Figure 23 displays the diamine chemical structures. Among the diamines, we synthesized the 5,5'-(propane-2,2-diyl) bis(furan-5,2-diyl) methenamine (PBFA) (**10**) from bio-based furfuryl amine according to the Skoutas' work. ^[144]

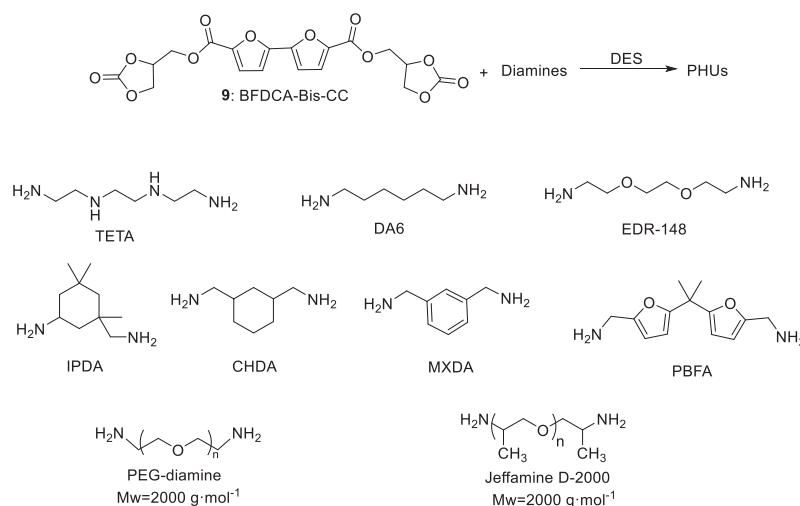


Figure 23. Structures of the diamines evaluated in the study

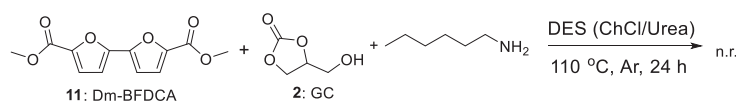
The different reactions were launched according to the “optimal” protocol described in the Chapter 2. After the reaction, water was used to wash the mixture and purify

²⁰³ Shen G.; Andrioletti B. *Molecules*, **2022**, *27*, 4131.

the PHUs, except for the reactions involving the TETA and the EDR-148 that were purified through dialysis in water. The use of the ChCl/Urea DES as the solvent avoids the need for additives (Lewis acid or alkali) or traditional toxic solvent (DMF). Consequently, it is relatively easy to obtain pure polymers after the reaction. The IR spectra of the synthesized PHUs indicated that the carbonyl of the urethane C=O appears around 1650 cm⁻¹, and the urethane N-H located around 1540 cm⁻¹ (see SI FT-IR). These results are in agreement with the data from the literature. [78, 204]

2.3 Possible by-product formation

Firstly, the dimethyl (2,2'-bifuran)-5,5'-dicarboxylate (**11**) (Dm-BFDCA, 1 mmol, 250 mg), glycerol carbonate (2 mmol, 236 mg), hexylamine (2 mmol, 202 mg) and 1 mL DES (ChCl/Urea) were introduced into flask. The mixture was heated at 110°C in Ar atmosphere for 24 h (Scheme 38). As after the reaction, we didn't detect any amide products by ¹H NMR or FT-IR, we could conclude that the amidification reaction does not take place in our conditions.



Scheme 38. Competitive reaction revealing the absence of amide formation

According to our discussion in the Chapter 1, nucleophilic amines can attack the ester carbonyl function at the expense of the cyclocarbonate, affording amides, especially when the reaction temperature is set above 100°C. In order to ascertain or exclude this possibility, we synthesized the N-hexyl-2,2-bifuryl-5,5-dicarboxamide (**12**) (Figure 24). The amide carbonyl vibration was identified at 1640 cm⁻¹ in the FT-IR spectrum, which is in agreement with the literature data. [205] Thus, the absence of the vibration at 1640 cm⁻¹ in the FT-IR spectrum demonstrated that the newly formed PHU did not

²⁰⁴ Benyahya, S.; Boutevin, B.; Caillol, S.; Lapinte, V.; Habas, J. P. *Polym. Int.* **2012**, *61*, 918–925.

²⁰⁵ Tanada, M.; Shibata, Y.; Maeda, M.; Sasaki, S. *Heterocycles* **2004**, *63*, 29–39.

contain any amide bonds.

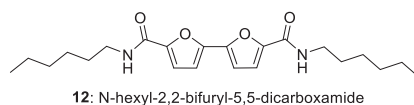


Figure 24. N-hexyl-2,2-bifuryl-5,5-dicarboxamide

3 Properties of PHUs

3.1 Structural analysis:

Table 6. *Mn* and *Mw* values for the synthesized PHUs.

Entry	Diamines	<i>Mw</i> (g·mol ⁻¹)	DPm	PDI
1 ^a	TETA	1,200	2	1.3
2 ^a	EDR-148	1,200	2	1.3
3	DA6	6,900	13	2.3
4	MXDA	3,000	5	1.3
5	CHDA	6,700	12	1.8
6	PBFA	11,000	17	3.5
7	IPDA	2,000	3	1.6
8	Jeffamine D-2000	4,500	1	1.7
9 ^b	Jeffamine D-2000	--	--	--
10	PEG-diamine	7,500	3	2.5

2,2-Bifuryl-5,5-Dicarboxyl glycerol carbonate (1 mmol, 422 mg), diamine (1 mmol, xx mg), and 1 mL DES were introduced into the flask. The mixture was heated at 110°C under Ar atmosphere for 24 h. After the reaction, the reaction was probably not completed, and the PHUs were washed with water. n.r.: no reaction. ^a Dialysis was used to purify the PHUs. ^b 90°C.

The SEC analyses showed that a large range of molecular weight were obtained. First, the linear amine exhibited *Mw* from 1200 to 11000 g·mol⁻¹ (Table 6). It seems that the polymerization leads to oligomers when TETA and EDR-148 (≈ 1200 g·mol⁻¹) are used (Table 6, entry 1 and 2) whereas higher molecular weights was obtained using the DA6 (≈ 7000 g·mol⁻¹) (Table 6, entry 3). The cyclic diamines showed molecular weights around 3000 g·mol⁻¹ to 11000 g·mol⁻¹ (Table 6, entries 4 to 6), which means that the

polymerization well occurred. Nevertheless, the IPDA exhibited a lower molecular weight (Table 6, entry 7). Using the DES as solvent to launch the aminolysis reaction between Jeffamine D-2000 and BFDCA-Bis-CC, M_w around 4500 g.mol⁻¹ (Table 6, entry 8) were measured. It can be linked to the lower reactivity of α sterically hindered amine. Indeed, the primary amine might react, but the α -methyl amine takes longer thus, a shorter polymer was obtained. In addition, we could not obtain the PHU at a lower temperature (90°C) in DES (Table 6, entry 9). Unlike Jeffamine D-2000, the other large amine used, the PEG 2000 exhibited a relatively higher molecular weight (Table 6, entry 10), M_w around 7500 g.mol⁻¹.

As aminolysis is a polycondensation reaction, the polymerization is not controlled which led to a broad range of molecular weight. That is why the polydispersity (PDI) is quite high for the different samples. If we increase the reaction time, we can obtain high molecular weight products in the aliphatic diamines based PHUs, the low molecular weight owing to short reaction time. Otherwise, we still afford the low molecular weight products; thus, the aliphatic diamines and bis-cyclocarbonate (entries 1, 2, 8 and 10) probably produce circle products. Some low molecular weight can be explained by side reaction such as amidification or cyclization of the polymer. [100, 103, 108] Some low PDI could be contributed to the unsuitable reference in analysis of the M_w and the residue monomers.

3.2 Thermal analysis

First DSC analyses were carried out to determine the glass transition temperature (T_g) of the polymers synthesized. As shown in Table 7, a broad range of T_g were obtained. Indeed, the use of aliphatic diamine such as, EDR-148, DA6, PEG-diamine and Jeffamine D-2000 exhibited low glass transition from -40°C to -50°C (Table 7, entries 2, 3, 8, and 10). These results are coherent with the structure of the polymer. Moreover, when aliphatic or aromatic rings are used (MXDA, CHDA, PBFA and IPDA) the T_g were improved to reach values around 70°C (Table 7, entries 4-7). These values are coherent since the rings are known to confer rigidity to the polymer matrix.

Table 7. Thermodynamic properties of PHUs.

Entry	Diamines	T _{d 5%} °C	C Residue at 700 °C (mass%)	T _g (°C)
1 ^a	TETA	146	8.3	-38
2 ^a	EDR-148	166	9.2	-38
3	DA6	167	16.8	-43
4	MXDA	217	25.0	71
5	CHDA	216	20.7	72
6	PBFA	227	28.8	71
7	IPDA	196	4.0	68
8	D-2000	198	1.8	-50
9 ^b	D-2000	n.r.	--	--
10	PEG-diamine	146	3.0	-44

2,2-Bifuryl-5,5-Dicarboxyl glycerol carbonate (1 mmol, 422 mg), diamine (1 mmol, xx mg), and 1 mL DES were introduced into the flask. The mixture was heated at 110°C under Ar atmosphere for 24 h. After the reaction, the PHUs were washed with water. n.r.: no reaction. ^a Dialysis was used to purify the PHUs. ^b 90°C. ^c DMF as solvent.

The PEG-diamine presented two unique phenomena in this study using DSC. Indeed, an exothermic peak of crystallization is observed around -16°C and the fusion of the polymer is observed around 42°C (Figure 25). Thus, this sample is the only non-amorphous polymer that was obtained.

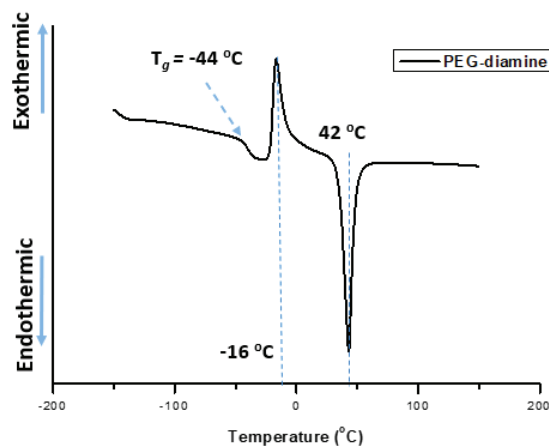


Figure 25. The DSC trace of the PEG-diamine based PHUs

Next, the thermal stability of the polymer was explored using a TGA analyzer (Table 7). The short aliphatic diamines (TETA, EDR-148, and DA6) showed the lowest thermal stability with around $T_{d\ 5\%}$ around 150 °C to 160 °C (Table 7, entries 1-3). When, the chain length of the amine is extended, *e.g.* with PEG-diamine the $T_{d\ 5\%}$ was observed around 150 °C (Table 7, entry 10). The PEG diamine structure did not improve the thermal stability since the structure with ether linkage is not highly stable toward temperature. [206] The D-2000 amine structure also contains ether linkage, nevertheless, the $T_{d\ 5\%}$ is also improved at about 200 °C (Table 7, entry 8). The longer chain length could explain the difference between the D-2000 and PEG-diamine PHUs. Moreover, the D-2000 structure contains methyl groups that can improve the $T_{d\ 5\%}$ depending on the structuration. The aromatic and cyclic diamine exhibited $T_{d\ 5\%}$ around 200 °C . The aromatic structure improves the structuration of the final polymer. Thus, the $T_{d\ 5\%}$ is improved compared to the short aliphatic amine. The effect was also observed on the mass left at 700 °C . Indeed, the mass left at 700 °C was about 20% to 29% with CHDA, PBFA and MXDA (Table 7, entries 4-6). The IPDA had a surprisingly low residual mass at 700 °C (Table 7, entry 7). Even if it is not an aromatic amine, the char at 700 °C was expected higher. The low char amount could be linked to the low polymerization observed by GPC. The aliphatic amines based PHUs (entries 1, 2, 3 and 10) presented a low $T_{d\ 5\%}$ degradation temperature, and the phenomenon could be

²⁰⁶ Chen, H.; Shi, X.; Zhu, Y.; Zhang, Y.; Xu, J. *Front. Chem. Eng. China* **2008**, *2*, 102–108.

attributed to multiple factors such as containing water or starting material. Next we will dry the samples at 100 °C under reduced pressure. The aliphatic amine containing ether or secondary amine linkages are easily degraded with the temperature. Thus, as expected the TETA and EDR-148 had low mass left at 700°C (Table 7, entry 1 and 2). However, DA6 had 16% mass left at 700°C, which is unexpected with aliphatic chain (Table 7, entry 3). This char formation can be linked to the chemical structure of the polymer.

4 Conclusion

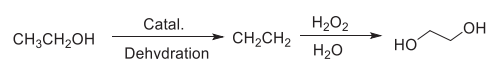
In this work, using ChCl/Urea DES as a green solvent to promote the aminolysis reaction between BFDCA-Bis-CC and diamines, even the poorly reactive α -methyl primary amines were proven good partners. The starting material BFDCA-Bis-CC and diamine of PBFA originate from the biomass. A large range of M_w were obtained from different PHUs and some of them exhibit different thermodynamic properties. The PHUs from the cyclic diamines present higher T_g temperature (more than 100 °C) compared with the PHUs from the aliphatic diamines. Meanwhile, the cyclic-diamines based PHUs appear more stable than the aliphatic diamines PHUs in high temperature. However, the PHUs originating from the cyclic diamines did not give the expect higher T_d 5%°C. Interesting, the PHUs contained the ether bond present more easy degradation in high temperature. The PEG-diamine based PHU is the only non-amorphous polymer.

Chapter 4

Chapter 4. Bio-based diols-bridged furancarboxylate cyclocarbonate

Introduction

Main diols originate from fossil resources and are pivotal bulk chemicals which are applied in a wide range of areas, including polymers, solvents, fuels, and pharmaceuticals. [195, 207-208] With the energy crisis and the pollution arising from the consumption of fossil resources, researchers are looking for alternative renewable resources. [209]



Scheme 39. Chemical pathways to ethylene glycol from the bio-based ethanol

Nowadays, ethylene glycol (EG) can be synthesized from ethylene deriving from the bio-based ethanol through a chemical processes developed recently by the researchers (Scheme 39). [210] Meanwhile, a consequent amount of works dedicated to the production of 1,3-propanediol (1,3-PDO) from the bio-based glycerol through a heterogenous catalyst system and metabolic engineering have been published in the past decades. [211-212, 213]

Especially, the Dupont company achieved the biological production of 1,3-butanediol (1,3-BDO) and 2,3-butanediol (2,3-BDO) for commercial-scale in the early 2000's. [214-215] The Genomatica company commercialized the synthesis of 1,4-butanediol (1,4-

²⁰⁷ Jiang, Y.; Liu, W.; Zou, H.; Cheng, T.; Tian, N.; Xian, M. *Microb. Cell Fact.* **2014**, *13*, 1–17.

²⁰⁸ Deng, C. Q.; Jiang, Q. Z.; Deng, J.; Fu, Y. *Green Chem.* **2021**, *23*, 2169–2176.

²⁰⁹ Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411–2502.

²¹⁰ Zhang, M.; Yu, Y. *Ind. Eng. Chem. Res.* **2013**, *52*, 9505–9514.

²¹¹ Zhao, X.; Wang, J.; Yang, M.; Lei, N.; Li, L.; Hou, B.; Miao, S.; Pan, X.; Wang, A.; Zhang, T. *ChemSusChem* **2017**, *10*, 818–824.

²¹² Chanklang, S.; Mondach, W.; Somchuea, P.; Witoon, T.; Chareonpanich, M.; Faungnawakij, K.; Seubsai, A. *Catal. Today* **2022**, *397*, 356–364.

²¹³ Chen, Z.; Liu, D. *Biotechnol. Biofuels* **2016**, *9*, 1–15.

²¹⁴ Nakamura, C. E.; Whited, G. M. *Curr. Opin. Biotechnol.* **2003**, *14*, 454–459.

²¹⁵ Saxena, R. K.; Anand, P.; Saran, S.; Isar, J. *Biotechnol. Adv.* **2009**, *27*, 895–913.

BDO) from sugars through metabolic engineering of *Escherichia coli*.^[216] The main applications of the short chain diols and their isomers are shown in the Figure 26.^[217] EG, 1,3-PDO, and 1,4-BDO are important building blocks to synthesize polyethylene terephthalate (PET), polypropylene terephthalate (PTT), and polybutylene terephthalate (PBT) in the polymer industry.

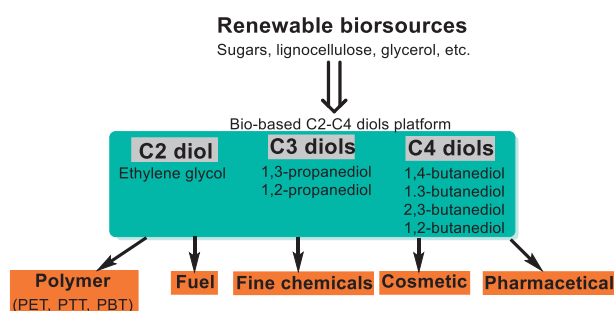
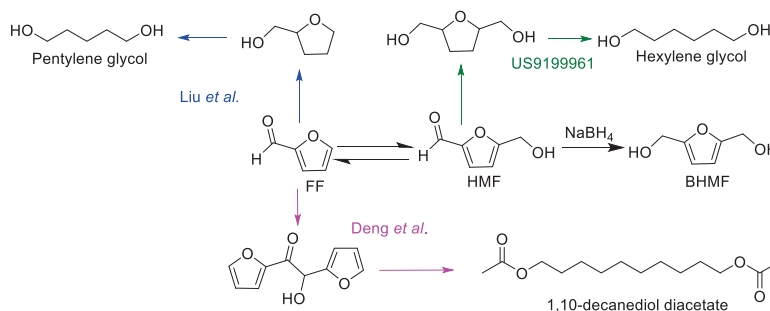


Figure 26. Applications of C2-C4 diols and their isomers

As it has been recalled in the introduction chapter, FF and HMF are two important bio-based platform molecules used to produce other sub-derivatives (Scheme 40). 1,10-decanediol is an important raw material as Deng *et al.*^[207] developed an efficient and sustainable pathway to synthesize 1,10-decanediol diacetate from FF (Scheme 40).



Scheme 40. Diols from furanic platforms

Liu *et al.*^[218] using the Pd-added Ir -ReOx/SiO₂ as catalysts carried out a two-step

²¹⁶ Yim, H.; Haselbeck, R.; Niu, W.; Pujol-Baxley, C.; Burgard, A.; Boldt, J.; Khandurina, J.; Trawick, J. D.; Osterhout, R. E.; Stephen, R.; Estadilla, J.; Teisan, S.; Schreyer, H. B.; Andrae, S.; Yang, T. H.; Lee, S. Y.; Burk, M. J.; Van Dien, S. *Nat. Chem. Biol.* **2011**, *7*, 445–452.

²¹⁷ Zhang, Y.; Liu, D.; Chen, Z. *Biotechnol. Biofuels* **2017**, *10*, 1–20.

²¹⁸ Liu, S.; Amada, Y.; Tamura, M.; Nakagawa, Y.; Tomishige, K. *Green Chem.* **2014**, *16*, 617–626.

reaction to synthesize pentylene glycol from FF in one-pot at different temperatures. In a related work, hexylene glycol can be produced by hydrogenation of HMF as it has been reported in a U.S. Patent.^[219] 2,5-furandimethanol, a six-carbon monomer for polymer synthesis, mainly originates from HMF through hydrogenation, which is mature pathway.^[220]

Isosorbide is a C6 diol containing two hydroxyl functions and its bicyclic structure provides a relatively high chemical stability. It is commercially available from sugar, (Figure 27).^[195] The hydroxyl group reactivity is affected by the stereochemistry, thus, it aroused attention more than its isomers isomannide and isoidide.^[221]

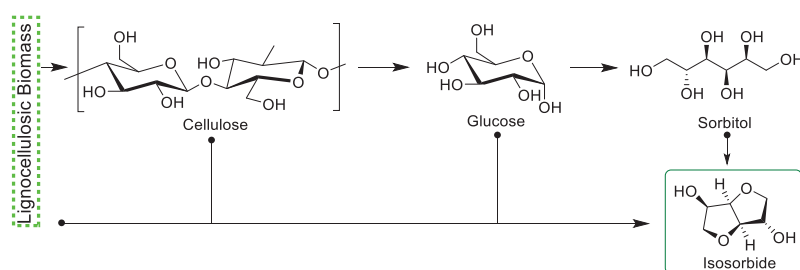


Figure 27. Conversion of lignocellulosic biomass and sub-derivatives to isosorbide

The use of isosorbide as a renewable monomer building block to synthesize high-performance polymers has been developed (Figure 28).^[222] The increase of the glass transition temperature of the materials containing the rigid isosorbide has been demonstrated, and isosorbide-based polymers present other outstanding properties including impact, abrasion, strong resistance to UV irradiation, and chemical degradation.^[223]

²¹⁹ De Vries, J. G.; Phua, P. H.; Cabrera, I. V. M.; Heeres, H. J. US, Patent, US9199961, **2015**.

²²⁰ Chen, S.; Wojcieszak, R.; Dumeignil, F.; Marceau, E.; Royer, S. *Chem. Rev.* **2018**, *118*, 11023–11117.

²²¹ Flèche, G.; Huchette, M. *Starch - Stärke* **1986**, *38*, 26–30.

²²² Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. A Review. *Prog. Polym. Sci.* **2010**, *35*, 578–622.

²²³ Saxon, D. J.; Luke, A. M.; Sajjad, H.; Tolman, W. B.; Reineke, T. M. *Prog. Polym. Sci.* **2020**, *101*, 101196.

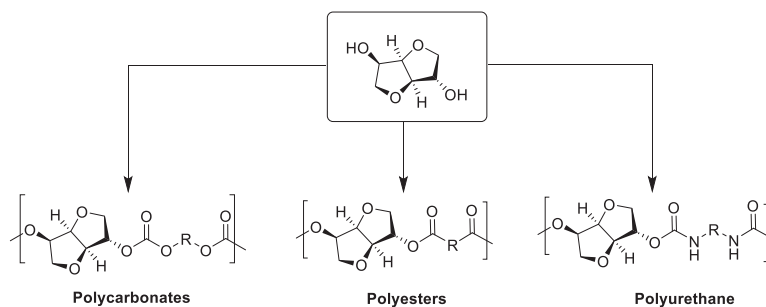
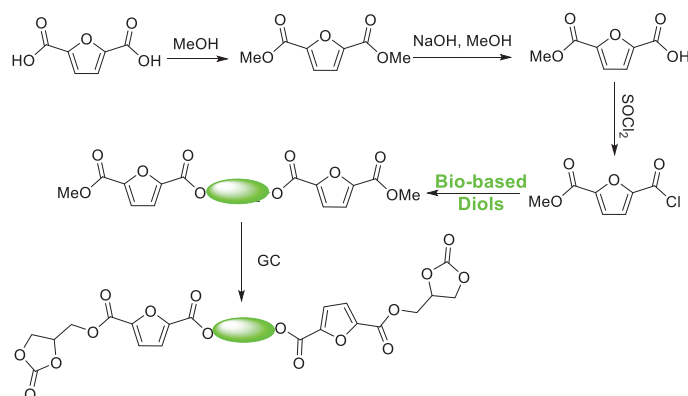


Figure 28. Isosorbide-based polymers

Polymeric materials play a pivotal role in the modern human life. Developing sustainable polymers has become more and more attractive in academia and industry. Thus, we explored the use of bio-based diols to connect the aromatic, bio-based furan-bis-cyclocarbonate to synthesize PHUs (Scheme 41).



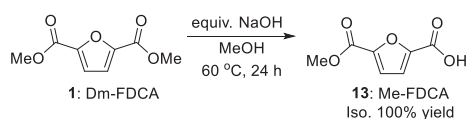
Scheme 41. Synthetic pathway to PHUs using fully bio-based bis cyclocarbonate

2 Synthesis of furandicarboxylate-mono-cyclocarbonate

2.1 Synthesis of Me-FDCA

As discussed in the Chapter 2, the methyl-ester function of Dm-FDCA present different reactivities that can be controlled towards the synthesis of unsymmetrical FDCA-based monomers (Scheme 42). Hence, Shen *et al.* ^[224] reported the synthesis of 5-(methoxycarbonyl)furan-2-carboxylic acid (Me-FDCA) (**13**) from Dm-FDCA (**1**).

²²⁴ Shen, Y.; Yao, B.; Yu, G.; Fu, Y.; Liu, F.; Li, Z. *Green Chem.* **2017**, *19*, 4930–4938.

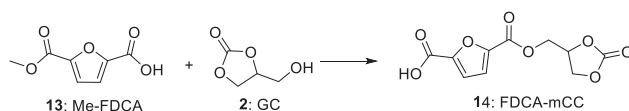


Scheme 42. Synthesis of Me-FDCA

2.2 Catalysts screening for the furandicarboxylate-mono-cyclocarbonate

In order to match the green chemistry concept, we decided to use the GC both as a starting material and solvent, which is helpful to increase the conversion in an equilibrated reaction. We first launched the transesterification of Me-FDCA by GC using CaO as catalyst and GC as solvent at 100°C. Unfortunately, after the reaction, we didn't detect any product (Table 8, entry 1). We also explored the use of alkali metal alkoxides such as Ti(BuO)₄ as catalyst, but the results indicated that the starting materials remained unreactive under the reaction conditions (Table 8, entry 2). From the Chapter 2, we know that DMAP is an excellent catalyst for the transesterification but it didn't work with Me-FDCA (Table 8, entry 3). Therefore, we used the stronger NaOH base as the catalyst, but to our desperation, we still didn't detect any products (Table 8, entry 4).

Table 8. Catalysts screening for the furandicarboxylate-mono-cyclocarbonate.



Entry	Catalyst	T (°C)	Yield (%)
1	CaO	100	n.r.
2	Ti(BuO) ₄	100	n.r.
3	DMAP	100	n.r.
4	NaOH	100	n.r.
5	CaO	120	n.r.
6	Ti(BuO) ₄	120	n.r.
7 ^a	DMAP	120	Traces
8	NaOH	120	Not detected

Me-FDCA (0.5 mmol, 85 mg), catalyst (10%, xx mg) and 1 mL GC as solvent were introduced into the flask. The flask was kept open and heated at xx°C for 24 h. n.r.: no reaction. ^a: there are many unknown by-products.

Subsequently, we decided to increase the reaction temperature to 120°C to identify the best catalyst for the reaction. Both CaO and Ti(BuO)₄ didn't give any interesting results (Table 8, entries 5 and 6). To our delight, we could detect trace of desired product using DMAP at 120°C (Table 8, entry 7), but too many unknown by-products were formed. Meanwhile, using NaOH as the catalyst at 120°C resulted in the destruction of the starting materials (Table 8, entry 8).

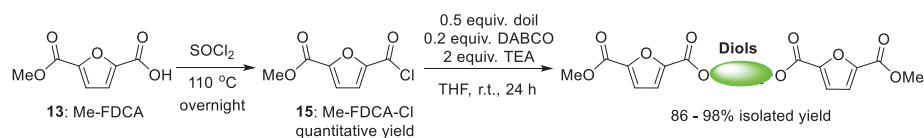
All the results indicated that the carboxylic acid profoundly affect the reactivity of the methyl ester of Me-FDCA. In particular, the use of a basic catalyst resulted in the deprotonation of the carboxylic acid and/or saponification of the methyl ester, inducing a loss of catalytic activity.

3 Synthesis of a bio-based diol-connected FDCA-cyclic carbonate

3.1 Synthesis of bio-based diol-connected Me-FDCA

As described above, the use of bio-based diols to synthesize polymer has been a hot topic in the recent years. Thus, we picked out some star bio-based diols to connect the Me-FDCA, and then, reacted the products with GC to obtain a bis cyclocarbonate through transesterification.

As the transesterification of Me-FDCA did not appear fruitful, we decided to perform the synthesis of the bio-based diol-connected Me-FDCA using the traditional 2-steps acyl-chloride/esterification strategy (Scheme 43). Using an excess of thionyl chloride as solvent at high temperature afforded quantitative yield of methyl 5-(chlorocarbonyl) furan-2-carboxylate (Me-FDCA-Cl) (**15**).^[223] The different bio-based diols, using the similar approach, 8 intermediates which structures are drawn in the Figure 29 were prepared in isolated yields ranging from 86 to 98% (see supporting information).



Scheme 43. Two-steps strategy to synthesize bio-based diol-connected Me-FDCA

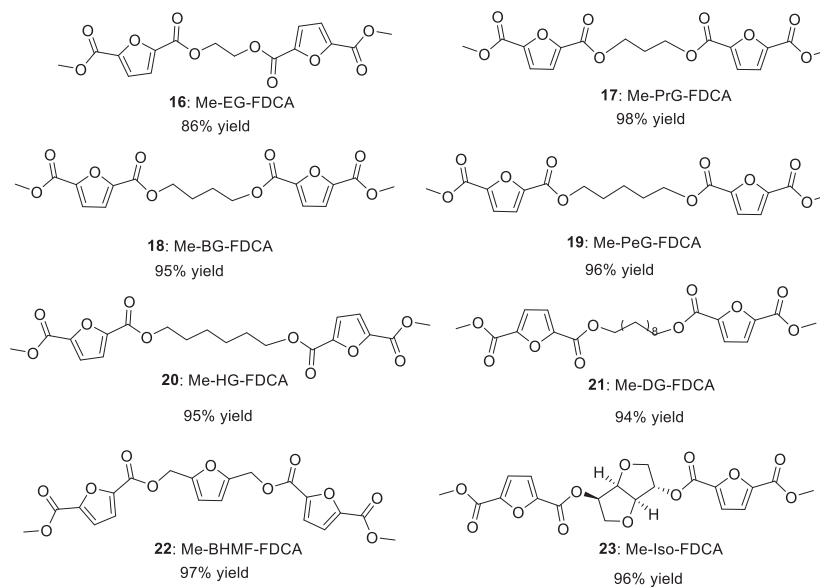
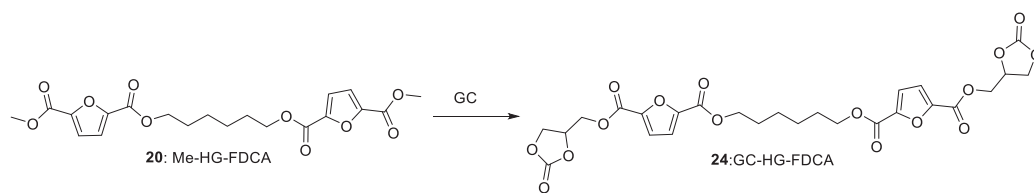


Figure 29. Structures of bio-based diols connecting Me-FDCA

3.2 Synthesis of GC-HG-FDCA

We first chose the Me-EG-FDCA (**16**) and GC as partners for a test reaction to explore the activity of the catalysts. However, the starting materials were easily destroyed even under mild reaction conditions (DMAP as catalyst, 60°C). Hence, no useful information could be obtained using those 2 partners. Therefore, we chose Me-HG-FDCA (**20**) as starting material in order to explore the transesterification conditions to synthesize glycerol carbonate 5-(hexylene glycol) furan-2-carboxylate (GC-HG-FDCA) (**24**). The different conditions screened are gathered in the Table 9.

Table 9. Catalysts screening for the GC-HG-FDCA.



Entry	Catalyst	T (°C)	Yield (%)
1	NaOCH ₃	70	n.r.
2	NaOCH ₃	80	Not detected
3	DMAP	80	n.r.
4	DMAP	85	Traces
5	DMAP	90	35
6	DMAP	100	Not detected
7	CaO	90	n.r.
8 ^a	DMAP	80	n.r.
9 ^b	DMAP	100	n.r.

HG-Me-FDCA (0.5 mmol, 211 mg), catalyst (10%, xx mg), and 1 mL GC as the solvent and were introduced into the flask. The flask was kept open and was heated at xx°C for 24 h. n.r.: no reaction.

^a 2.2 equiv. GC, and 1 mL MeTHF as the solvent. ^b 2.2 equiv. GC, 1 mL Tol. as the solvent.

0.5 mmol HG-Me-FDCA, 10 mol% NaOCH₃ as the catalyst and 1 mL of GC acting both as a solvent and a reagent were combined and the reaction was brought to 70°C for 24 h. Unfortunately, no product was detected (Table 9, entry 1). Next, the reaction temperature was increased to 80°C, but the target product was not identified either. Of note, the starting material was destroyed at 80°C (Table 9, entry 2). For this reason, we switched to DMAP as the catalyst. After 24 h of reaction, we only detected the starting materials or traces products at relatively low temperature (80 and 85°C) respectively (Table 9, entries 3 and 4). Surprisingly, we could isolate the desired GC-HG-FDCA product at 90°C in 35% yield (Table 9, entry 5). At 100°C, the starting materials disappeared but we could not detect the target product and didn't find any interesting by-products (Table 9, entry 6). Next, we investigated the use of CaO as the catalyst because a heterogeneous catalyst is generally better for the development of sustainable chemistry. However, under the optimal conditions, we didn't detect the

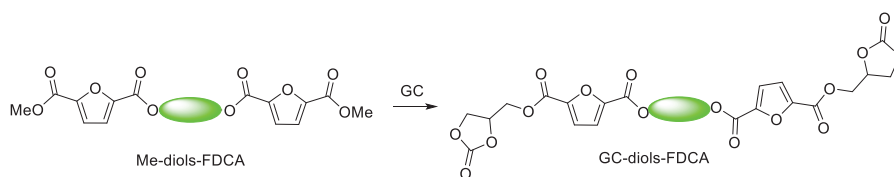
desired product (Table 9, entry 7).

Considering that the starting materials are very fragile in concentrated GC solutions, because of possible CC ring opening or transesterification, we investigated the use of the bio-based Me-THF as the solvent. In a preliminary set of conditions, 10% of DMAP as the catalyst, and 2.2 equiv. of GC as co-substrate were reacted to synthesize GC-HG-FDCA at 80°C (Table 9, entry 8). Unfortunately, we only detected the starting materials after the reaction. In order to bring the reaction at higher temperature, toluene was chosen as the solvent. Although, the starting materials remain stable in these conditions, the expected product could not be detected (Table 9, entry 9). Hence, the best conditions appeared to be those reported in the Table 9, entry 5.

3.3 Synthesis of GC-diols-FDCA

Based on the most promising conditions determined above (i.e. 10% DMAP as the catalyst, 1 mL GC as the solvent and 90°C), we screened the other bio-based diols to connect Me-FDCA and synthesize the corresponding GC-diols-FDCA: glycerol carbonate 5-(ethylene glyceryl) furan-2-carboxylate (GC-EG-FDCA), glycerol carbonate 5-(propylene glycol) furan-2-carboxylate (GC-PrG-FDCA), glycerol carbonate 5-(butylene glycol) furan-2-carboxylate (GC-BG-FDCA), glycerol carbonate 5-(pentylene glycol) furan-2-carboxylate (GC-PeG-FDCA), glycerol carbonate 5-(hexylene glycol) furan-2-carboxylate (GC-HG-FDCA), glycerol carbonate 5-(decene glycol) furan-2-carboxylate (GC-DG-FDCA) (**25**), glycerol carbonate 5-2,5-furandimethanol furan-2-carboxylate (GC-BHMF-FDCA), glycerol carbonate 5-isosorbide furan-2-carboxylate (GC-Iso-FDCA).

Table 10. Screening of the different substrates for the synthesis of the GC-diols-FDCA.



Entry	T (°C)	Products	C number	Yield (%)
1	60	GC-EG-FDCA	2	Not detected
2	60	GC-PrG-FDCA	3	Not detected
3	80	GC-BG-FDCA	4	n.r.
4	90	GC-BG-FDCA	4	Traces
5	90	GC-PeG-FDCA	5	Traces
6	90	GC-HG-FDCA	6	35
7	60	GC-BHMF-FDCA	--	n.r.
8	90	GC-BHMF-FDCA	--	Not detected

Me-XX-FDCA (0.5 mmol, XX mg), DMAP (10%, 6 mg), and 1 mL GC as solvent were introduced into the flask. The flask kept open and was heated at xx°C for 24 h.

The 2 and 3 carbon alkyl diols (e.g. ethylene and propylene glycols) connecting Me-FDCA appeared very fragile in the reaction conditions at 60°C (Table 10, entries 1 and 2) and were not detected. For diols displaying a longer alkyl chain, the Me-diols-FDCA containing 4 carbon are stable even at relatively high temperature (Table 10, entry 3). Interestingly, we were able to identify traces of GC-BG-FDCA and GC-PeG-FDCA at 90°C (Table 10, entries 4 and 5). Finally, we were able to isolate the desired products when using hexanediol (Table 10, entry 6) or decanediol. Unfortunately, we haven't been able to isolate the pure above two products, especially the GC-DG-FDCA because they were proven difficult to separate from the by-products. Me-BHMF-FDCA did not react with the GC at low temperature (Table 10, entry 7) but was proven fragile above 90°C (Table 10, entry 8). Hence, we could only detect the product where the GC had reacted only once (mono-GC adduct) ($[M+H]^+$ 537.1, $[M+Na]^+$ 559.0). An interesting aspect of the reaction is linked to the fact that the MS analysis appeared very clean as no other by-products peak was identified in the MS spectrum (See appendix).

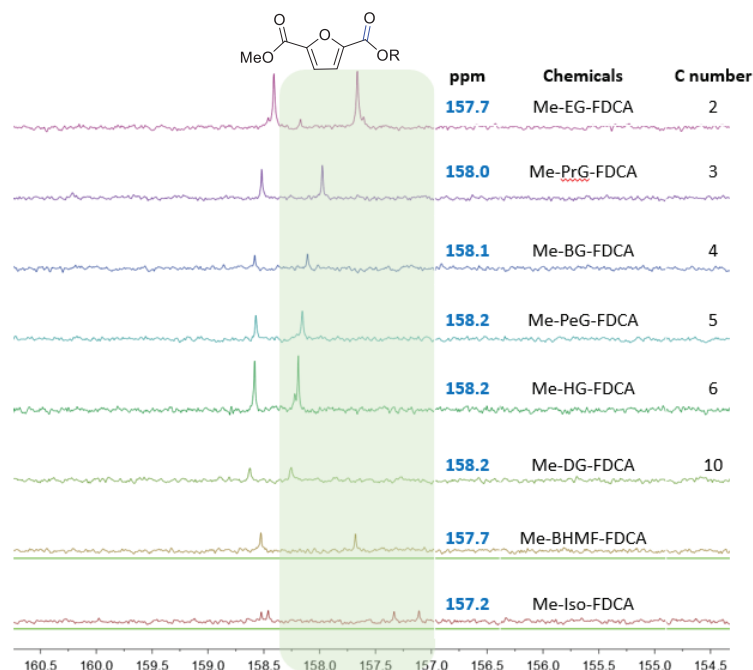


Figure 30. The Me-diols-FDCA carbonyl ppm in NMR

Of note, an interesting observation arose from the ^{13}C NMR analyses of the Me-diols-FDCA (Figure 30). Indeed, the chemical shifts of the carbonyl groups appeared to be indicative of the stability of the ester bond. It is acknowledged that the chemical shifts of the carbonyl functions are more shielded when substituted by electron rich groups. Generally, it is admitted that the electron releasing effect should follow the following order: BG>PrG>EG. Thus, the chemical shifts of the carbonyl ester functions are expected to follow the order : BG-carbonyl_more shielded/PrG-carbonyl in the middle/EG-carbonyl_less shielded. However, from the Figure 30, we can observe the reverse order. A hypothesis that could be proposed to explain this observation is illustrated in the Figure 31 using the EG connector as a model. Indeed, it could be envisioned that one oxygen of a carbonyl group partly compensate the electro deficiency of the second carbonyl inducing a shielding effect. When the connector is longer this intramolecular interaction could be disfavored for entropic reasons, inducing a stronger stability.

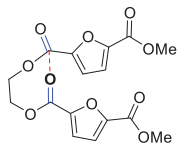


Figure 31. Possible interaction between Me-EG-FDCA carbonyl groups

4. Conclusion

We have attempted to synthesize a series of new FDCA-based bis-carbonates exhibiting a bio-based diol connecting the Me-FDCA. Different catalysts were screened to prepare the GC-diols-FDCA from the Me-diols-FDCA through transesterification. Finally, we could only isolate the fully bio-based GC-HG-FDCA in 35% yield and impure GC-DG-FDCA. The “clean” MS analysis of the latter let us hope that it should be possible to synthesize GC-Iso-FDCA according to the same protocol. Work will be ongoing to ascertain this hypothesis.

General conclusion and perspectives

General conclusion and perspectives

In the thesis, we developed three projects about the PHUs, and their starting material Bis-CC are all originated from the bio-based molecules. The aminolysis reaction medium avoid the traditional toxic solvent, achieving additives-free activity of α -methyl primary amine to attack the cyclocarbonate.

In the chapter 2, we designed a pathway to synthesize the FDCA-Bis-CC from the Dm-FDCA and GC via the transesterification, to avoid using the toxic chemical DCC as catalyst. In the reaction, we found the by-product could influence the reaction, so that we should remove the MeOH from the system in time, otherwise, the MeOH would destroy the reaction, resulting in some unknown products. Next, the DES (ChCl/Urea) was chosen as solvent, we obtained the PHUs under ambient conditions compared with the traditional aminolysis reaction. We found the urea also plays catalyst role in the reaction; thus, we can obtain the PHUs from the α -methyl primary amine in a short time. By the way, the interesting by-product of hexylurea from the reaction between urea the amine was evidenced. After the reaction, the solvent of DES could be removed through dialysis or water washing, thus, we affording the pure polymers easily.

In the chapter 3, the BFDCA and GC from the top 14 high value-added platform molecules of FF and glycerol respectively. We also obtained the fully bio-based BFDCA-Bis-CC through the relatively low toxic SOCl_2 . Meanwhile we could recycle the SOCl_2 after the reaction through distillation. We extended the scope of diamines including short chain aliphatic diamines (DA6, EDR-148, TETA), long chain aliphatic diamines (Jeffamines, PEG-diamines), and the aliphatic and aromatic ring diamines (IPDA, CHDA, MXDA, and PBFA). Aminolysis being a polyaddition reaction, the polymerization is not controlled which result in a large range of molecular weight. The cyclic diamines based PHUs (70°C) presented higher Tg temperature compared to the aliphatic diamines

based PHUs (-40°C), contributing to the cyclic coherent property. Although the cyclic diamines based PHUs did not give the expect higher $T_{d 5\%}$, they are more stable than aliphatic chain diamines based PHUs in high temperature. Especially, the BFDCA-Bis-CC and the PBFA all originated from the biomass, the corresponding PHUs are fully bio-based. And the PHUs containing the ether bond more easily degrade at high temperature.

In the chapter 4, we took advantage that the two methyl esters have different activity in the transesterification, and the bio-based molecules usually contain hydroxyl in general. The PHUs containing aliphatic chain will have a relatively lower T_g . Therefore, we first synthesized a series of bio-based diols connecting Me-FDCA, and we also tried to afford diols connecting FDCA-CC through the transesterification reaction. Nevertheless, the short chain diols connecting Me-FDCA are unstable in the transesterification conditions. Fortunately, we finally obtained GC-HG-FDCA and other two diols connecting FDCA-CC of GC-DG-FDCA and GC-Iso-FDCA are waiting for purification.

Overall, my past three years of work open a fire window for other researchers in the sustainable synthesis of PHUs. PHUs as an alternative of PUs have been proposed recent decades, and many researchers have explored that in different aspects. Bio-based PHUs focus on vegetable oil in the past works, thus, they are more applied in flexible polymers. Therefore, developing the similar chemical property and structure bio-based monomers in PHUs with traditional monomers for PUs is necessary.

Bio-based molecules aims at replacing petroleum products since they were proposed. Developing and modifying bio-based molecules has been a hot research, and bio-based monomers for polymer have been developed. Bio-based products used in polymer will broaden the application and market volume of biomass molecules and solve plastic source from petroleum problem.

Meanwhile, green chemistry principles are respected in chemical reaction and industrial production in recent 30 years. To achieve the sustainable development, researchers are also concerned about the chemical process. The DES based on ChCl and urea was first reported 20 years ago, and then, the DES family members have fully developed. They can substitute of the traditional solvent and also could play a catalyst in some reactions such as redox, esterification, alkylation and etc... DES as an excellent solvent will help researchers to solve a series of chemical process problems (toxicity, pollution, cost).

Of note, the final fate of plastics is another concerned question, as we all know they result in terrible pollution over the past hundred years. The plastic degradation mainly depends on chemical properties of the monomers, and relative electron-rich compounds are more easily oxidized in the natural environment. Next, we will explore our PHUs property in biodegradation.

All in all, exploring and utilization of biomass products to synthesize bio-based and biodegraded polymers according to green and sustainable principles will help ourself to solve the energy crisis, environment pollution problem, and human health.

Experimental section

Experimental section

General information

The reagents and solvents were purchased from Alfa Aesar, Sigma-Aldrich, TCI and Huntsman company, utilized without any purification unless mentioned specifically. The solvents for the column chromatography were purchased from Carlo Erba company. The thin-layer chromatography (TLC) analysis was conducted on the aluminum-backed plates pre-coated 0.2mm silica gel 60. The flash chromatographies were performed using Merck Si 60 silica gel (40-63 μm). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer (^1H : 300, 400 or 500 MHz; ^{13}C : 75, 100 or 125 MHz). The solvent DMSO- d_6 peak ^1H locate in 2.50 ppm, and the ^{13}C locate in 39.52. The solvent CDCl_3 peak ^1H locate in 7.26 ppm, and the ^{13}C locate in 77.16. The High-resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-Q II XL spectrometer using ESI as ionization source. The FTIR spectra were recorded using a Nicolet iS50 spectrometer. The procedure to investigate the physicochemical properties of monomers and PHUs follows the method in references.

General procedure

Synthesis of the DESs

The hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) were introduced into the round flask in the appropriate ratio. The mixture was heated and stirred until a homogeneous colorless liquid was formed with no visible precipitate.

DES (ChCl/Urea)

Using the general procedure, 10 mmol urea and 5 mmol choline chloride (ChCl) were stirred at 75°C until a homogenous solution was produced. ^[148]

PHUs syntheses

Bis-CC and the appropriate diamine were added into a round bottom flask. DES of ChCl/urea (1:2) was introduced, and the reaction mixture was stirred under argon until the monomer was consumed. After the reaction, the DES and the short oligomers was removed through water washing or by dialysis.

Dialysis process

After the reaction, cooling to room temperature, the mixture was introduced into the dialysis bag (MWCO = 3500), and using 500 mL water extracted three times every three hours. The water was evaporated to achieve the purification of product.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) analyses were carried out through a NETZSCH DSC200F3 calorimeter, which was calibrated using indium, n-octane, n-octadecane, biphenyl, adamantane, bismuth, tin and zinc standards. N₂ was used as purge gas. Roughly 10 mg of sample were put in a perforated aluminum pan and the thermal properties were recorded between -150°C and 120°C at 20°C.min⁻¹ to observe the glass transition temperature. Using the second heating ramp gave the T_g values to erase the thermal history of the polymer. All the reported temperatures are average values on three different experiments.

Thermal gravimetric analysis

Thermogravimetric analyses (TGA) of the cured foams were carried out to determine the thermal stability and were performed on a Netzsch TG 209F1 apparatus under 40 mL.min⁻¹ N₂ flow. Using N₂ as the protective gas with a 20 mL.min⁻¹ flow. Roughly 10-12 mg of sample were put in an alumina crucible and heated from room temperature to 800°C with a 20°C.min⁻¹ heating rate.

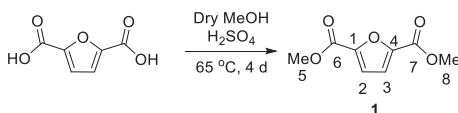
Size-exclusion chromatography

Size-exclusion chromatograms (SEC) were recorded using a triple-detection GPC (Gel

permeation chromatography) from Agilent Technologies with its corresponding Agilent software, dedicated to multidetector GPC calculation. The system contained two PL1113-6300 ResiPore 300 × 7.5 mm columns with a flow rate of 1 mL min⁻¹ of THF as the eluent. Using a 390-LC PL0390-0601 refractive index detector as the detector. The entire SEC-HPLC system was thermostated at 35°C. PMMA standards were used for calibration. The typical sample concentration was 20 mg mL⁻¹.

Chapter 2 Experimental section

Synthesis and characterizations of dimethyl furan-2,5-dicarboxylate (Dm-FDCA) (**1**).



To a solution of 2,5-furandicarboxylic acid (70 mmol, 10.9 g) in dry MeOH (500 mL) was added aqueous 98% sulfuric acid (0.7 mL) and the resulting solution heated at 65 °C for 4 d. The solution was cooled and concentrated *in vacuo*. The residue was filtered and washed with saturated aqueous NaHCO₃ solution (60 mL x 4) and washed with water until neutral pH. We obtained 97% yield of dimethyl furan-2,5-dicarboxylate (Dm-FDCA) (12.5 g) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.19 (s, 2H; H₂, H₃), 3.89 (s, 6H; H₅, H₈).

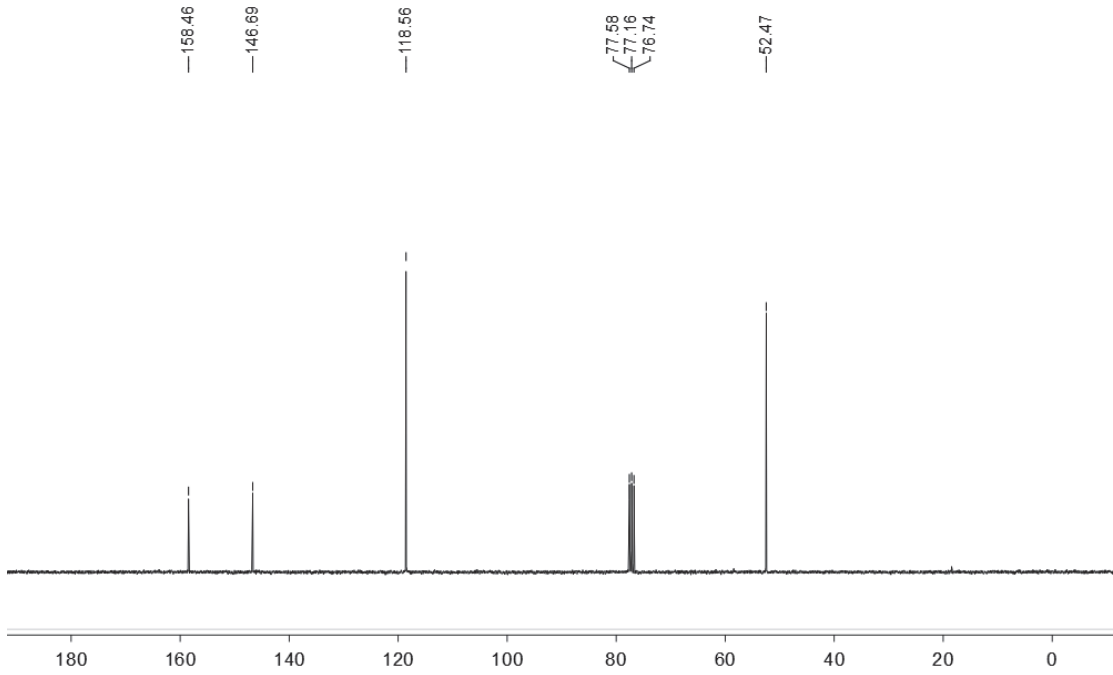
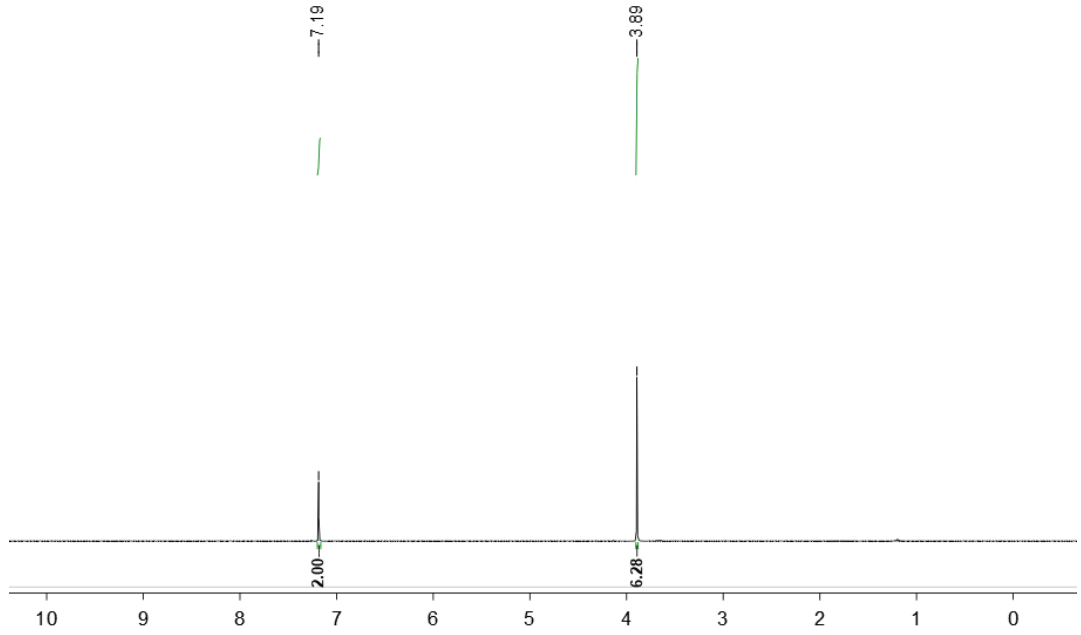
¹³C NMR (75 MHz, CDCl₃) δ 158.5 (s; C₆, C₇), 146.7 (s; C₁, C₄), 118.6 (s; C₂, C₃), 52.5 (s; C₅, C₈).

These results are in agreement with the literature. ^[225]

IR (V_{\max} cm⁻¹): 1720 (stretching vibration of ester C=O).

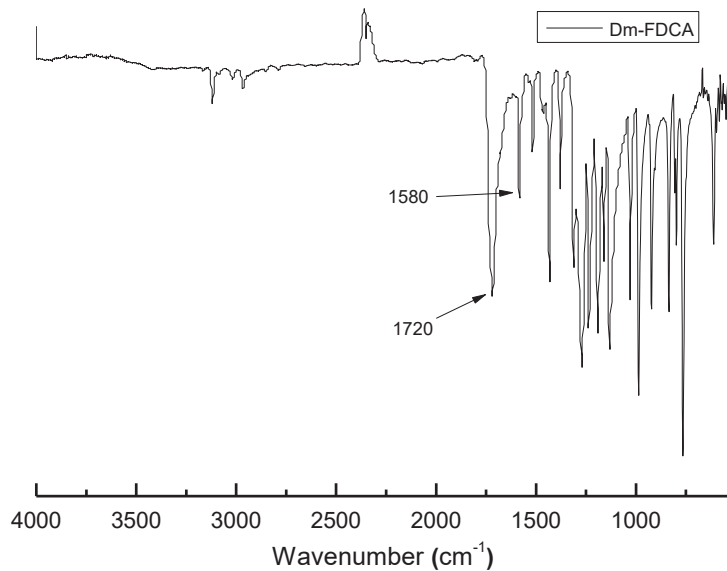
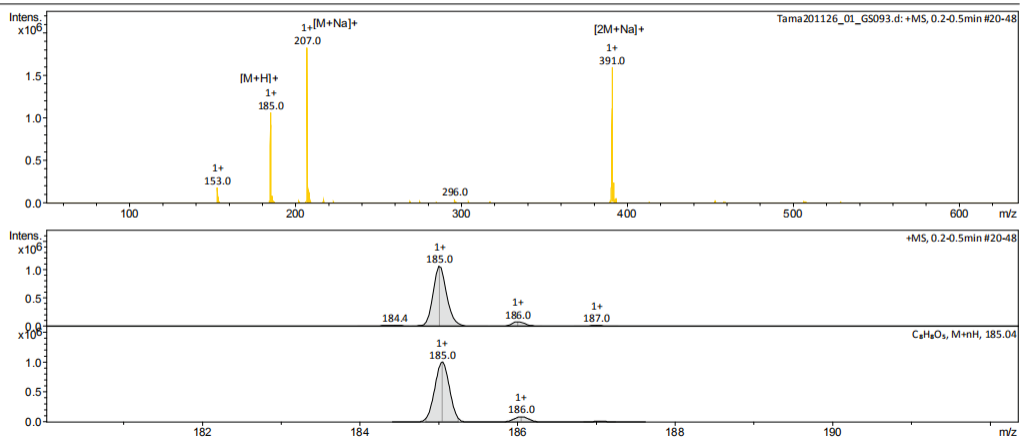
MS [M+H]⁺ 185.0, [M+Na]⁺ 207.0.

²²⁵ Li, F.; Li, X. L.; Li, C.; Shi, J.; Fu, Y. *Green Chem.* **2018**, *20*, 3050–3058.

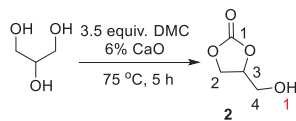


Acquisition Parameter

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SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of glycerol carbonate (GC) (**2**).



Glycerol (0.4 mol, 36.84 g), DMC (1.4 mol, 126 g) and CaO (6% mmol, 1.35g) were loaded into a 250 mL round-bottom flask having condenser and reacted at 75°C for 5 h. Cooling to room temperature, the catalyst was removed by filtration. And the MeOH and excess DMC were removed at 45°C under reduced pressure. Using the EA/cyclohexane (2:1, v/v) as the eluent, we obtained 86% yield (40.6 g) of glycerol carbonate (GC) as colorless oil.

^1H NMR (300 MHz, DMSO) δ 5.28 (t, J = 5.6 Hz, 1H; O-H₁), 4.80 (ddd, J = 5.9, 4.3, 2.8 Hz, 1H; H₃), 4.51 (t, J = 8.3 Hz, 1H; H₂), 4.30 (dd, J = 8.2, 5.8 Hz, 1H; H₂), 3.69 (ddd, J = 12.6, 5.5, 2.8 Hz, 1H; H₄), 3.52 (ddd, J = 12.6, 5.7, 3.3 Hz, 1H; H₄).

^{13}C NMR (75 MHz, DMSO) δ 155.3 (s; C₁), 77.1 (s; C₃), 66.0 (s; C₄), 60.7 (s; C₂).

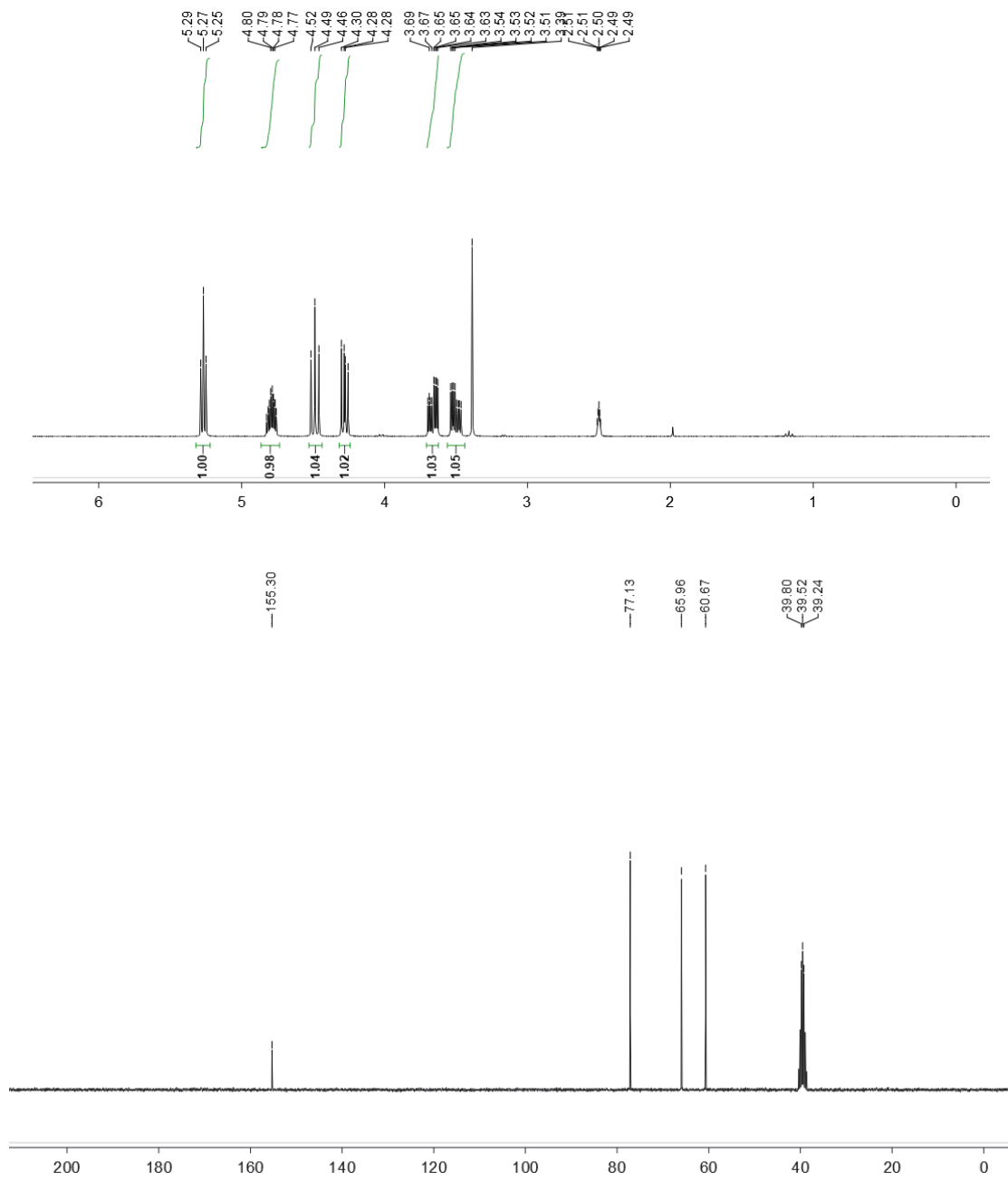
These results are in agreement with the literature.^[226-227]

IR (V_{max} cm⁻¹): 3411(stretching vibration of -OH), 1760 (stretching vibration of cyclic carbonate C=O).

MS: [M+H]⁺ 119.1, [M+Na]⁺ 141.0.

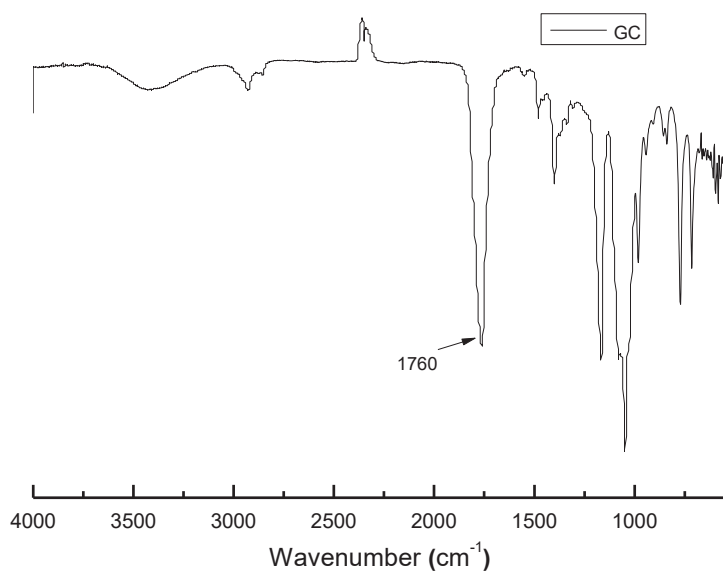
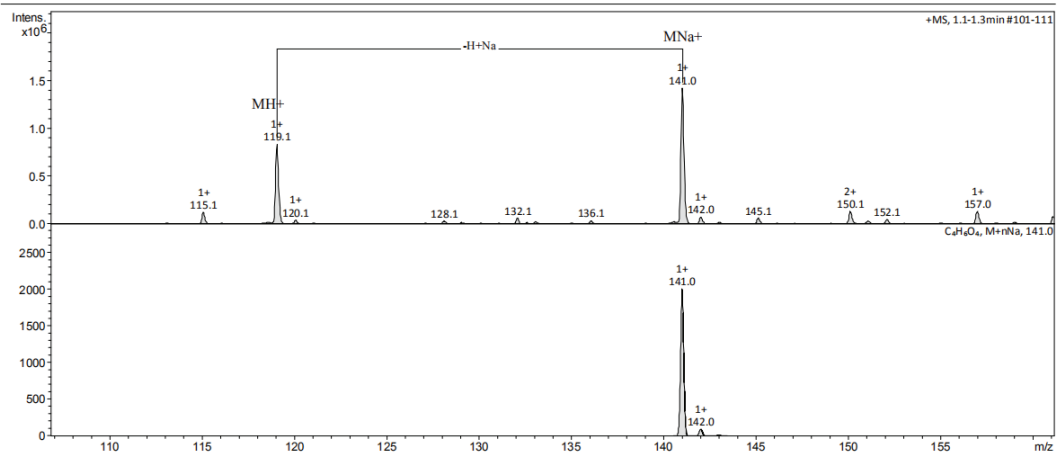
²²⁶ Zhang, Y.; Chen, G.; Wu, L.; Liu, K.; Zhong, H.; Long, Z.; Tong, M.; Yang, Z.; Dai, S. *Chem. Commun.* **2020**, *56*, 3309–3312.

²²⁷ Al-Qaisi, F. M.; Qaroush, A. K.; Okashah, I. K.; Eftaiha, A.; Vasko, P.; Alsoubani, F.; Repo, T. *Eur. J. Inorg. Chem.* **2022**.

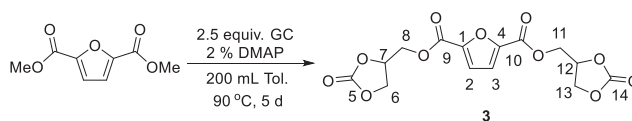


Acquisition Parameter

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SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of furan-2,5-dicarboxylate bis cyclic carbonate (FDCA-Bis-CC) (**3**).



Dimethyl furan-2,5-dicarboxylate (55 mmol, 10.1 g), GC (2.5 equiv., 16.2 g) and DMAP (2%, 134.2 mg) were dissolved in 200 mL dry Tol. The reaction mixture was stirred at 90°C for 5 d, by-product of MeOH was released. After the reaction, the residue was filtered and washed with the acetone (20 mL x 3). Finally, we obtained 95% yield (18.6 g) of furan-2,5-dicarboxylate bis cyclic carbonate (FDCA-Bis-CC) as a white solid.

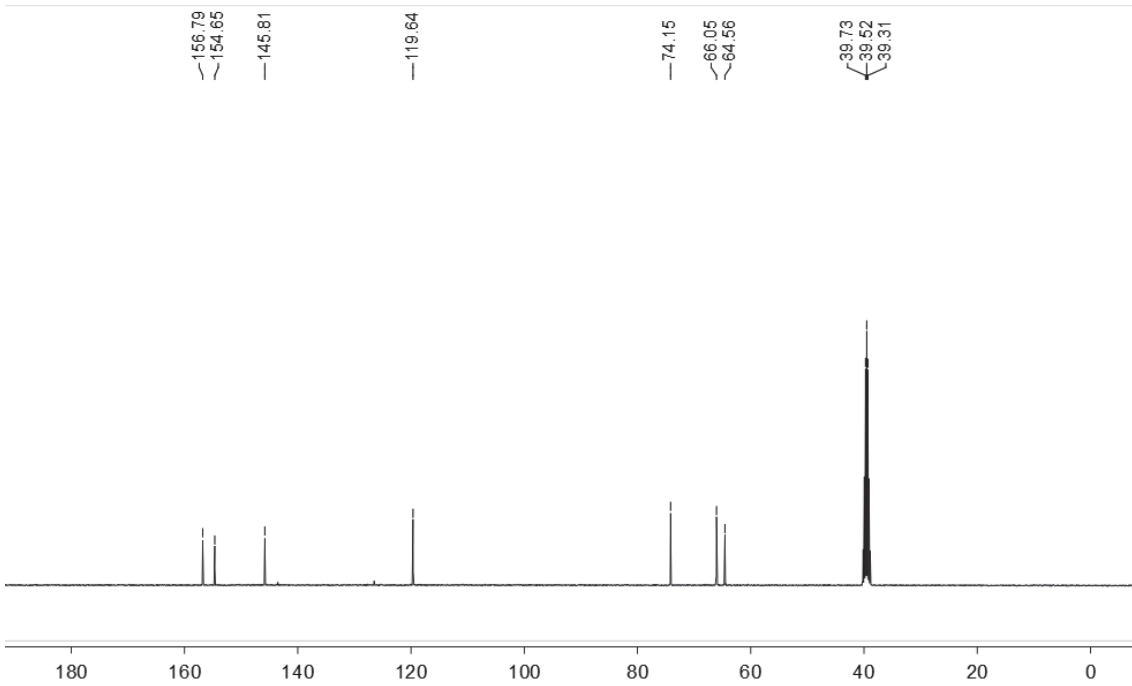
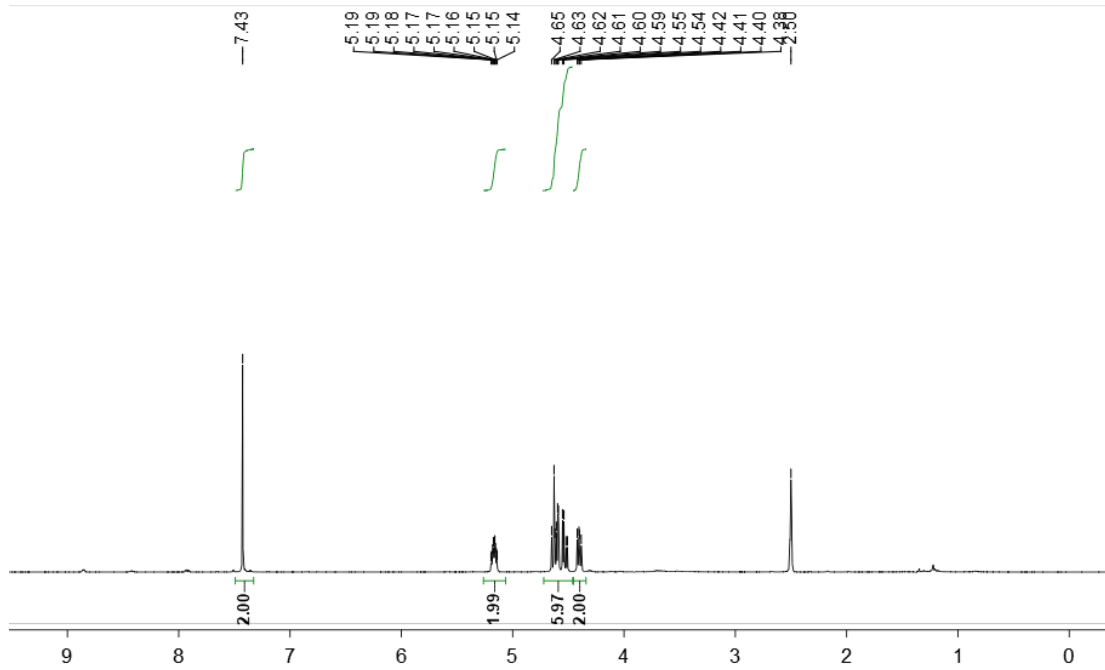
^1H NMR (400 MHz, DMSO) δ 7.43 (s, 2H; H₂, H₃), 5.26 – 5.06 (m, 2H; H₇, H₁₂), 4.72 – 4.46 (m, 6H; H₆, H₈, H₁₁, H₁₃), 4.40 (dd, $J = 8.4, 6.1$ Hz, 2H; H_{8'}, H_{11'}).

^{13}C NMR (101 MHz, DMSO) δ 156.8 (s; C₉, C₁₀), 154.6 (s; C₅, C₁₄), 145.8 (s; C₁, C₄), 119.6 (s; C₂, C₃), 74.2 (s; C₇, C₁₂), 66.0 (s; C₈, C₁₁), 64.6 (s; C₆, C₁₃).

These results are in agreement with the literature. ^[139]

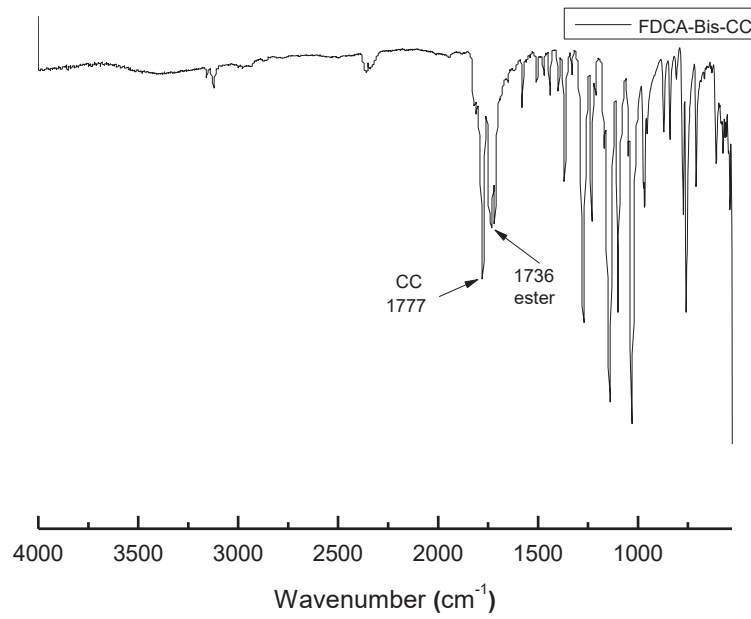
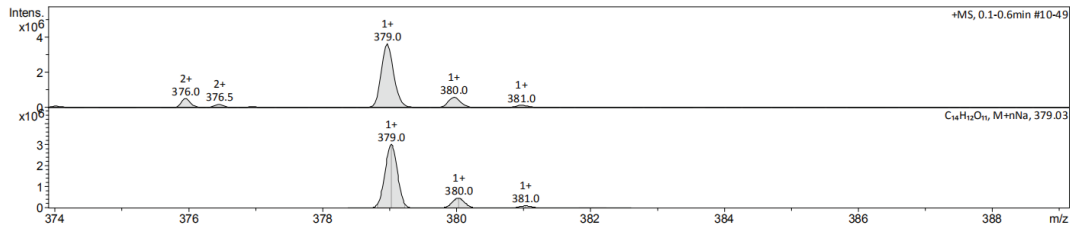
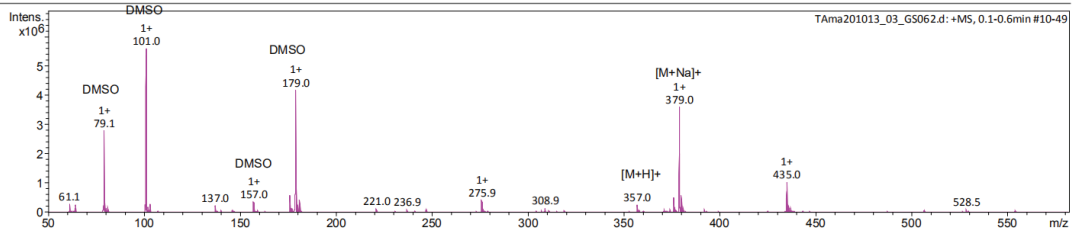
IR (V_{max} cm⁻¹): 1777 (stretching vibration of cyclic carbonate C=O), 1735 (stretching vibration of ester C=O)

MS: [M+H]⁺ 357.0, [M+Na]⁺ 379.0

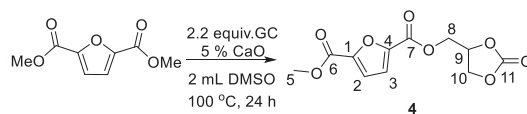


Acquisition Parameter

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Accumulation Time	528 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of Me-FDCA-cyclic carbonate (Me-FDCA-CC) (**4**).

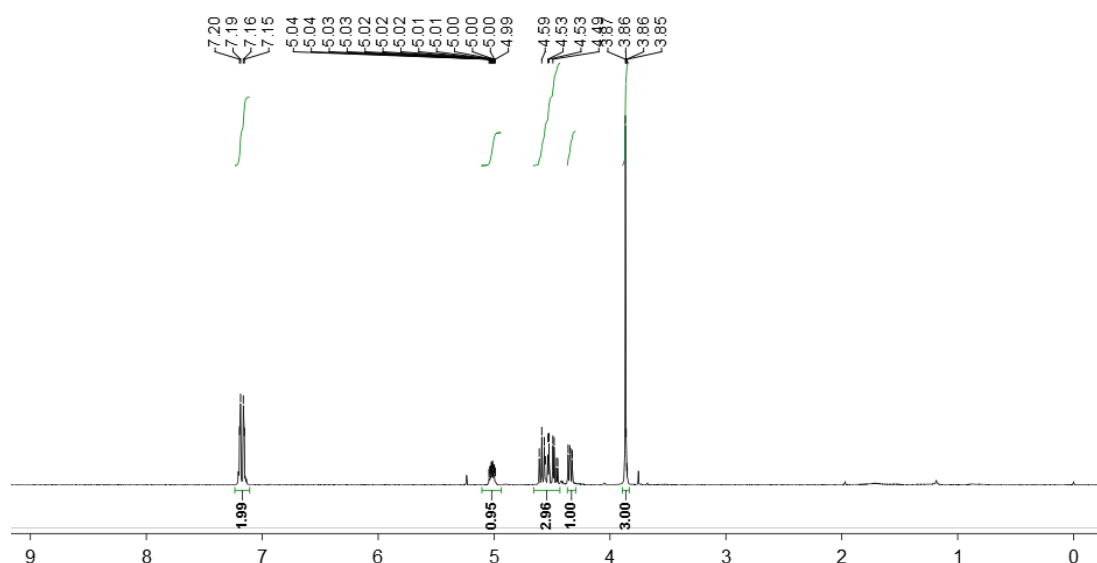


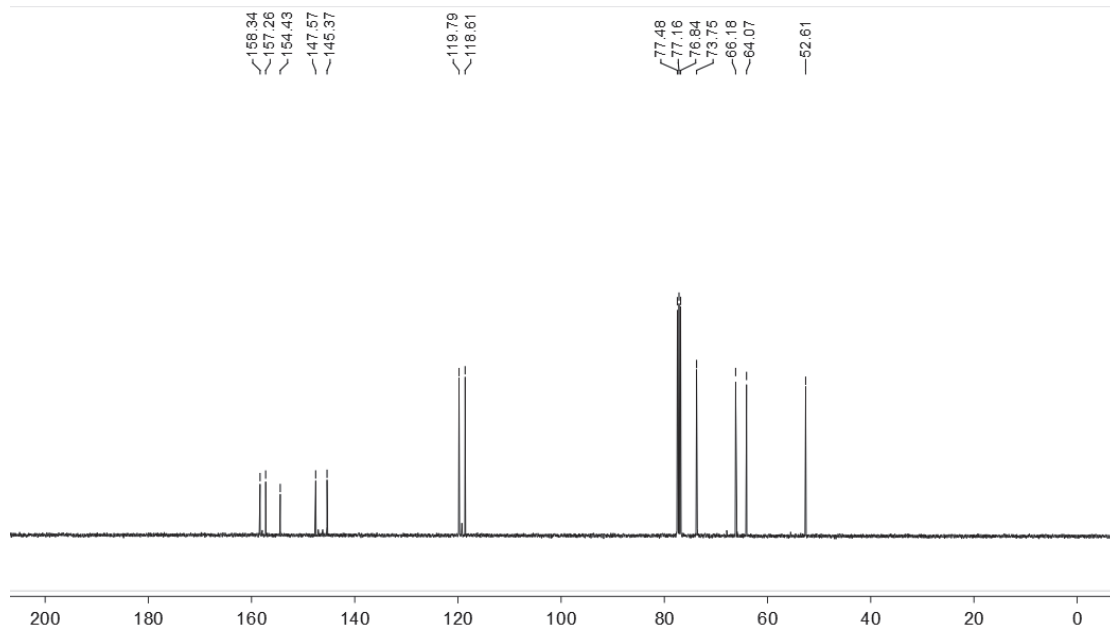
Dimethyl furan-2,5-dicarboxylate (1 mmol, 184 mg), GC (2.2 equiv., 259 mg), CaO (5%, 2.8 mg) were dissolved in 2 ml dry DMSO. The reaction mixture was stirred at 100°C for 24 h. After cooling to room temperature, added the 5 mL water in the flask, and then used the EA (5 mL) to extract 3 times. Next, the solvent was evaporated to dryness and the residue was purified by column chromatography (cyclohexane/ethyl acetate, 1:5, v/v) to give 22% yield (59.4 mg) of Me-FDCA-cyclic carbonate (Me-FDCA-CC) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.17 (dd, $J = 13.1, 3.7$ Hz, 2H; H_2, H_3), 5.10 – 4.94 (m, 1H; H_9), 4.66 – 4.43 (m, 3H; $\text{H}_8, \text{H}_{10}$), 4.34 (dd, $J = 8.9, 5.8$ Hz, 1H; H_8'), 3.89 – 3.83 (m, 3H; H_5).

^{13}C NMR (101 MHz, CDCl_3) δ 158.3 (C_6), 157.3 (C_7), 154.4 (C_{11}), 147.6 (C_1), 145.4 (C_4), 119.8 (C_2), 118.6 (C_3), 73.8 (C_9), 66.2 (C_8), 64.1 (C_{10}), 52.6 (C_5).

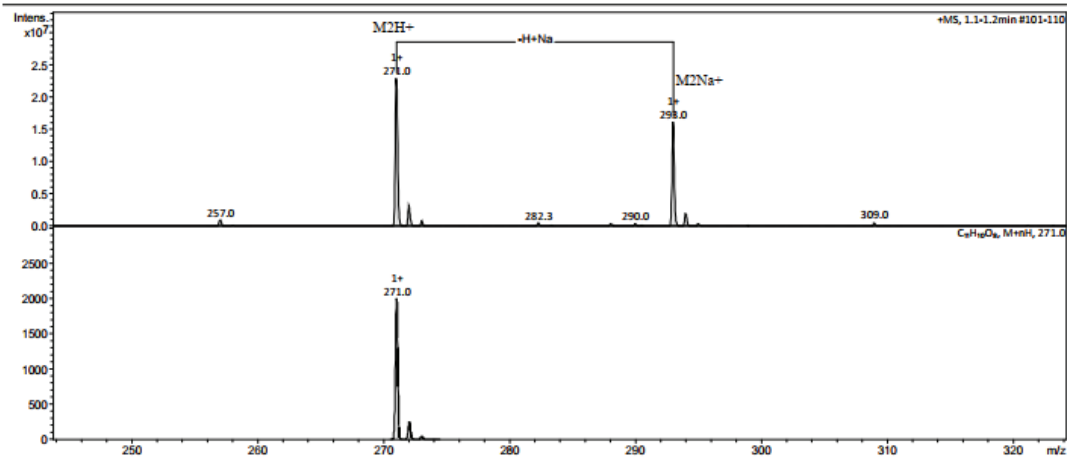
MS $[\text{M}+\text{H}]^+$ 271.0, $[\text{M}+\text{Na}]^+$ 393.0.



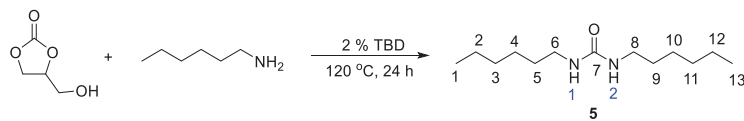


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	4101 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of 1,3-dihexylurea (**5**).



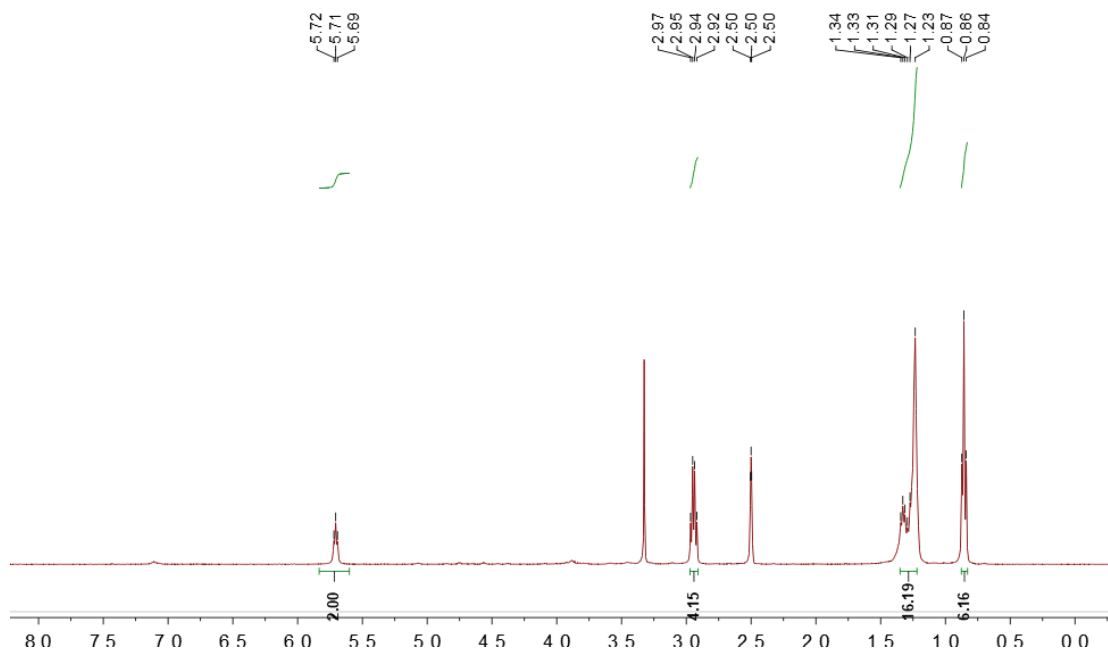
GC (2 mmol, 236 mg), hexylamine (2.2 equiv., 444.4 mg) and TBD (2%, 5.6 mg) were introduced into a round flask, and the mixture was heated at 120°C for 24 h. The urea was precipitated in the ice water, and several washing of the precipitate with the water, we obtained 53% yield (241.7 mg) of the 1,3-dihexylurea.

^1H NMR (400 MHz, DMSO) δ 5.71 (t, J = 5.5 Hz, 2H; N-H₁₋₂), 2.94 (dd, J = 12.7, 6.7 Hz, 4H; H₆, H₈), 1.35 – 1.22 (m, 16H; H₂₋₅, H₉₋₁₂), 0.86 (t, J = 6.9 Hz, 6H; H₁, H₁₃).

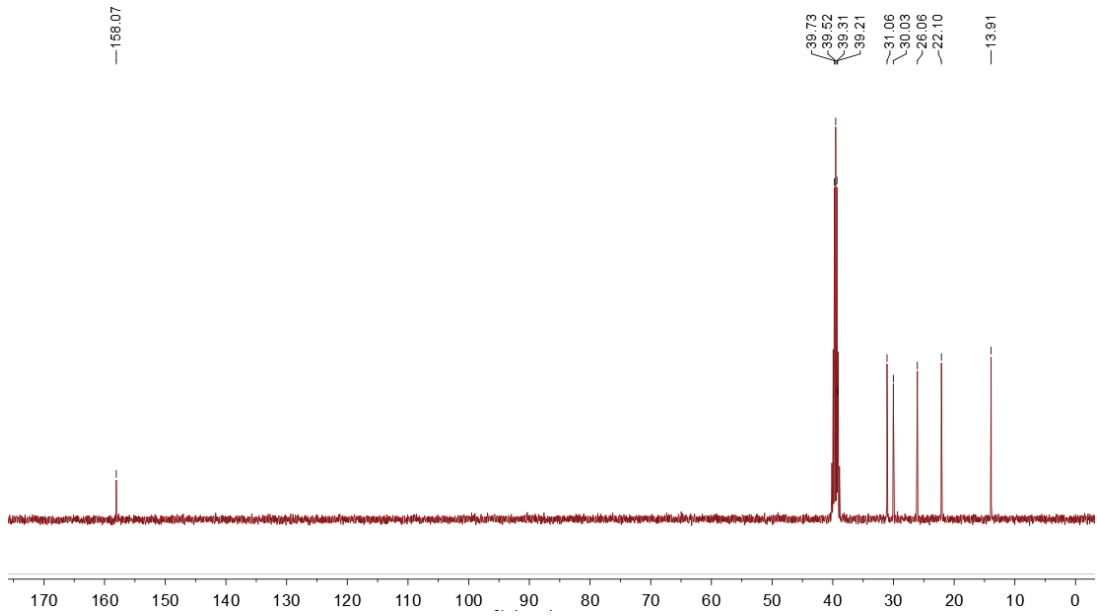
^{13}C NMR (101 MHz, DMSO) δ 158.1 (s; C₇), 39.2 (s; C₆, C₈), 31.1 (s; C₅, C₉), 30.0 (s; C₄, C₁₀), 26.1 (s; C₃, C₁₁), 22.1 (s; C₂, C₁₂), 13.9 (s; C₁, C₁₃).

These results are in agreement with the literature. ^[228]

MS: [M+H]⁺ 229.2, [M+Na]⁺ 251.2.

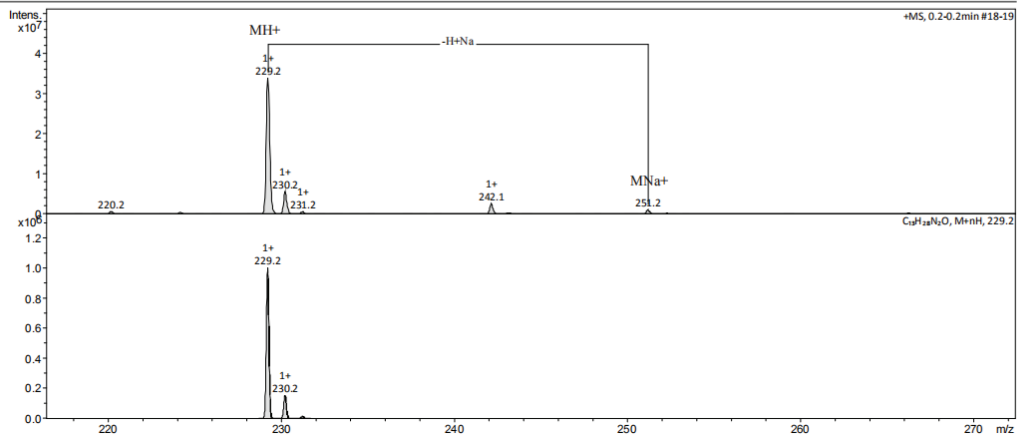


²²⁸ Liu, S.; Wang, H.; Dai, X.; Shi, F. *Green Chem.* **2018**, *20*, 3457–3462.

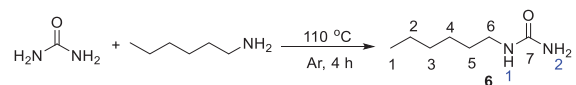


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	73 μ s	RF Level	55 %	Trap Drive	46.3
SPS Target Mass	300 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of hexylurea (**6**).



0.5 mL DES (ChCl/Urea=1:2) (around 10 mmol) and hexylamine (5 mmol, 505mg) were introduced into flask, and the mixture was heated at 110°C for 4 hours under Ar. And then, used the ice acetone to precipitate the DES, the acetone was evaporated. Using the ice water (5 mL x 3) to wash the residue to obtain the 4% yield (28.8 mg) of hexylurea.

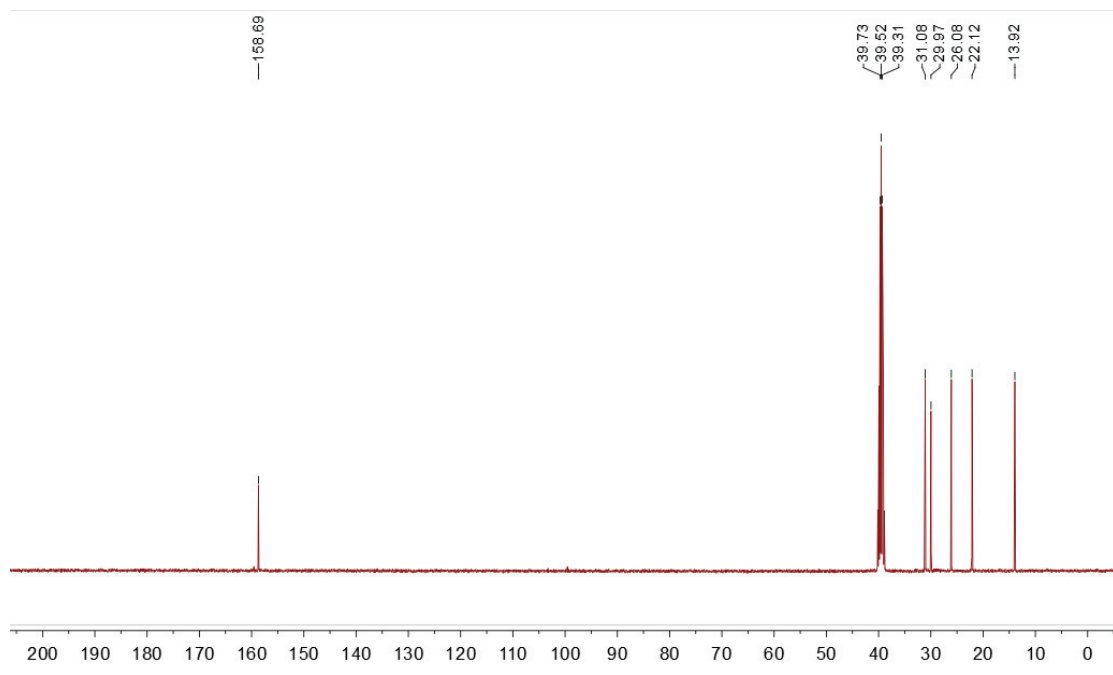
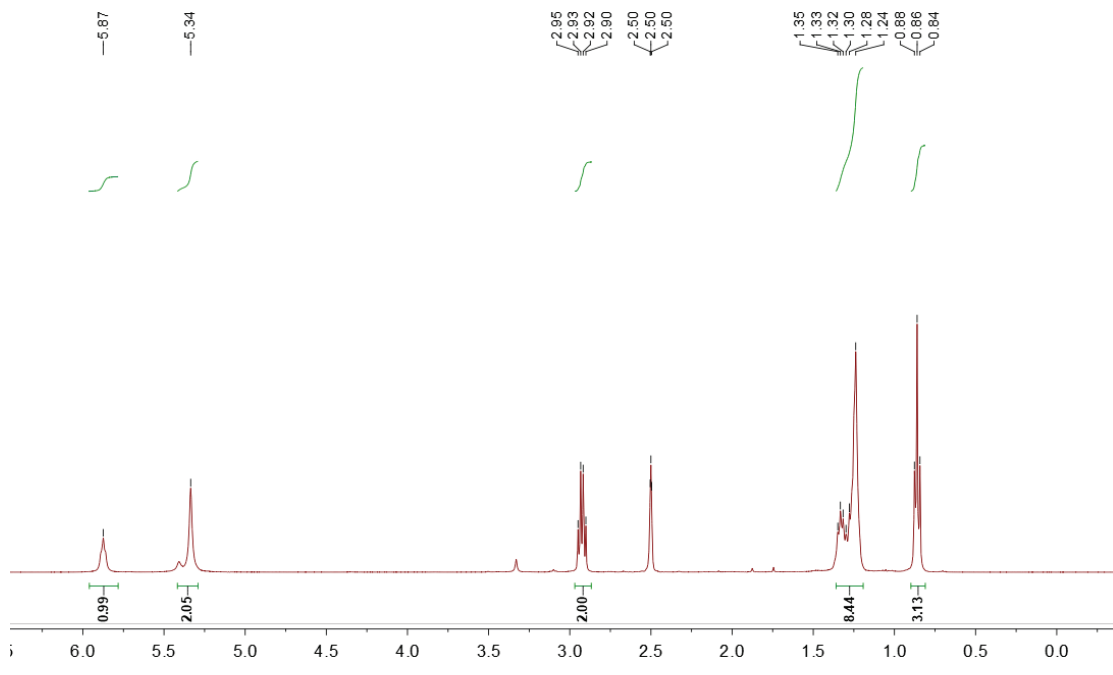
^1H NMR (400 MHz, DMSO) δ 5.87 (s, 1H; N-H₁), 5.34 (s, 2H; N-H₂), 2.93 (dd, $J = 12.7$, 6.7 Hz, 2H; H₆), 1.36 – 1.19 (m, 8H; H₂₋₅), 0.86 (t, $J = 6.8$ Hz, 3H; H₁).

^{13}C NMR (101 MHz, DMSO) δ 158.7 (s; C₇), 31.1 (s; C₅), 30.0 (s; C₄), 26.1 (s; C₃), 22.1 (s; C₂), 13.9 (s; C₁). (Note: C₆ peak is contained in DMSO peaks.)

These results are in agreement with the literature. ^[229]

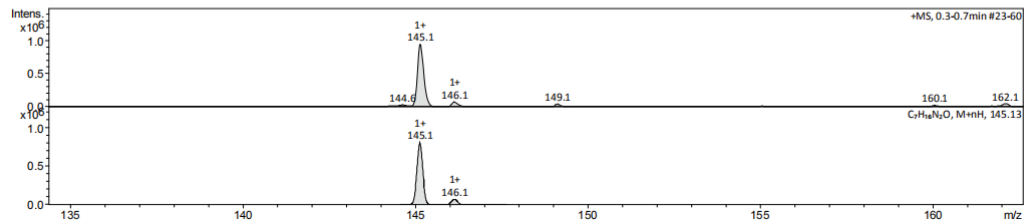
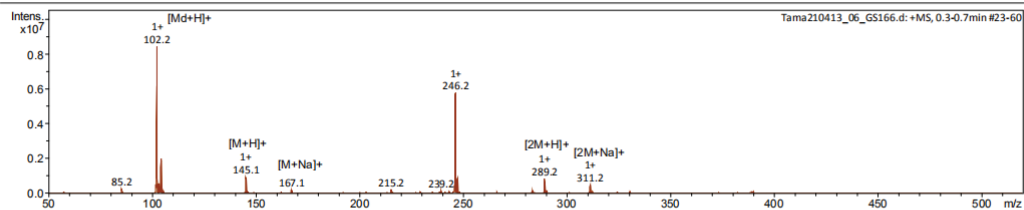
MS: [M+H]⁺ 145.1.

²²⁹ Mohy El Dine, T.; Chapron, S.; Duclos, M. C.; Duguet, N.; Popowycz, F.; Lemaire, M. *European J. Org. Chem.* **2013**, *24*, 5445–5454.

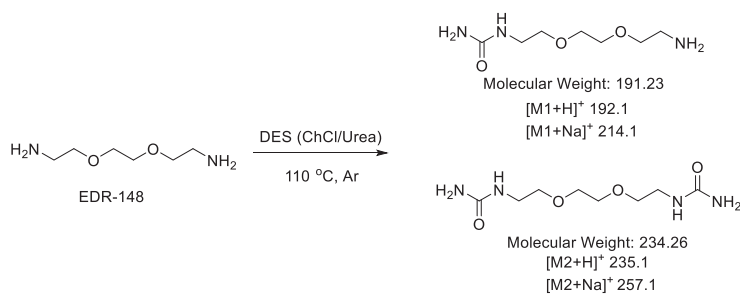


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	100 μ s	RF Level	32 %	Trap Drive	38.0
SPS Target Mass	100 m/z	Averages	5 Spectra	n/a	n/a

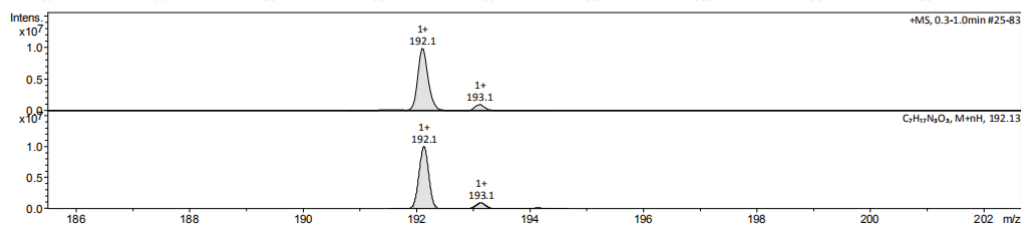
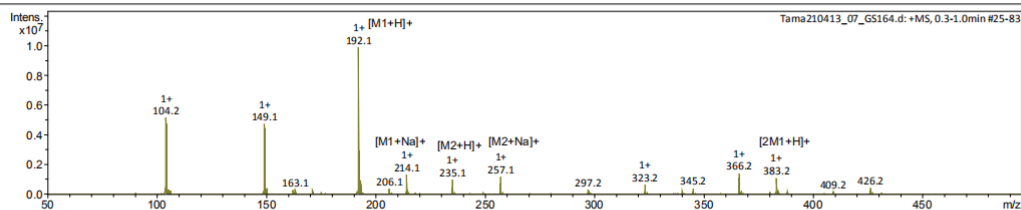


The by-products MS from diamine EDR-148 react with urea.



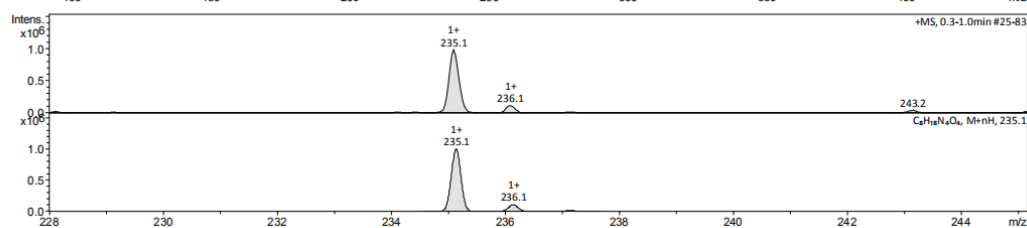
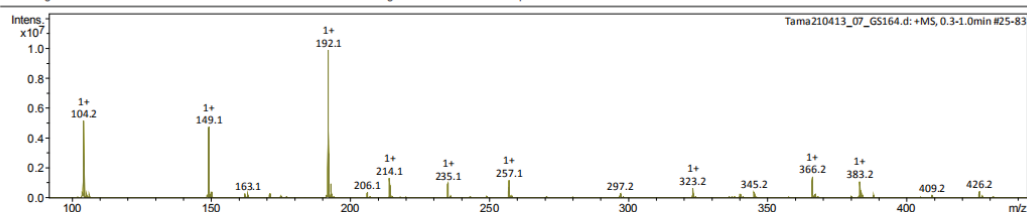
Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	62 μ s	RF Level	32 %	Trap Drive	38.0
SPS Target Mass	100 m/z	Averages	5 Spectra	n/a	n/a

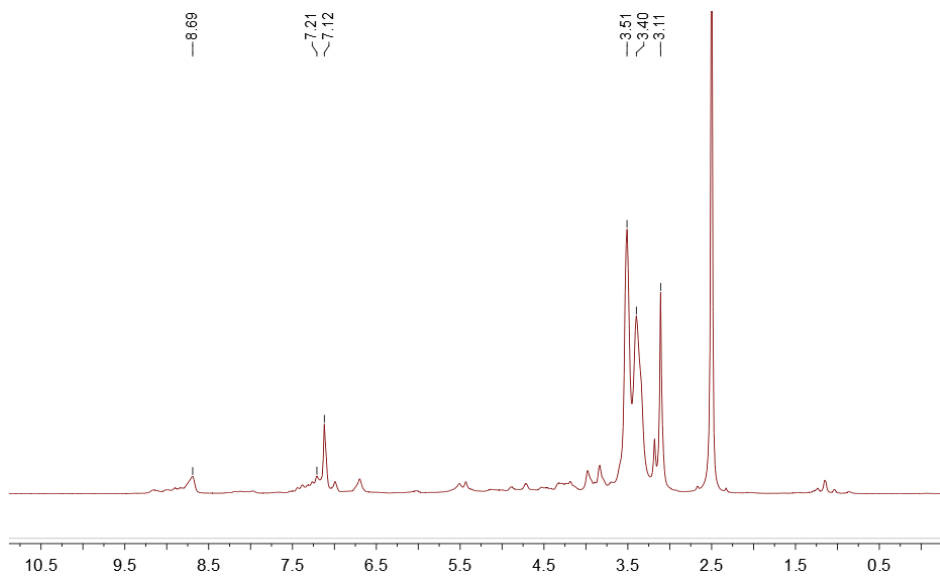
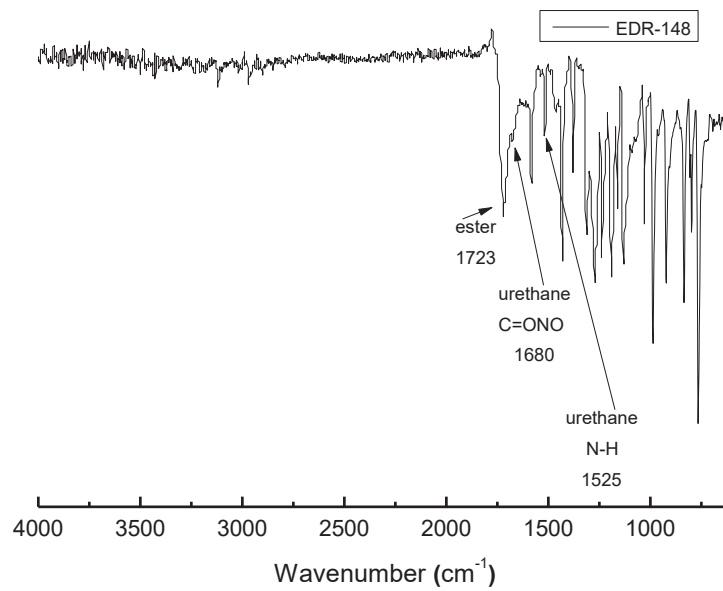


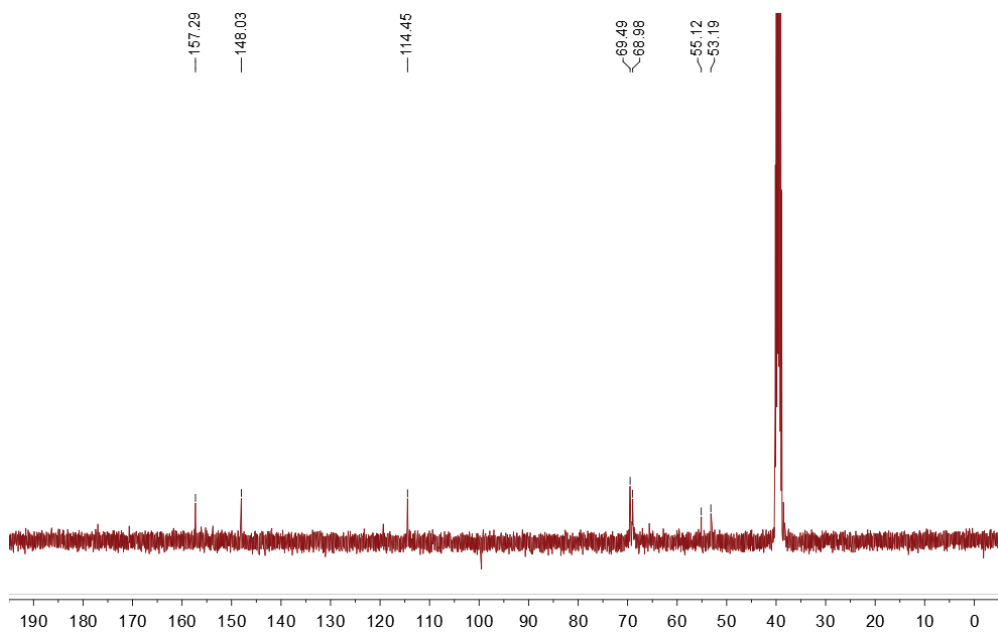
Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	62 μ s	RF Level	32 %	Trap Drive	38.0
SPS Target Mass	100 m/z	Averages	5 Spectra	n/a	n/a

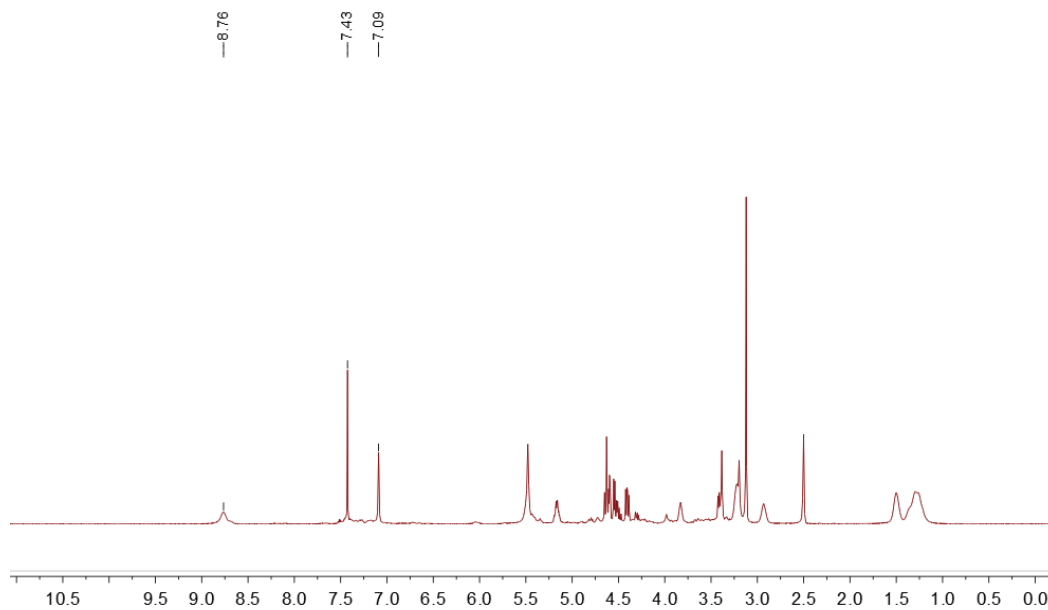
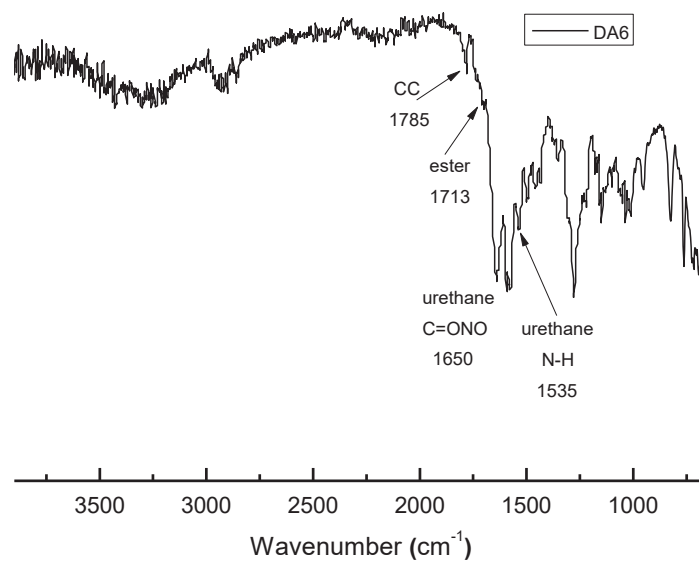


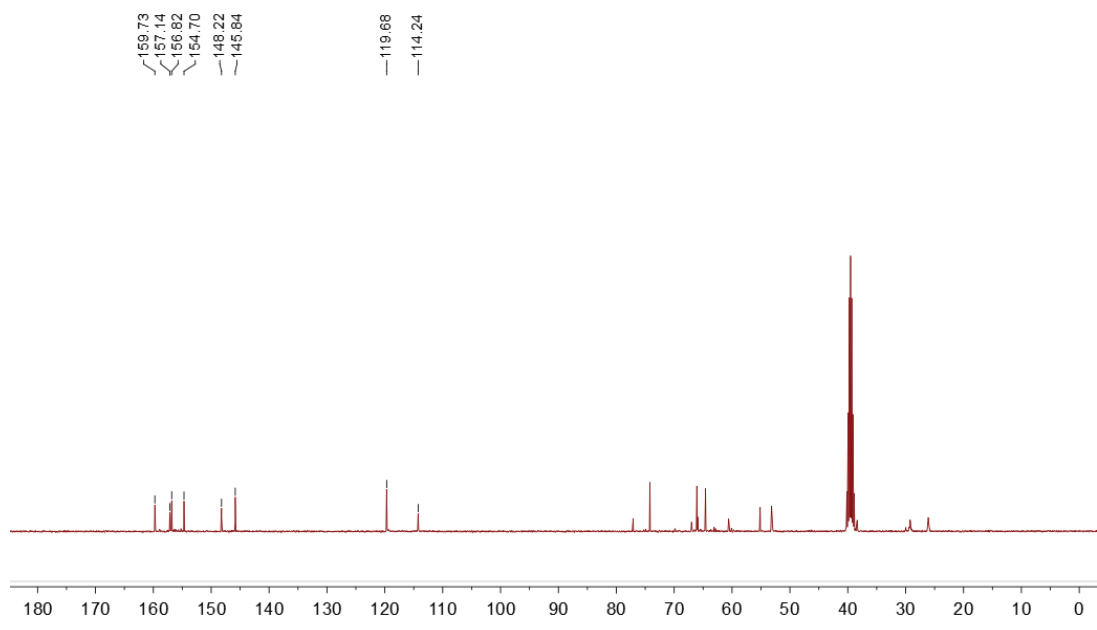
Characterizations of PHUs synthesized from EDR-148 in DES.



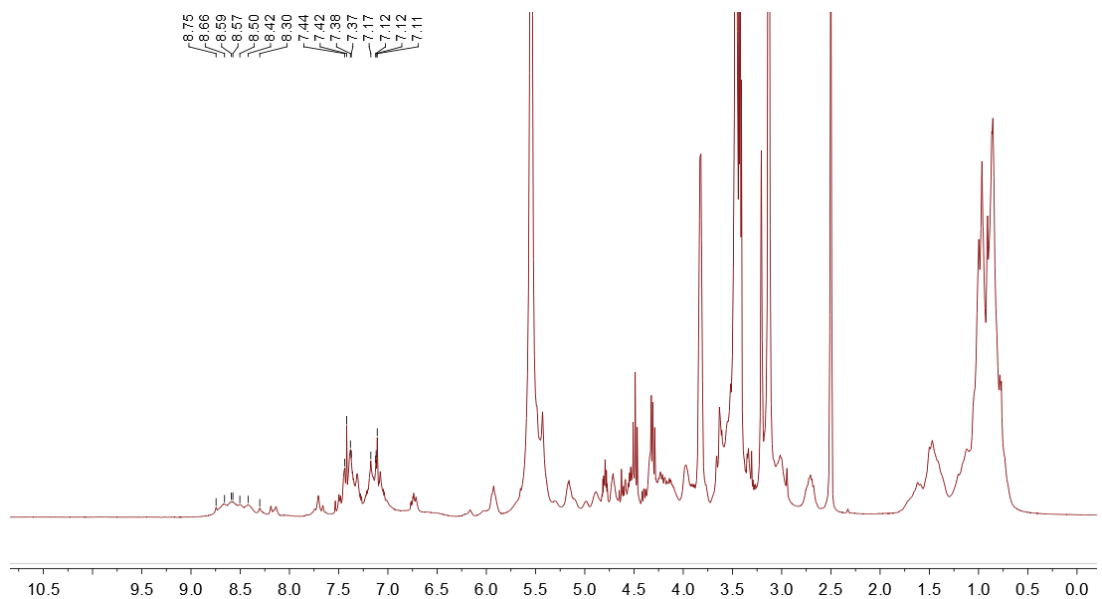
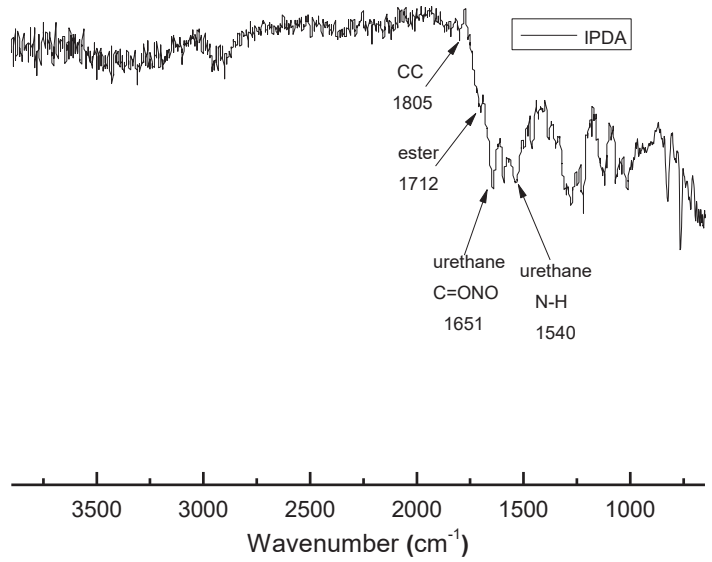


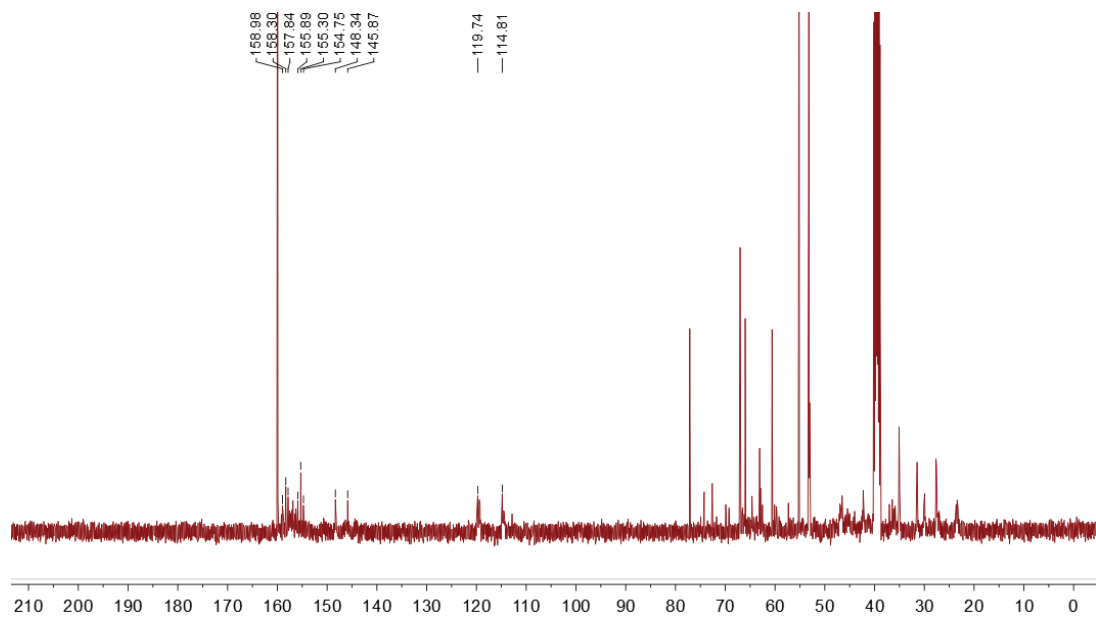
Characterizations of PHUs synthesized from DA6 in DES.



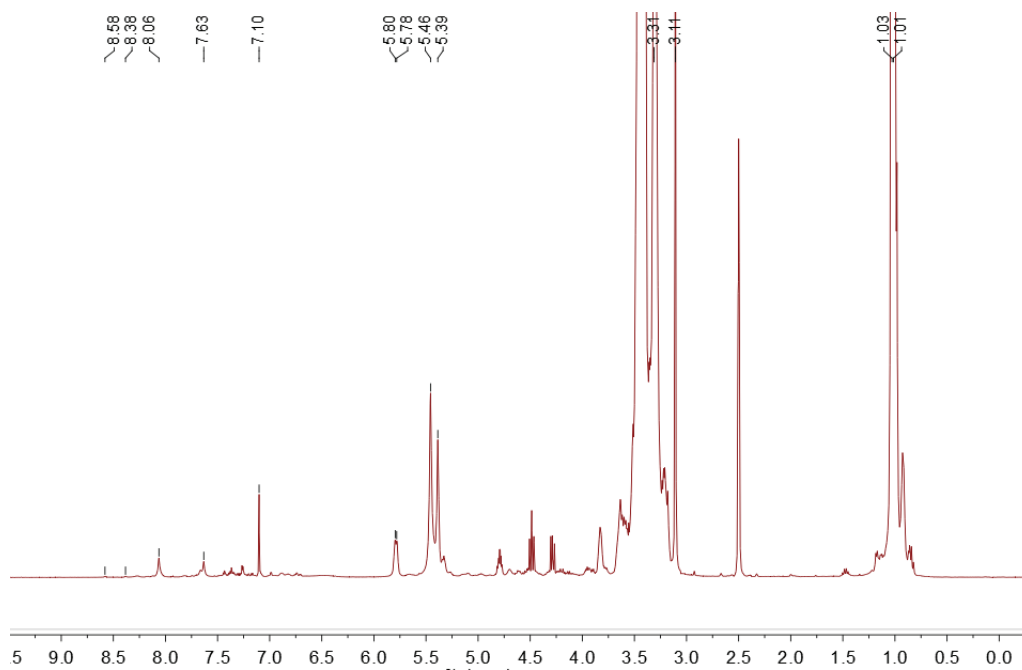
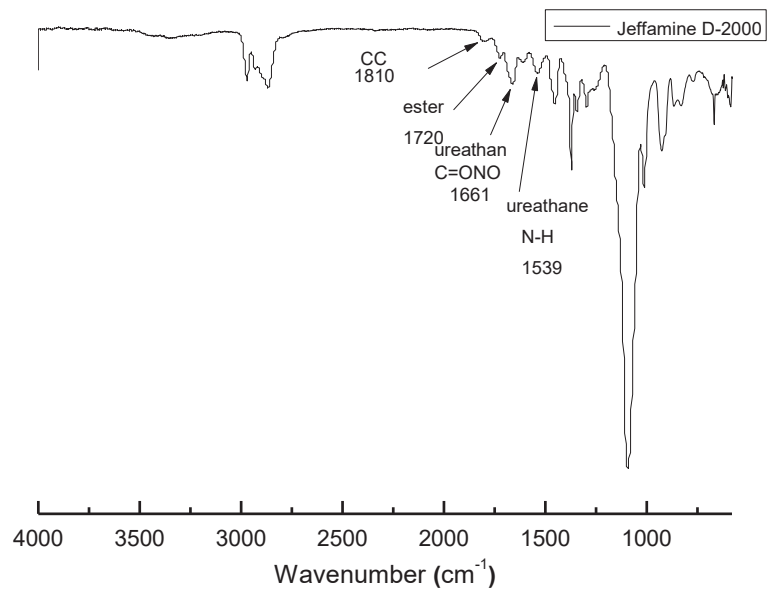


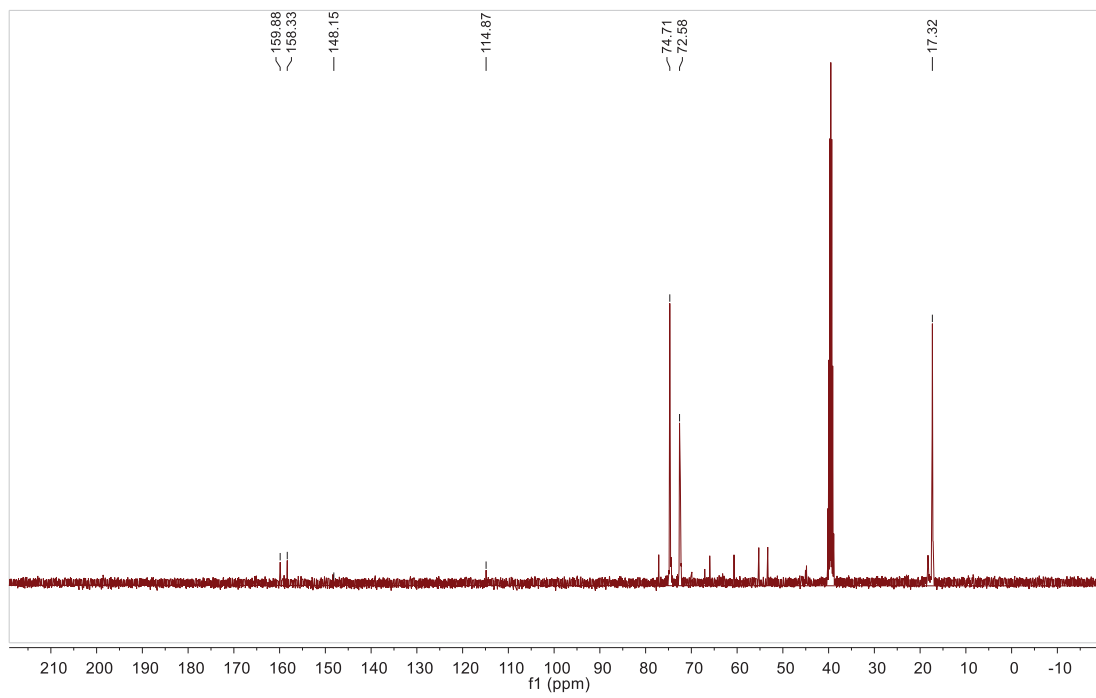
Characterizations of PHUs synthesized from IPDA in DES.



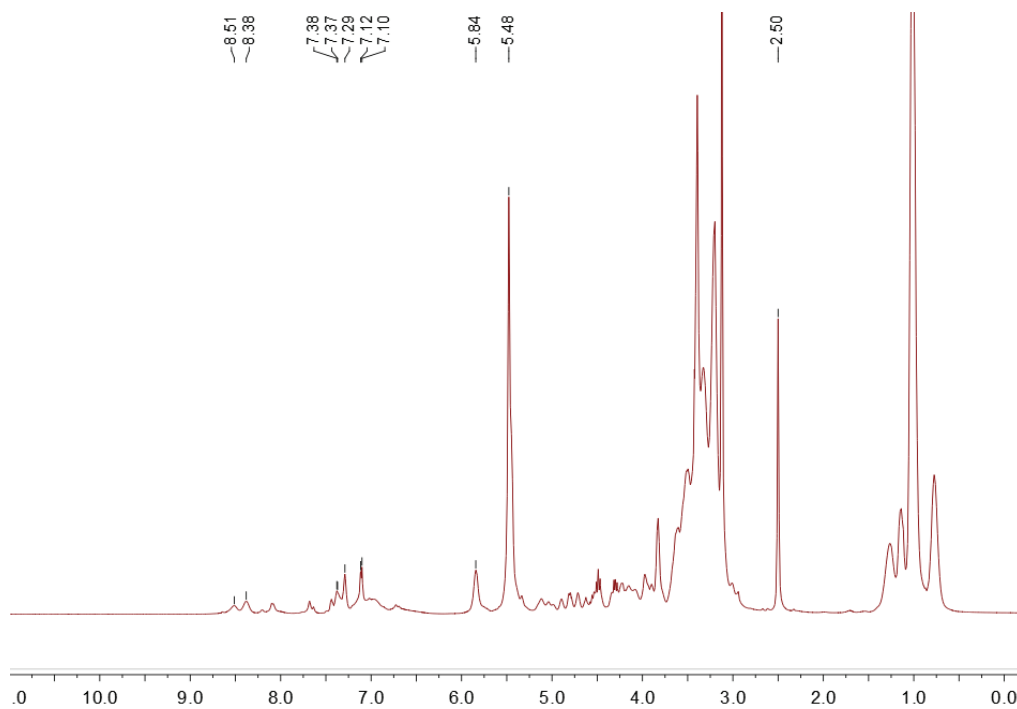
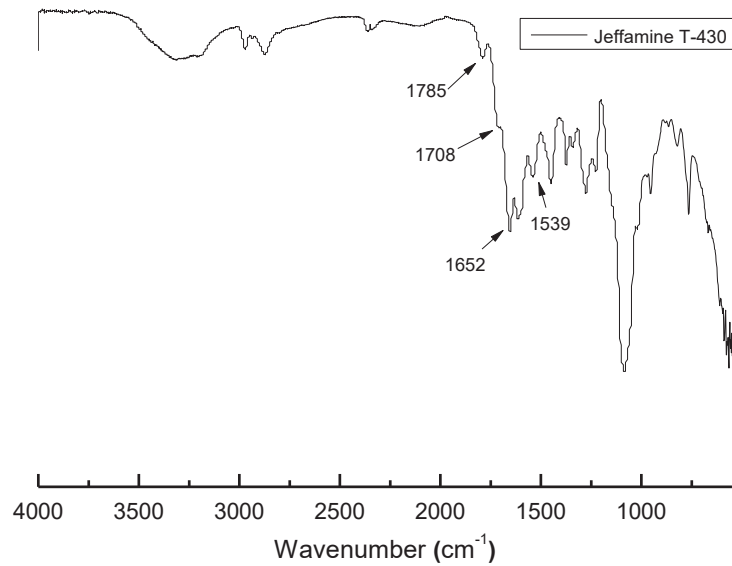


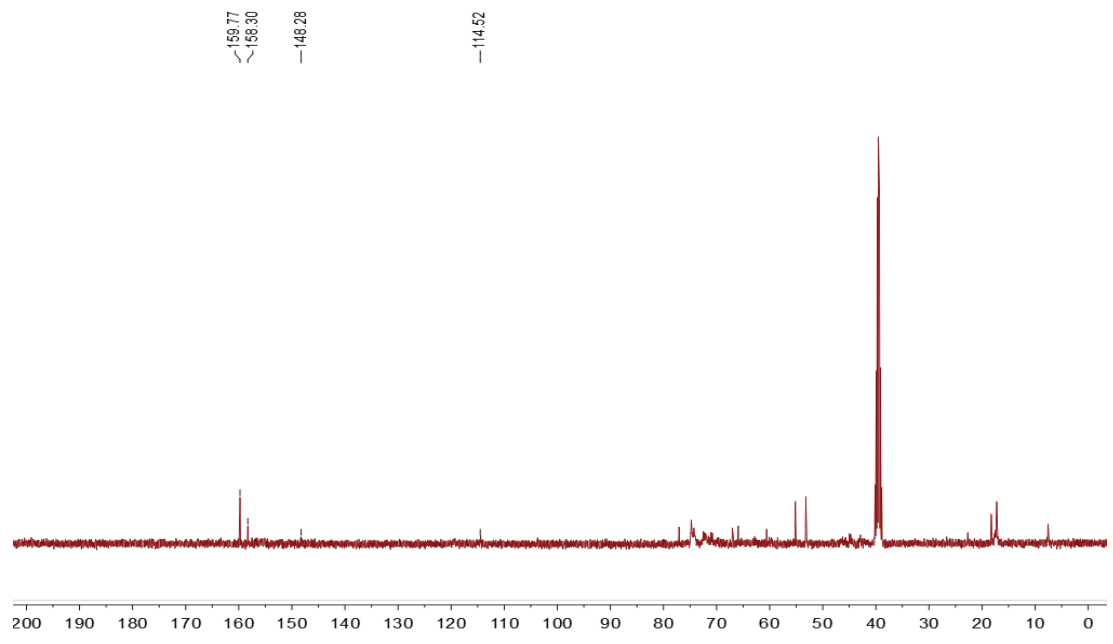
Characterizations of PHUs synthesized from Jeffamine D-2000.



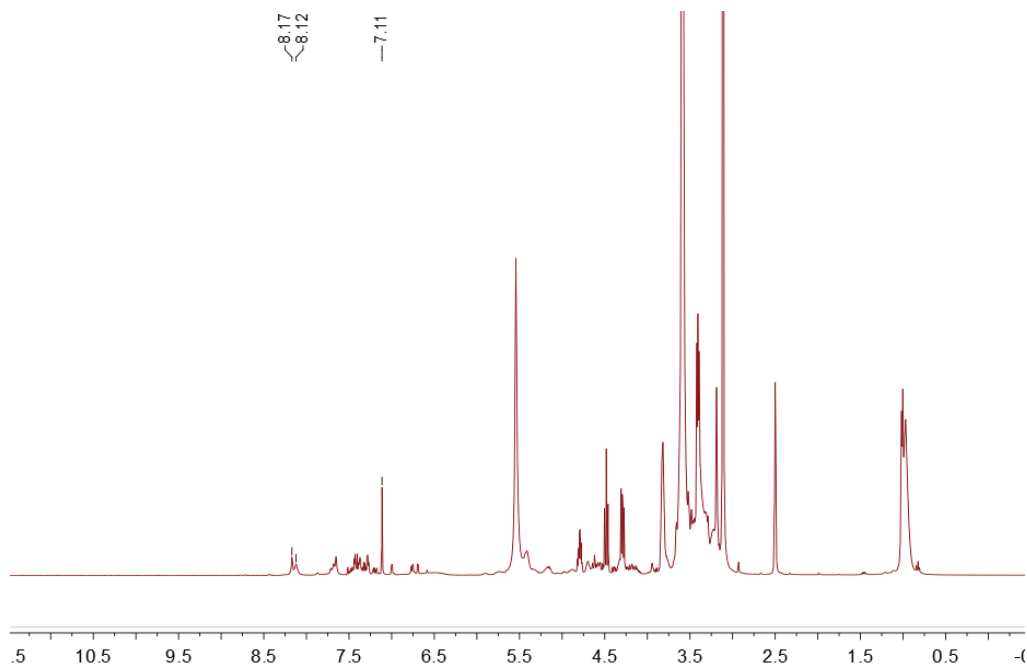
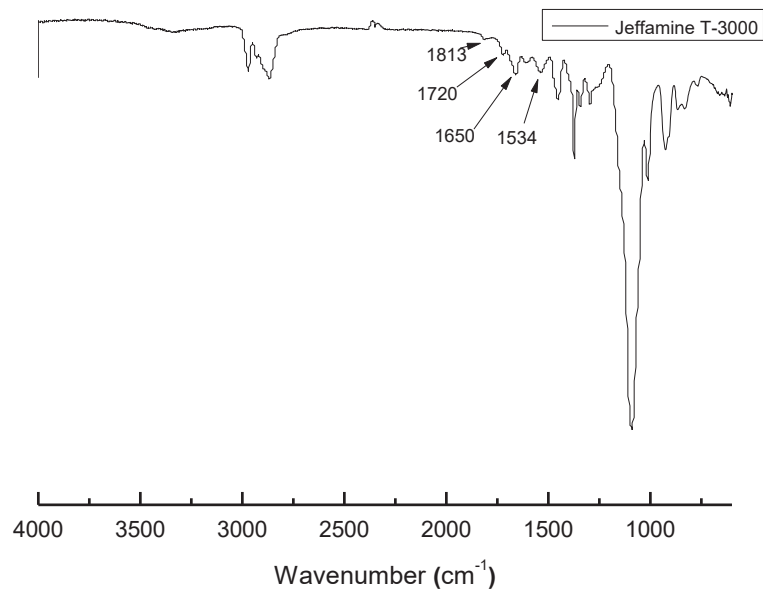


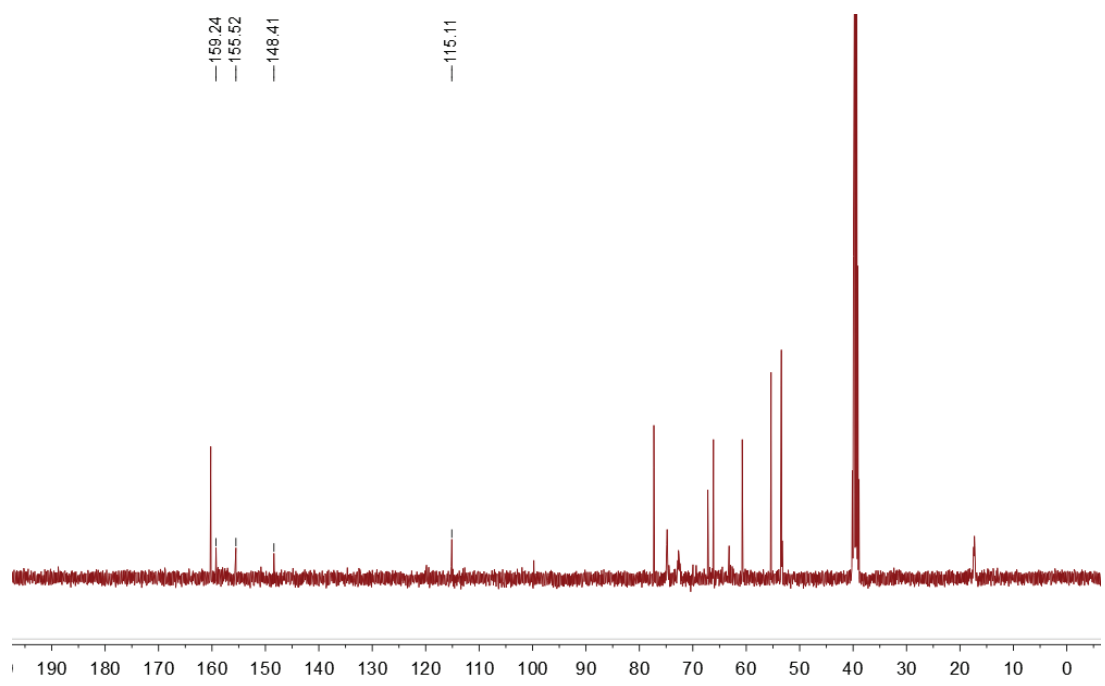
Characterizations of PHUs synthesized from Jeffamine T-403.





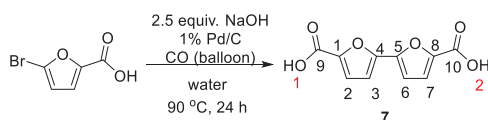
Characterizations of PHUs synthesized from Jeffamine T-3000.





Chapter 3 Experimental section

Synthesis and characterizations of 2,2-bifuryl-5,5-dicarboxylic acid (BFDCA) (**7**).



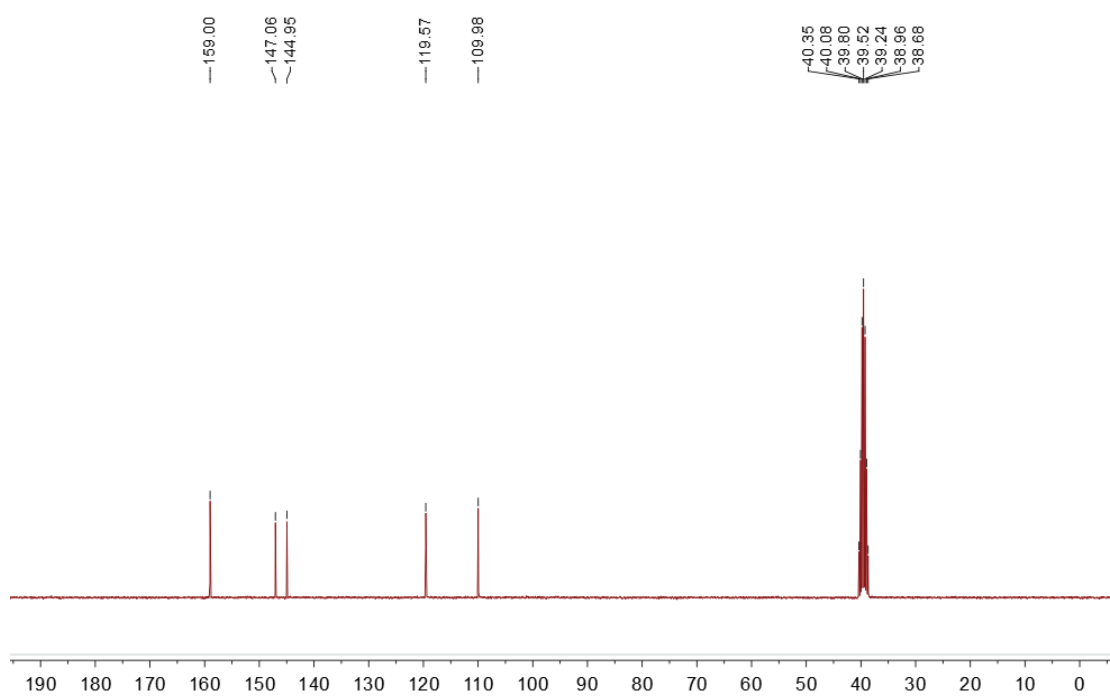
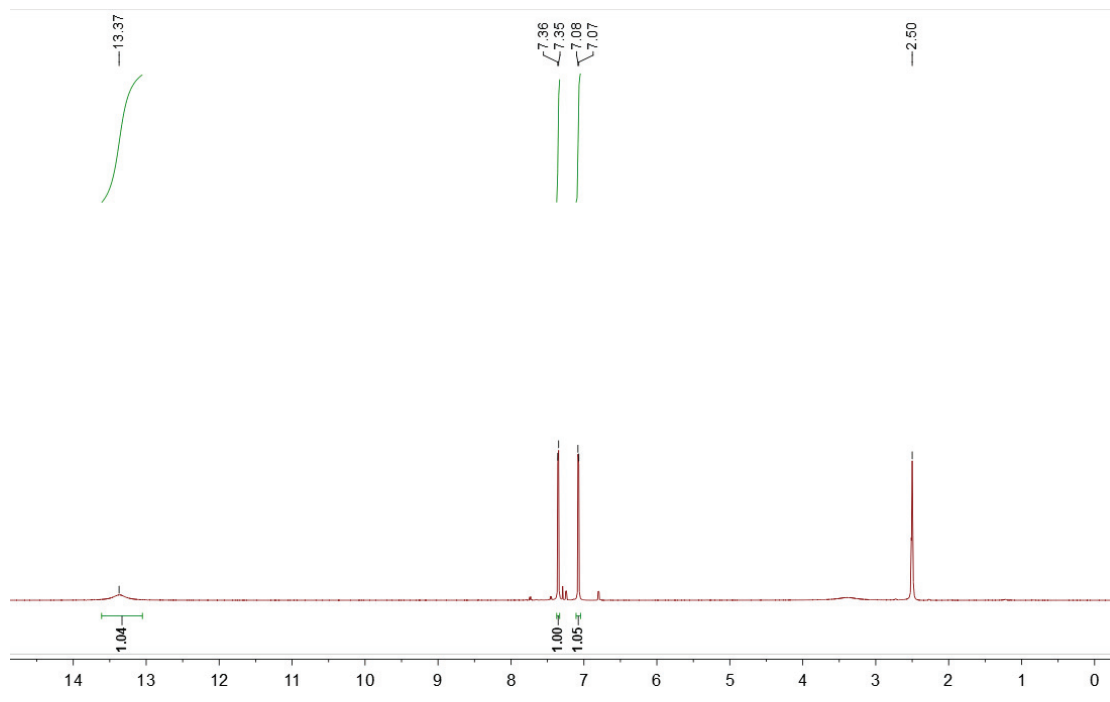
5-bromofuroic acid (26 mmol, 5 g), NaOH (65 mmol, 2.63 g), Pd/C (0.25 mmol, 620 mg,) and 150 mL H₂O were added to 250 mL flask. And then, used the CO exchanged the air five times, the flask was heated at 90°C for 24 h. After cooling to r.t., released the excess CO gas in the fuming hood. The Pd/C catalyst was removed through hot filtration, and using the 3 M HCl neutralized the filter water to pH 3. After filtration and drying the solid in oven, we obtained 2,2-bifuryl-5,5-dicarboxylic acid (BFDCA) in 97% yield (5.6 g) as a grey powder.

¹H NMR (300 MHz, DMSO) δ 13.32 (s, 2H; O-H₁₋₂), 7.35 (d, J = 3.6 Hz, 2H; H₂, H₇), 7.07 (d, J = 3.7 Hz, 2H; H₃, H₆).

¹³C NMR (75 MHz, DMSO) δ 159.0 (s; C₉, C₁₀), 147.1 (s; C₄, C₅), 145.0 (s; C₁, C₈), 119.6 (s; C₂, C₇), 110.0 (s; C₃, C₆).

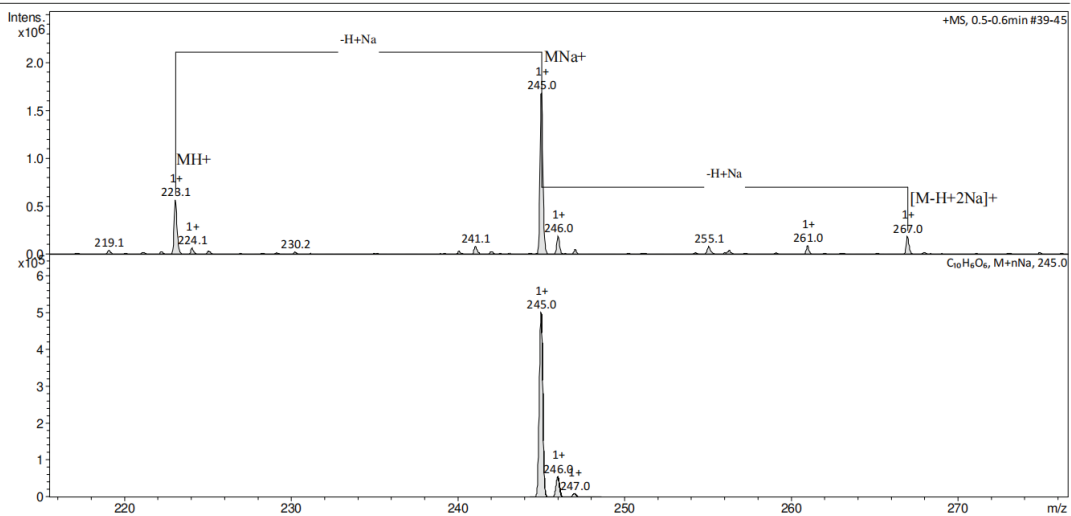
These results are in agreement with the literature. ^[200]

MS: [M+H]⁺ 223.1, [M+Na]⁺ 245.0.

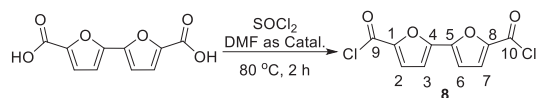


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	1234 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of 2,2-bifuryl-5,5-dicarboxyl chloride (BFDCA-Cl) (**8**).



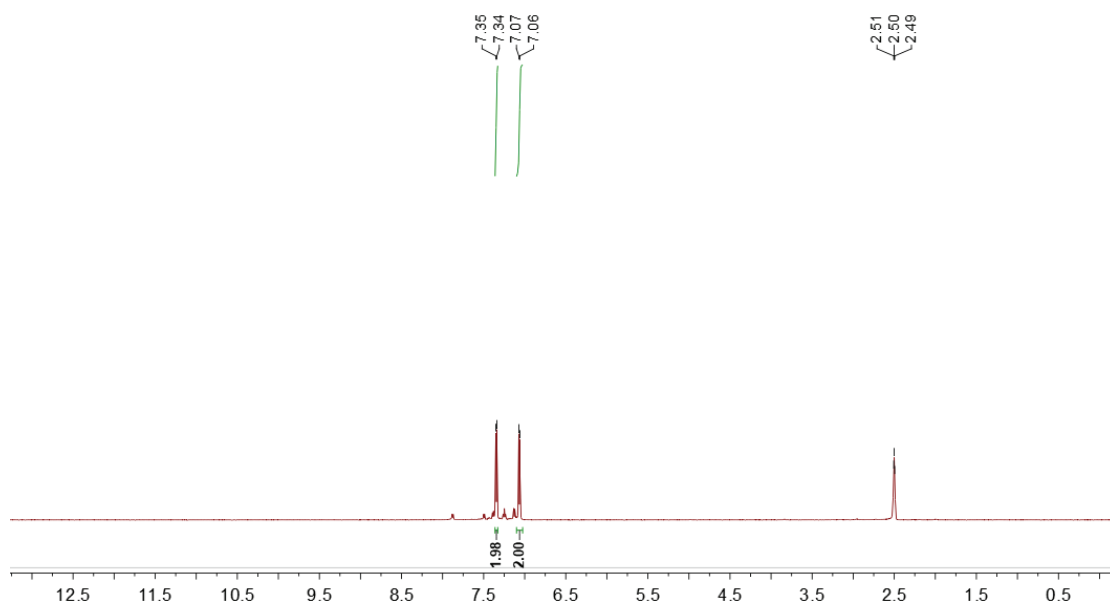
BFDCA (20 mmol, 4.4 g), SOCl_2 (40 mL), and 0.3 mL DMF as catalyst were introduced into 150 mL flask. The mixture was refluxed at 80°C for 2 h. Then, excess thionyl chloride was removed by distillation achieving recycle, and the residue was dried in vacuum at 80°C to afford desired product 2,2-bifuryl-5,5-dicarboxyl chloride (BFDCA-Cl) in almost quantitative yield (5.2 g) as a brown powder.

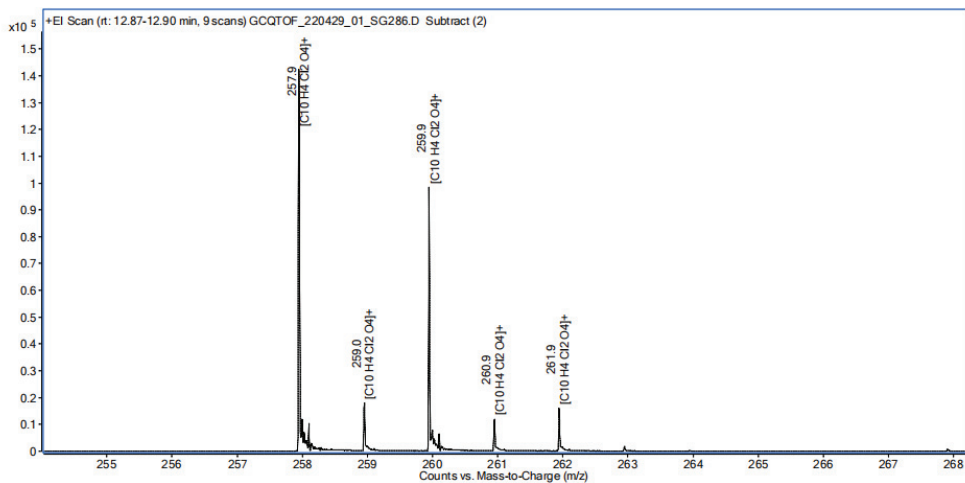
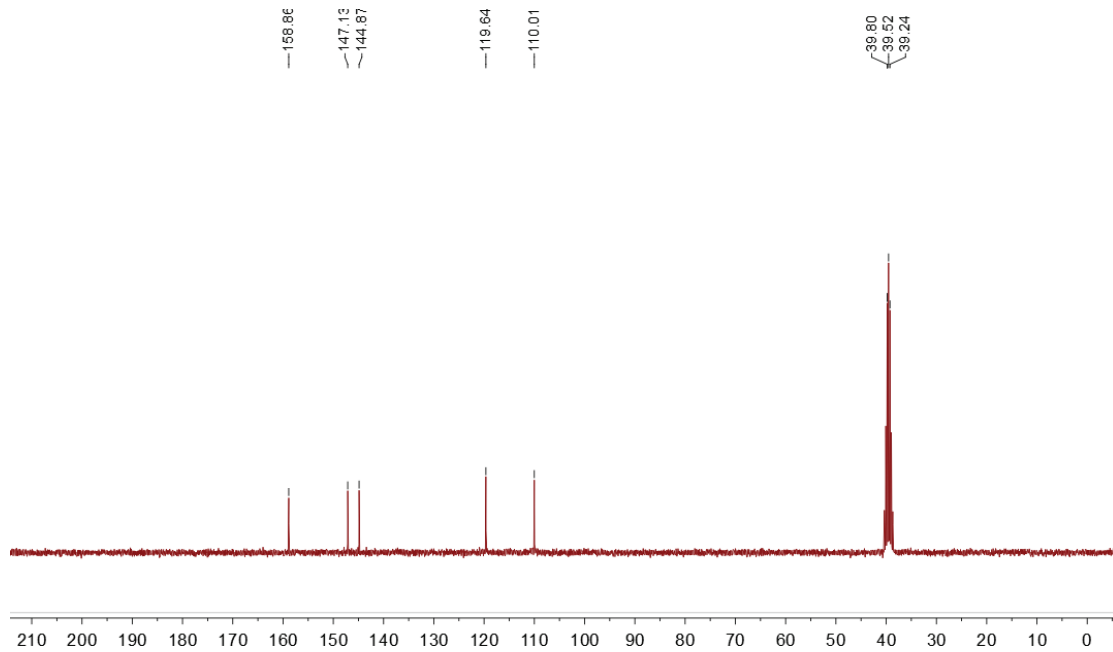
^1H NMR (300 MHz, DMSO) δ 7.35 (d, $J = 3.7$ Hz, 2H; H_2 , H_7), 7.07 (d, $J = 3.6$ Hz, 2H; H_3 , H_6).

^{13}C NMR (75 MHz, DMSO) δ 158.9 (s; C_9 , C_{10}), 147.1 (s; C_4 , C_5), 144.9 (s; C_1 , C_8), 119.6 (s; C_2 , C_7), 110.0 (s; C_3 , C_6).

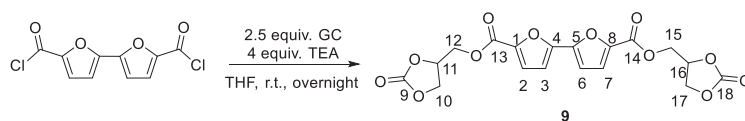
These results are in agreement with the literature. ^[199]

MS: $[\text{M}\cdot]^+$ 257.9.





Synthesis and characterizations of 2,2-bifuryl-5,5-dicarboxylate glycerol carbonate (BFDCA-Bis-CC) (**9**).

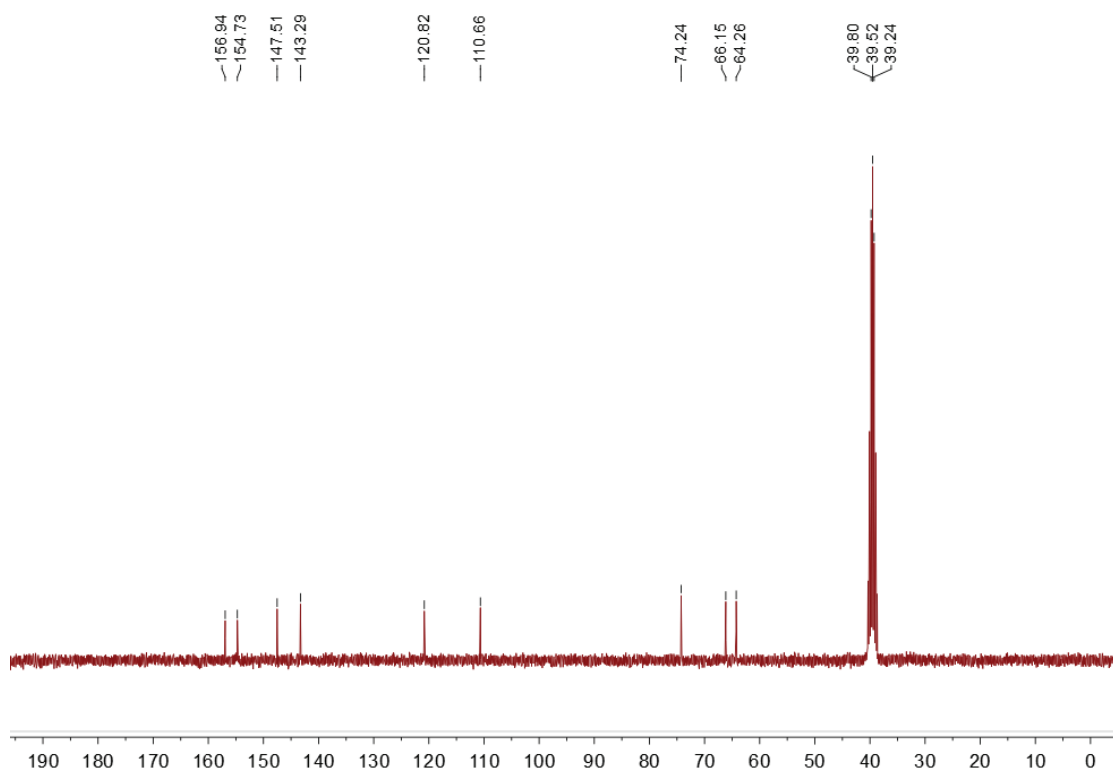
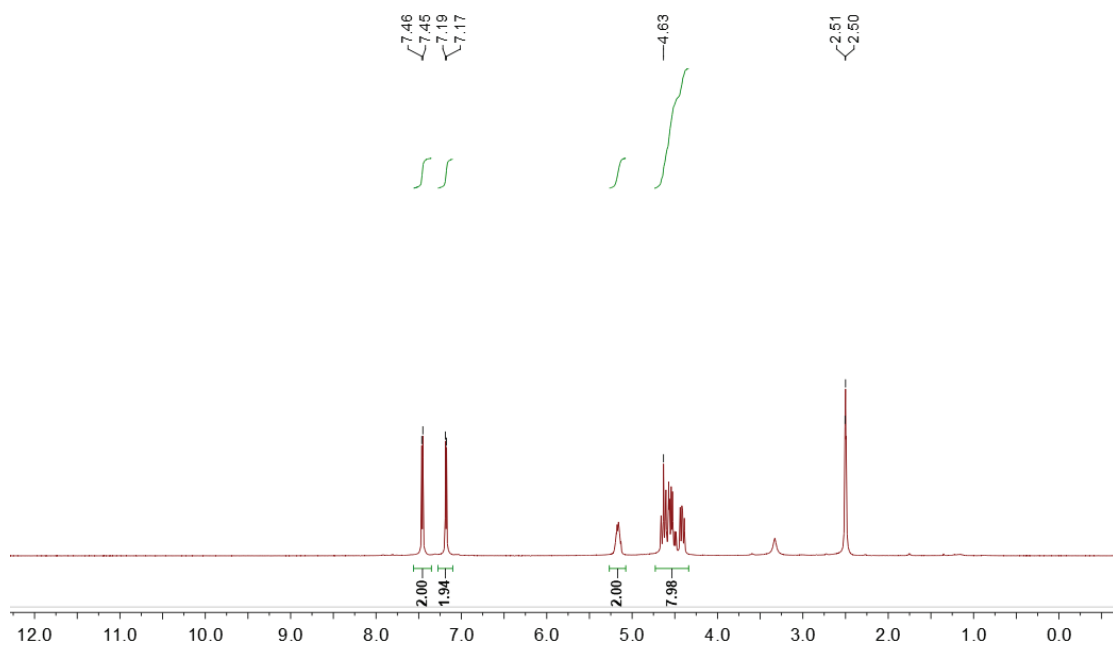


GC (50 mmol, 5.9 g), triethylamine (TEA, 80 mmol, 8.08 g) were introduced into a flask containing 120 mL of THF. A mixture of 2,2-bifuryl-5,5-dicarboxyl chloride (20 mmol, 5.18 g) and 50 ml THF was slowly added to the above solution. The mixture was stirred at r.t. overnight. After the reaction, THF was removed in vacuum, and a saturated aqueous NaHCO₃ solution (20 mL x 5) was used to wash the solid to afford 2,2-bifuryl-5,5-dicarboxylate glycerol carbonate (BFDCA-Bis-CC) in 94% yield (19.8 g) as a grey powder.

¹H NMR (300 MHz, DMSO) δ 7.46 (d, *J* = 3.7 Hz, 2H; H₂, H₇), 7.18 (d, *J* = 3.7 Hz, 2H; H₃, H₆), 5.17 (dtd, *J* = 8.5, 5.8, 2.7 Hz, 2H; H₁₁, H₁₆), 4.63 (s, 8H; H₁₀, H₁₂, H₁₅, H₁₇).

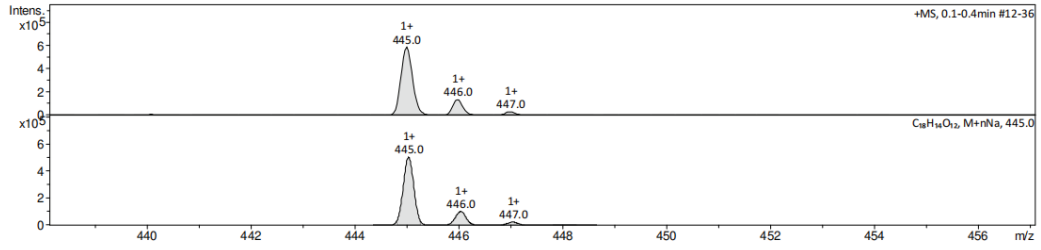
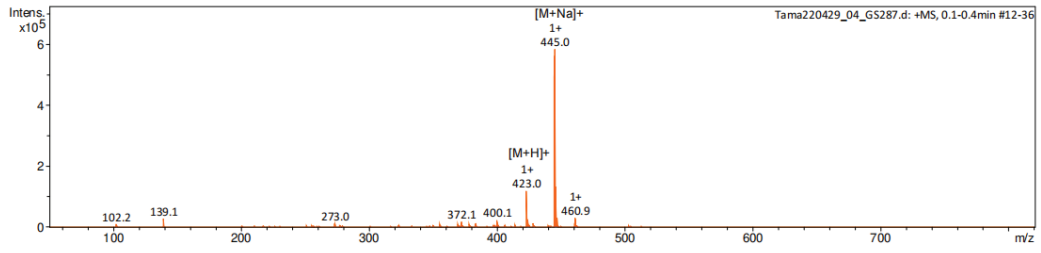
¹³C NMR (75 MHz, DMSO) δ 156.9 (s; C₁₃, C₁₄), 154.7 (s; C₉, C₁₈), 147.5 (s; C₄, C₅), 143.3 (s; C₁, C₈), 120.8 (s; C₂, C₇), 110.7 (s; C₃, C₆), 74.2 (s; C₁₁, C₁₆), 66.2 (s; C₁₂, C₁₅), 64.3 (s; C₁₀, C₁₇).

MS: [M+H]⁺ 423.0, [M+Na]⁺ 445.0.

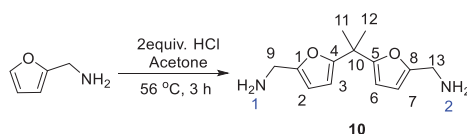


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	4703 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra		n/a



Synthesis and characterizations of (5,5'-(propane-2,2-diyl) bis(furan-5,2-diyl))methenamine (PBFA) (**10**).



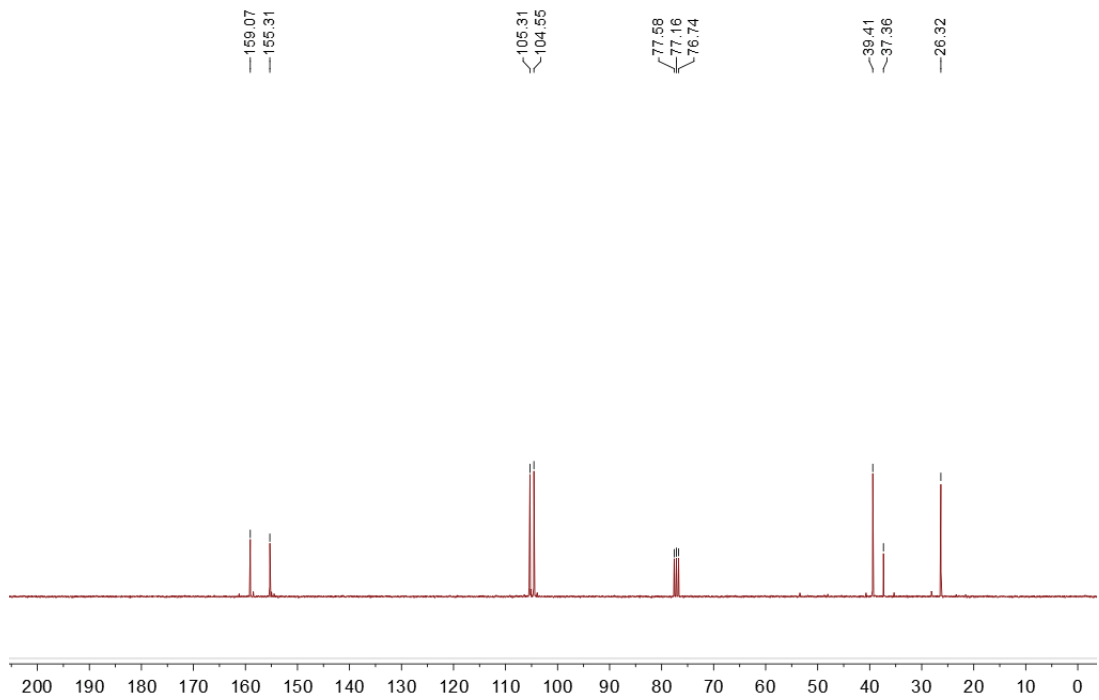
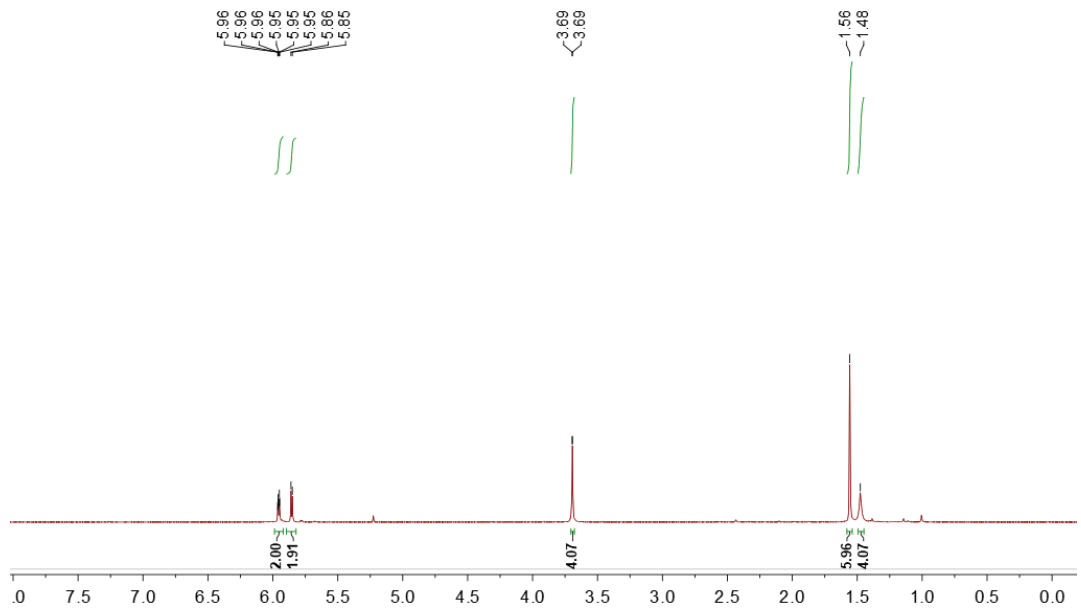
Furfuryl amine (10 mmol, 970 mg) was dissolved in concentrated hydrochloric acid (HCl, 20 mmol, 1.7 ml), and then 20 mL acetone was added to mixture. The reaction was stirred at 56°C for 3 h. After cooling to r.t., concentrated sodium hydroxide aqueous was used to neutralize the mixture to pH higher than 10. Using the EA/cyclohexane (7:3, v/v) (20 mL x 5) to extract the product, we received 5,5'-(propane-2,2-diyl) bis(furan-5,2-diyl) methenamine (PBFA) in 81% yield (0.95 g) as a brown oil.

^1H NMR (300 MHz, CDCl_3) δ 5.96 (dt, $J = 3.1, 0.7$ Hz, 2H; H_2, H_7), 5.86 (d, $J = 3.1$ Hz, 2H; H_3, H_6), 3.69 (d, $J = 0.4$ Hz, 4H; N- H_{1-2}), 1.56 (s, 6H; $\text{H}_{11}, \text{H}_{12}$), 1.48 (s, 4H; $\text{H}_9, \text{H}_{13}$).

^{13}C NMR (75 MHz, CDCl_3) δ 159.1 (s; C_4, C_5), 155.3 (s; C_1, C_8), 105.3 (s; C_2, C_7), 104.6 (s; C_3, C_6), 39.4 (s; C_{10}), 37.4 (s; $\text{C}_9, \text{C}_{13}$), 26.3 (s; $\text{C}_{11}, \text{C}_{12}$).

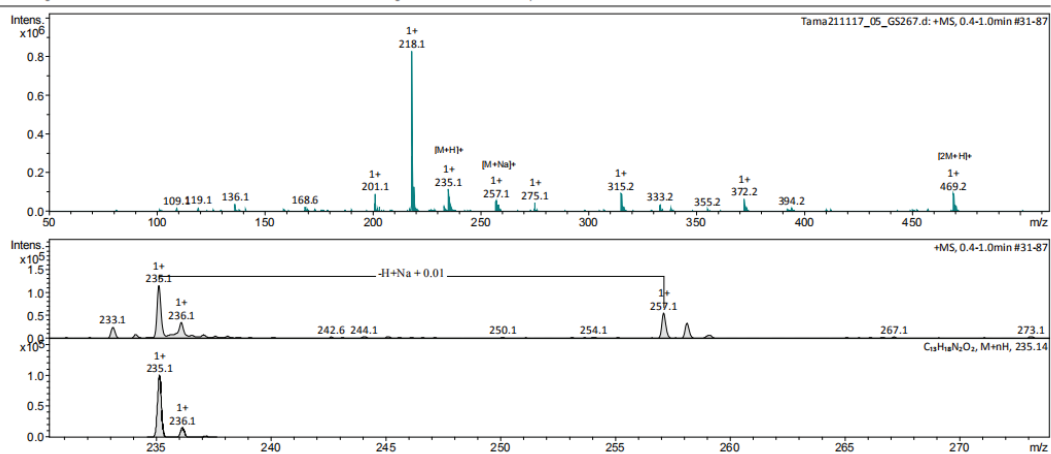
These results are in agreement with the literature. ^[144]

MS: $[\text{M}+\text{H}]^+$ 235.1, $[\text{M}+\text{Na}]^+$ 257.1.

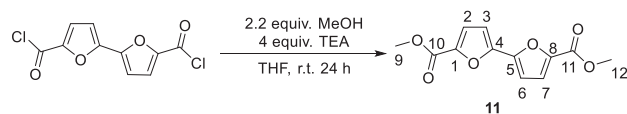


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	3262 μ s	RF Level	39 %	Trap Drive	40.1
SPS Target Mass	150 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of dimethyl (2,2'-bifuran)-5,5'-dicarboxylate (Dm-BFDCA) (**11**)

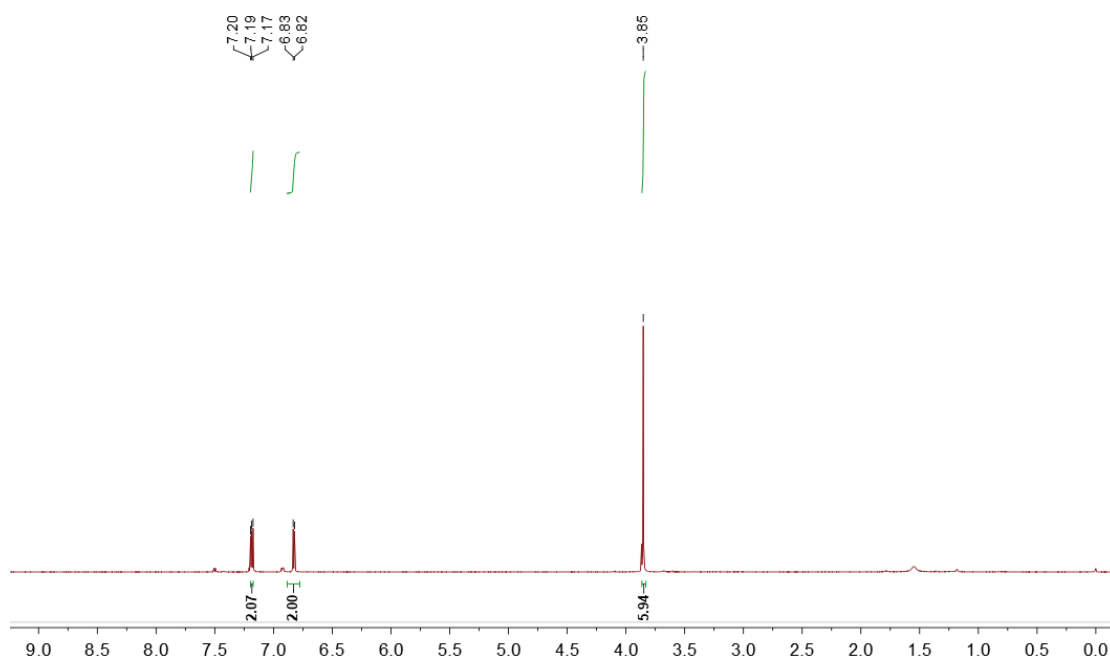


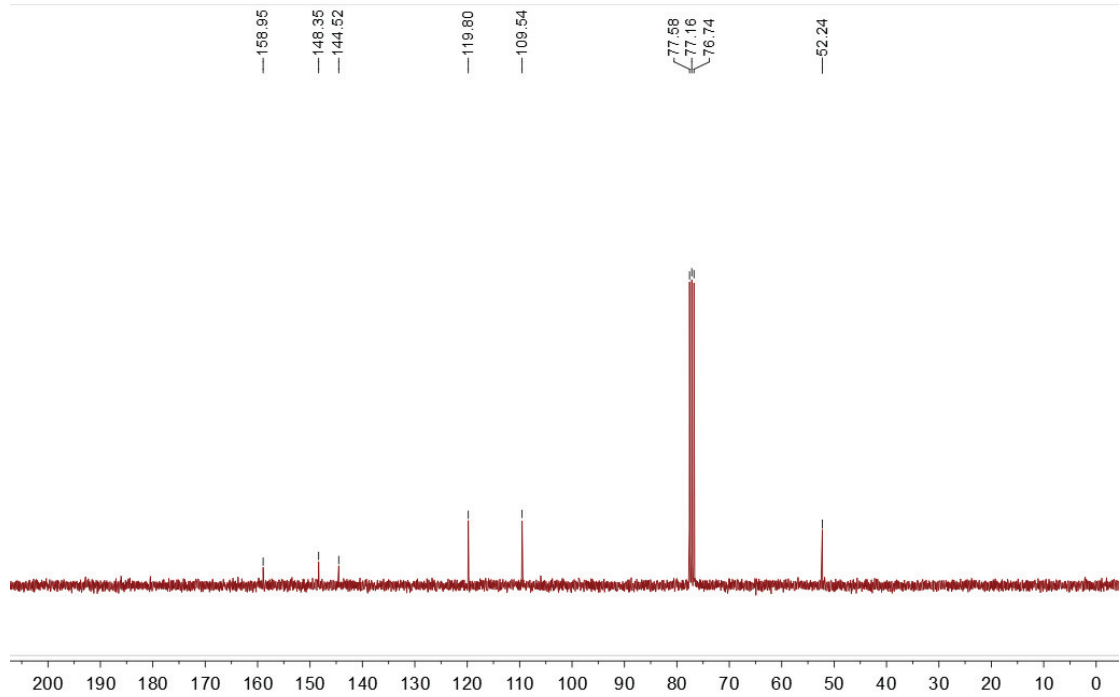
MeOH (11 mmol, 352 mg), triethylamine (TEA, 20 mmol, 2.02 g) were introduced into the flask contained 30 mL THF. A mixture of 2,2'-bifuranyl-5,5'-dicarbonyl chloride (5 mmol, 1.3 g) and 20 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and a saturated aqueous NaHCO₃ solution (20 mL x 3) was used to wash the solid to afford dimethyl (2,2'-bifuran)-5,5'-dicarboxylate (Dm-BFDCA) in 96% yield (1.2 g) as a grey powder.

¹H NMR (300 MHz, CDCl₃) δ 7.20 – 7.17 (m, 2H; H₂, H₇), 6.83 (d, *J* = 3.6 Hz, 2 H; H₃, H₆), 3.85 (s, 6 H; H₉, H₁₂).

¹³C NMR (75 MHz, CDCl₃) δ 159.0 (s; C₁₀, C₁₁), 148.4 (s; C₄, C₅), 144.5 (s; C₁, C₈), 119.8 (s; C₂, C₇), 109.5 (s; C₃, C₆), 52.2 (s; C₉, C₁₂).

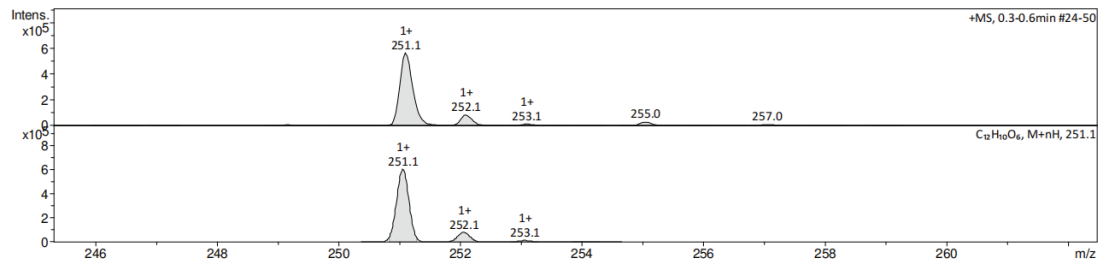
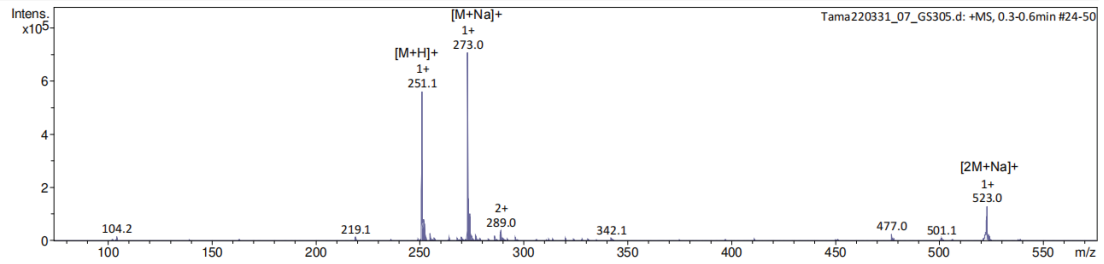
MS: [M+H]⁺ 251.1, [M+Na]⁺ 273.0.



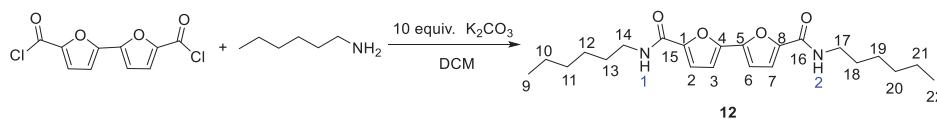


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	3133 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of N-hexyl-2,2-bifuryl-5,5-dicarboxamide (**12**).



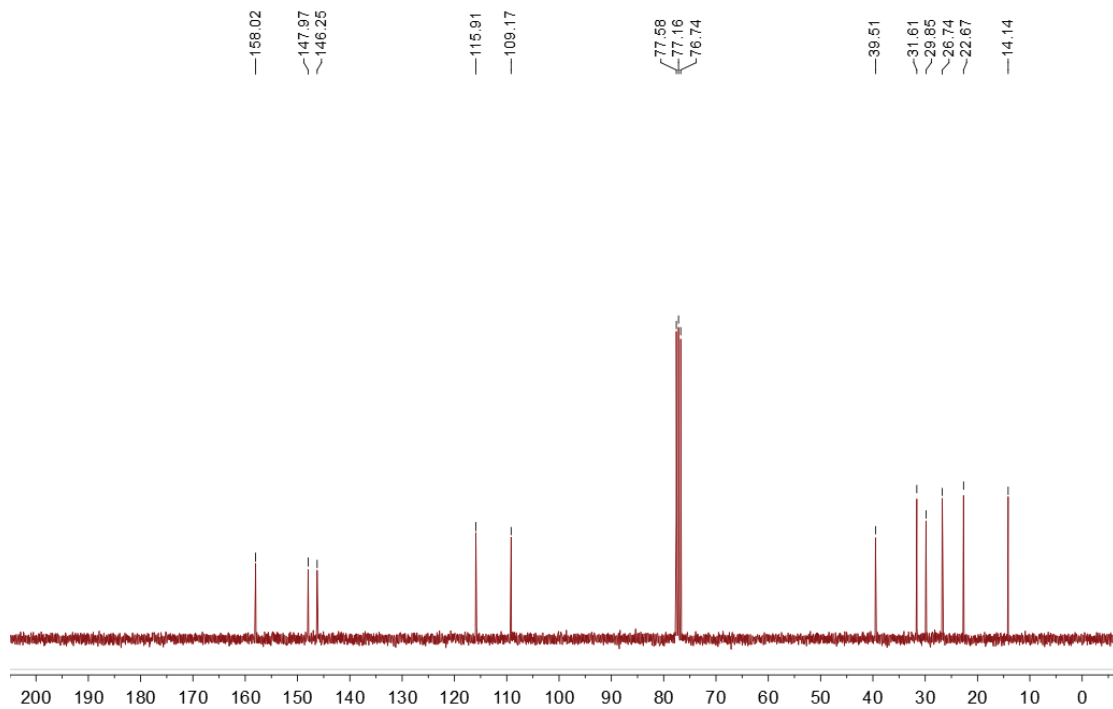
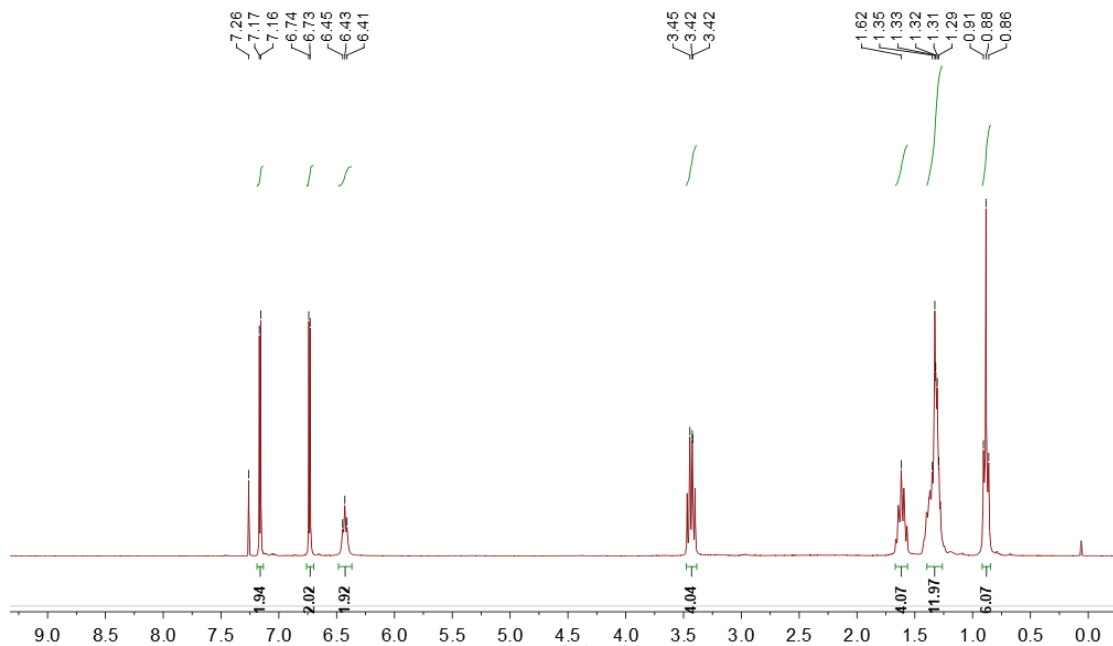
2,2-bifuryl-5,5-dicarboxyl chloride (2 mmol, 518 mg), hexylamine (2.2 equiv., 444 mg), K_2CO_3 (20 mol, 2.76 g) and 20 mL DCM were introduced into a flask. The mixture was stirred at r.t. overnight. After the reaction, DCM was removed in vacuum, a saturated aqueous $NaHCO_3$ (5 mL x 3) was used to wash the solid to afford N-hexyl-2,2-bifuryl-5,5-dicarboxamide in 95% yield (737.2 mg) as a grey powder.

1H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, $J = 3.6$ Hz, 2H; H_2, H_7), 6.74 (d, $J = 3.6$ Hz, 2H; H_3, H_6), 6.43 (t, $J = 5.6$ Hz, 2H; N- H_{1-2}), 3.48 – 3.39 (m, 4H; H_{14}, H_{17}), 1.62 (s, 4H; H_{13}, H_{18}), 1.40 – 1.26 (m, 12H; H_{10-12}, H_{19-21}), 0.88 (t, $J = 6.9$ Hz, 6H; H_9, H_{22}).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (s; C_{15}, C_{16}), 148.0 (s; C_4, C_5), 146.2 (s; C_1, C_8), 115.9 (s; C_2, C_7), 109.2 (s; C_3, C_6), 39.5 (s; C_{14}, C_{17}), 31.6 (s; C_{13}, C_{18}), 29.8 (s; C_{12}, C_{19}), 26.7 (s; C_{11}, C_{20}), 22.7 (s; C_{10}, C_{21}), 14.1 (s; C_9, C_{22}).

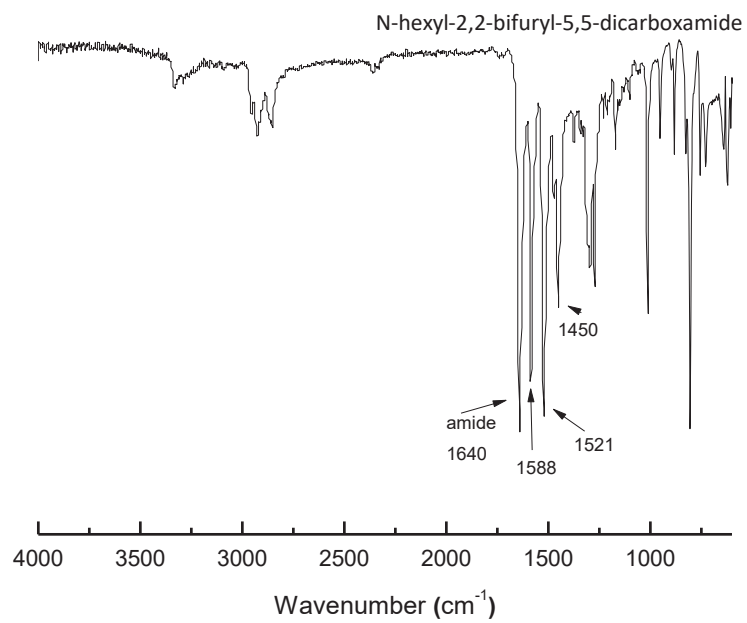
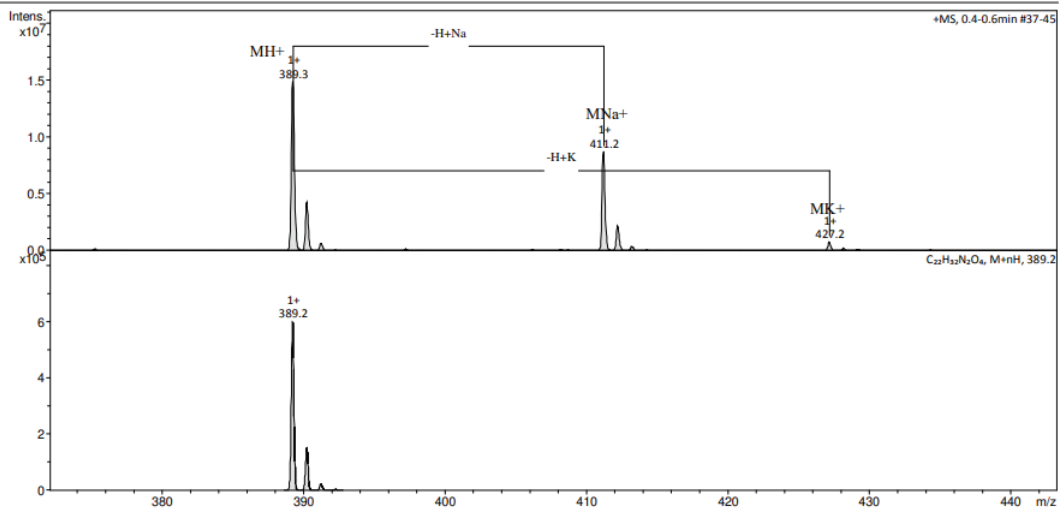
These results are in agreement with the literature. ^[205]

MS: $[M+H]^+$ 389.3, $[M+Na]^+$ 411.2.

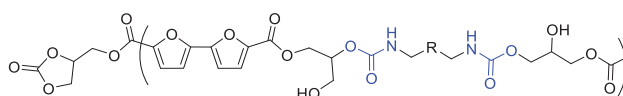


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	20 m/z	Scan End	1000 m/z
Accumulation Time	530 μ s	RF Level	24 %	Trap Drive	36.3
SPS Target Mass	60 m/z	Averages	5 Spectra		n/a



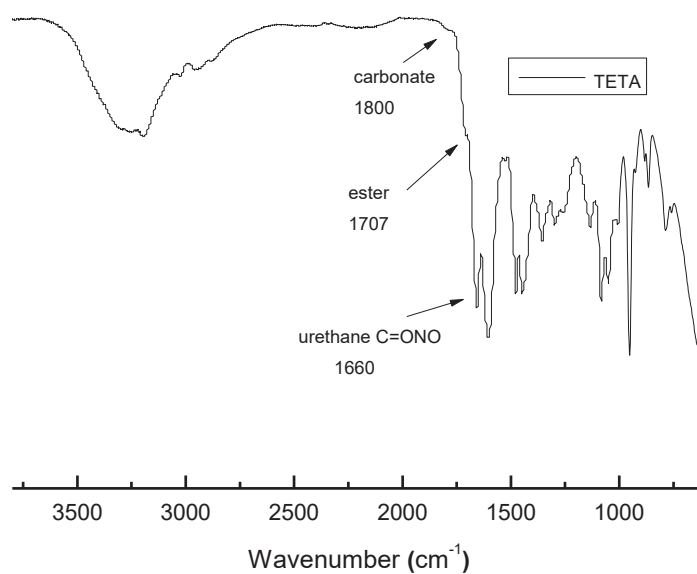
The PHUs polymer structure



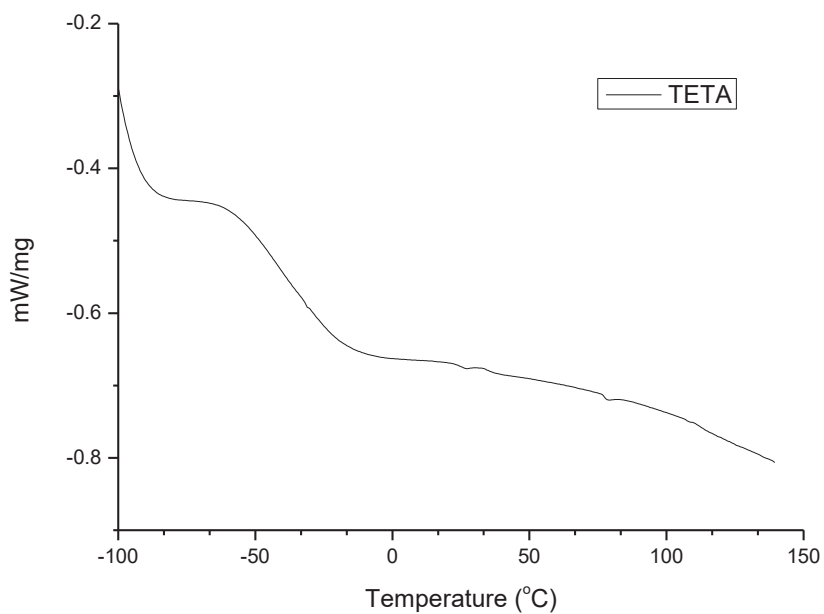
The cyclocarbonate carbonyl stretching vibration should be around 1790 cm^{-1} ; the ester carbonyl stretching vibration should be around 1710 cm^{-1} ; the urethane carbonyl stretching vibration should be range from 1650 to 1900 cm^{-1} ; the urethane N-H (amide II bending vibration) should be around 1540 cm^{-1} .

Characterizations of PHUs synthesized from TETA.

IR analysis

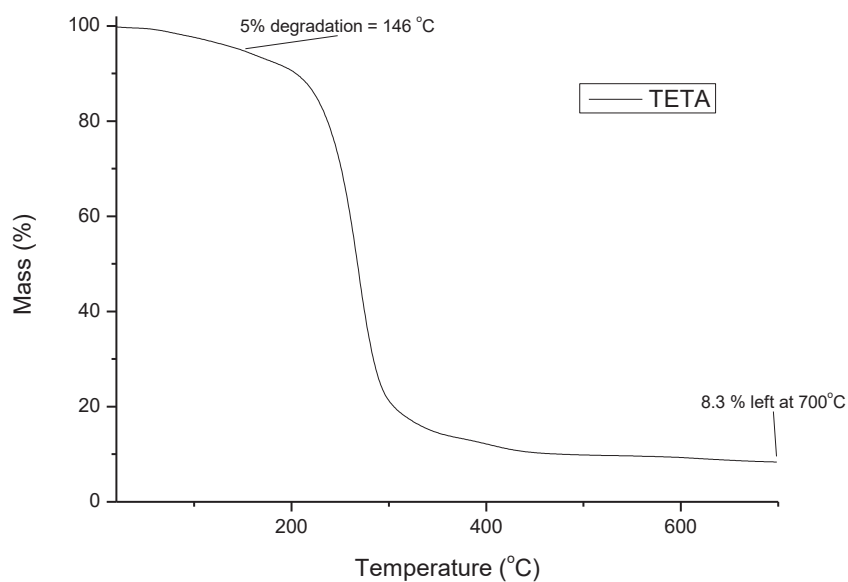


DSC



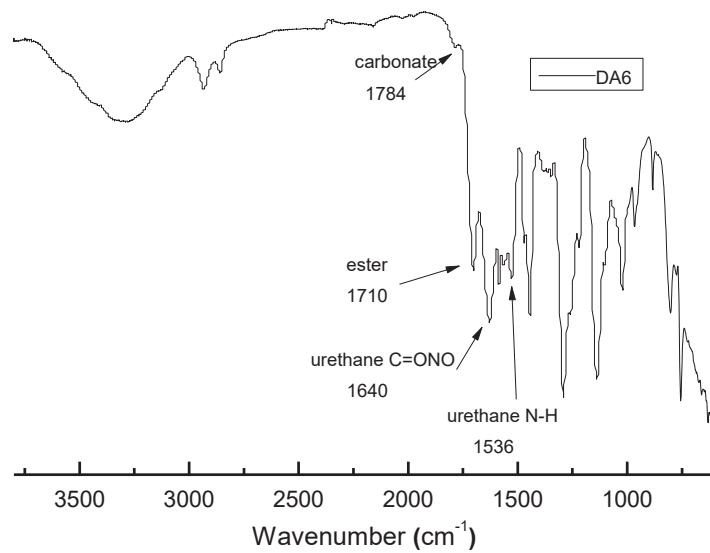
The DSC machine need to stabilize and work in relatively halcyon atmosphere. Otherwise, the DSC curve would display a slope around minus 100 °C, and have some waves.

TGA

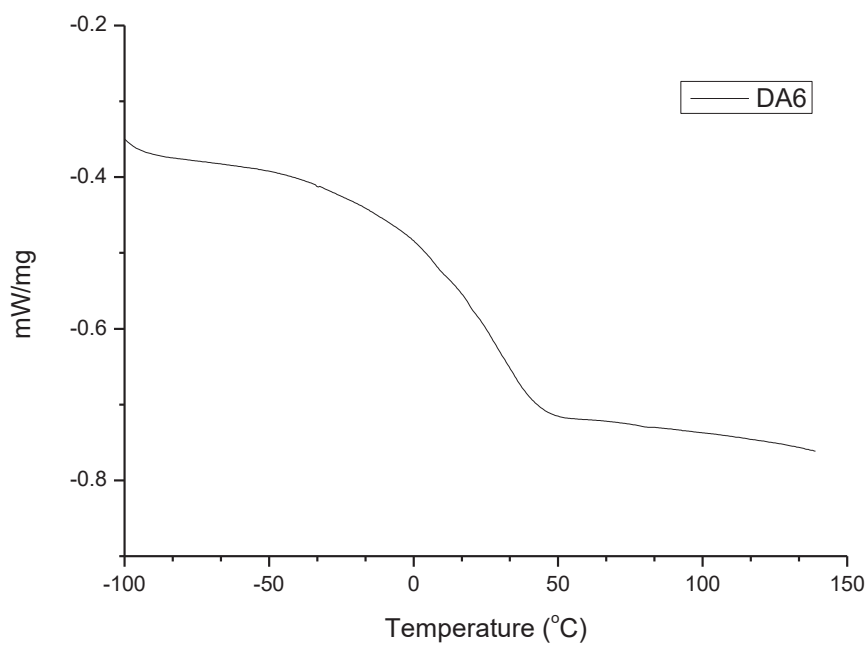


Characterizations of PHUs synthesized from DA6.

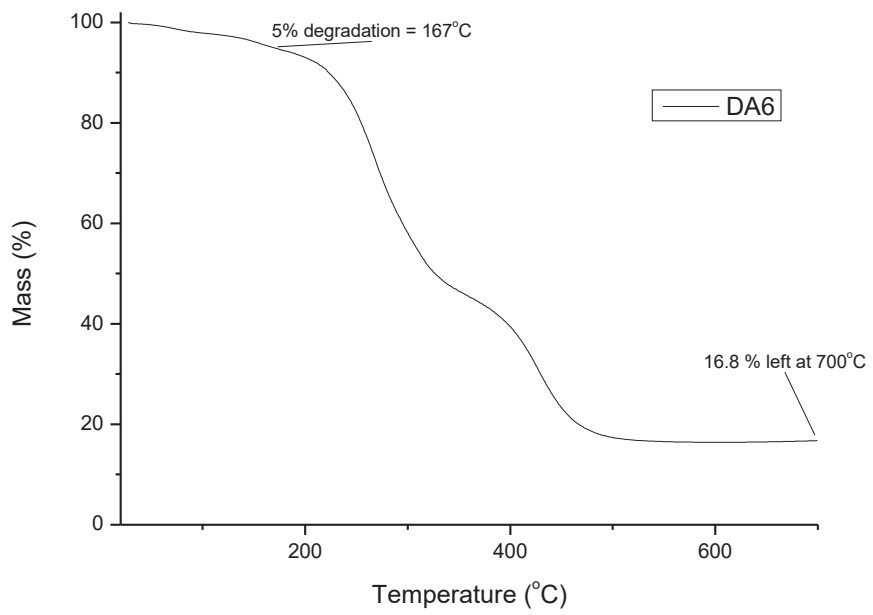
IR analysis



DSC

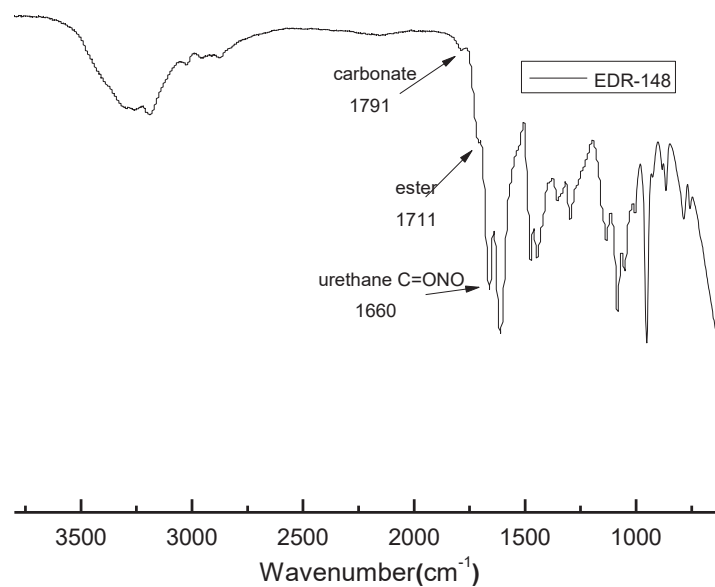


TGA

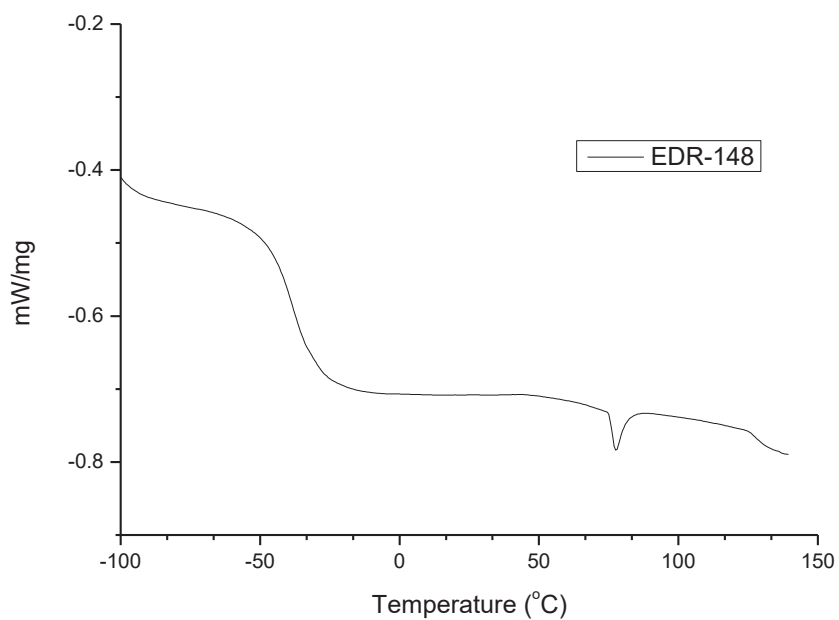


Characterizations of PHUs synthesized from EDR-148.

IR analysis

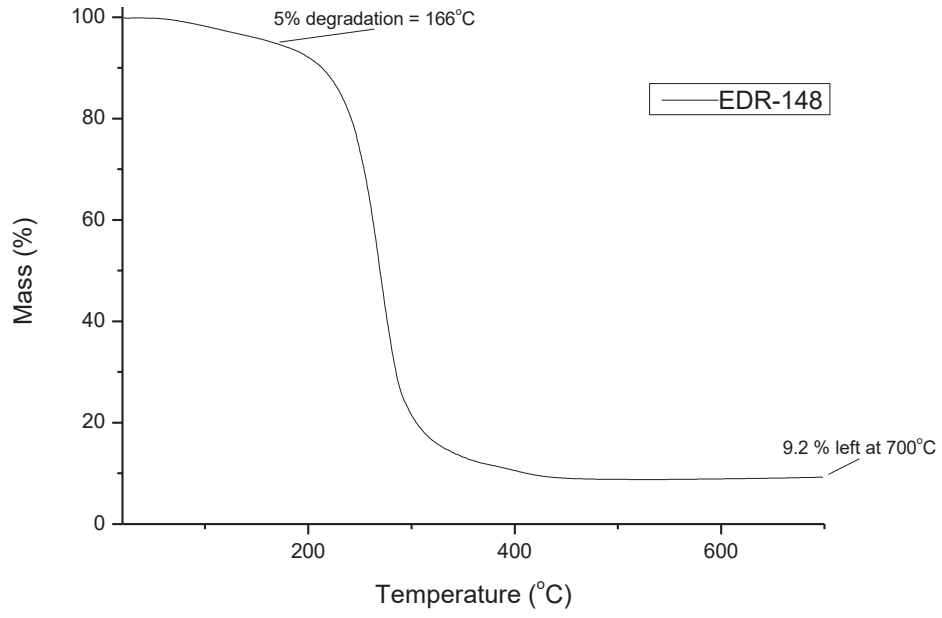


DSC



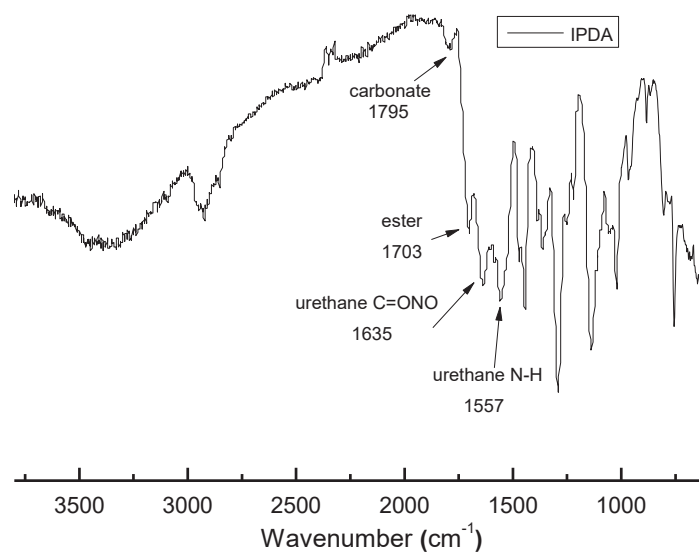
The curve is the second ramp analysis result, and the wave at around 80 °C in the curve is an endothermic peak, but we didn't observe the exothermic phenomenon. Thus, it's possible a machine deviation.

TGA

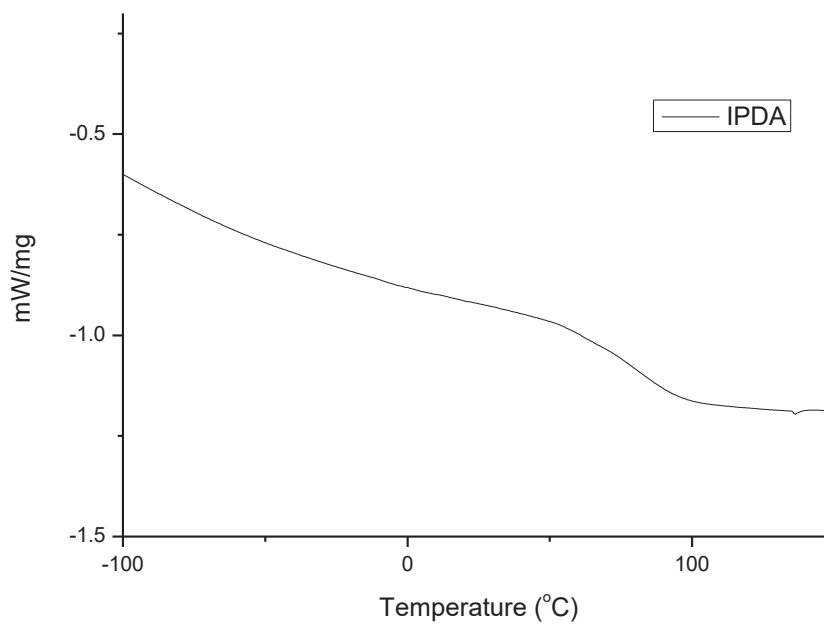


Characterizations of PHUs synthesized from IPDA.

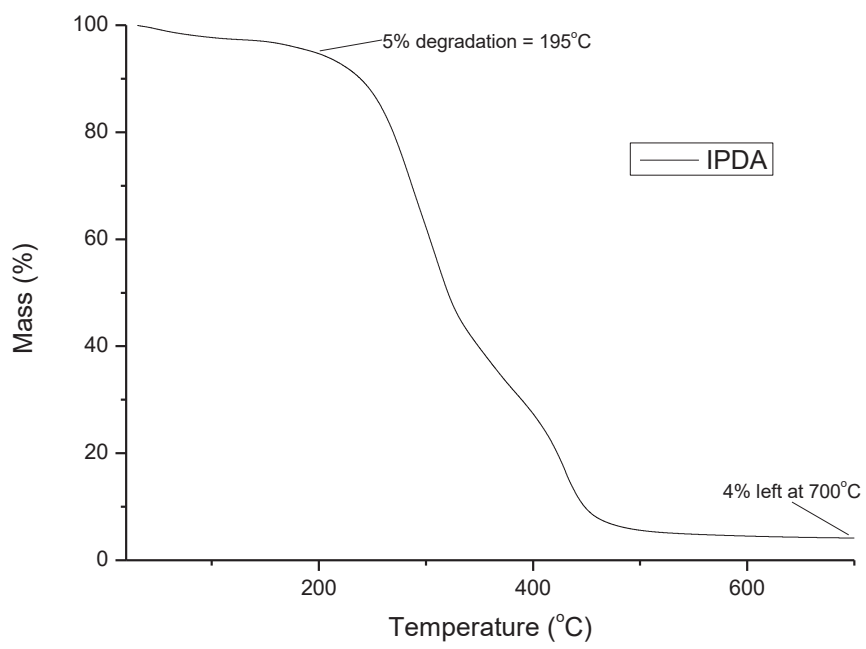
IR analysis



DSC

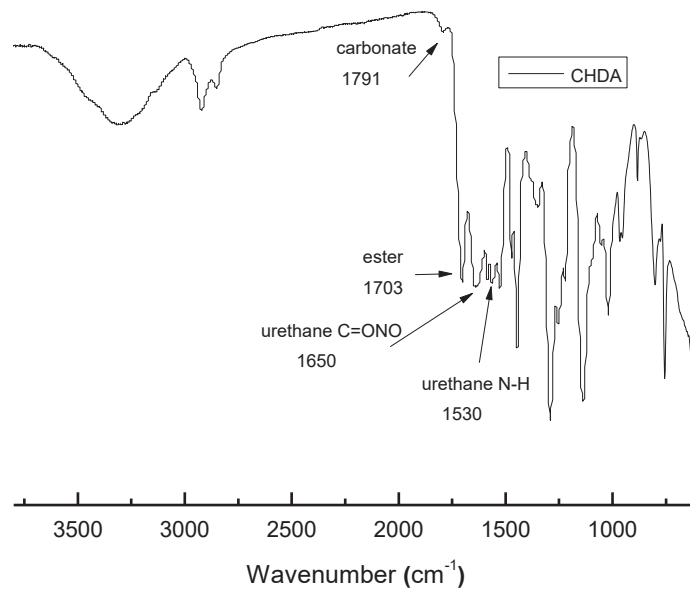


TGA

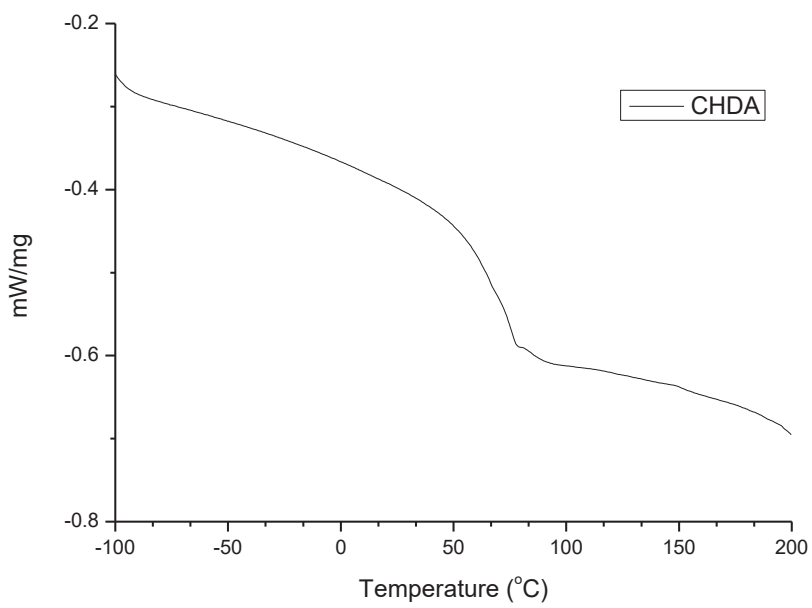


Characterizations of PHUs synthesized from CHDA.

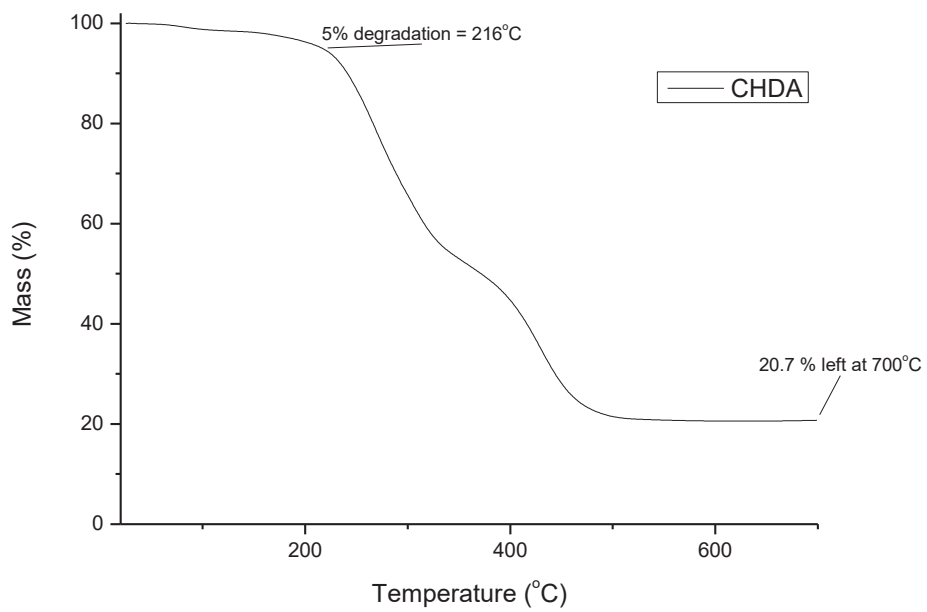
IR analysis



DSC

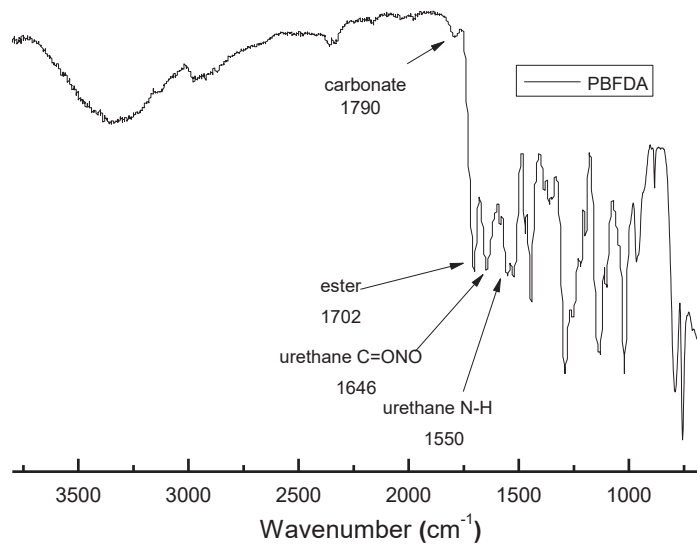


TGA

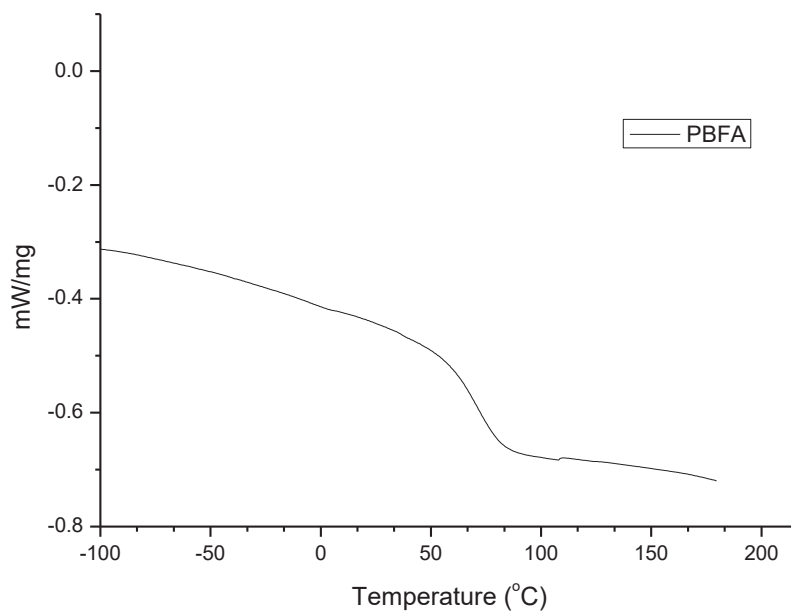


Characterizations of PHUs synthesized from PBFA.

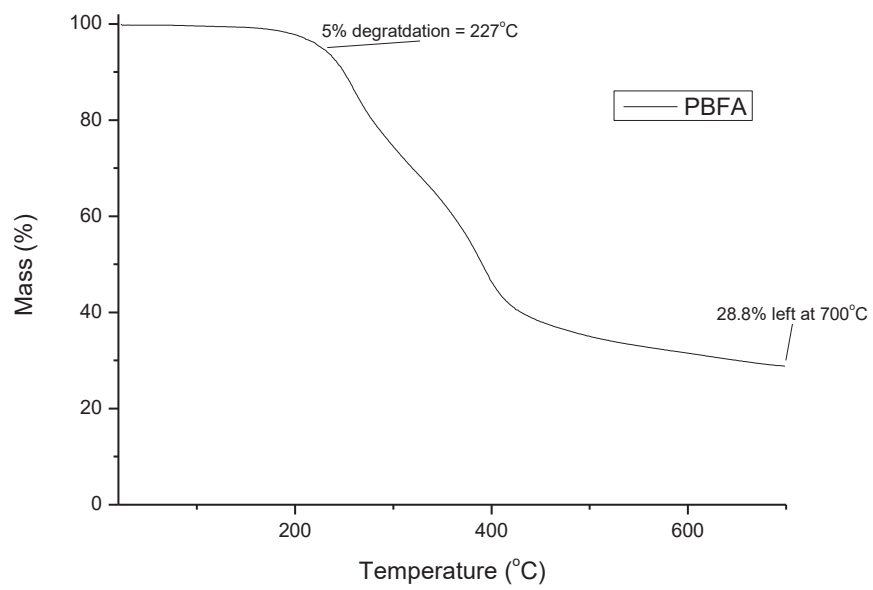
IR analysis



DSC

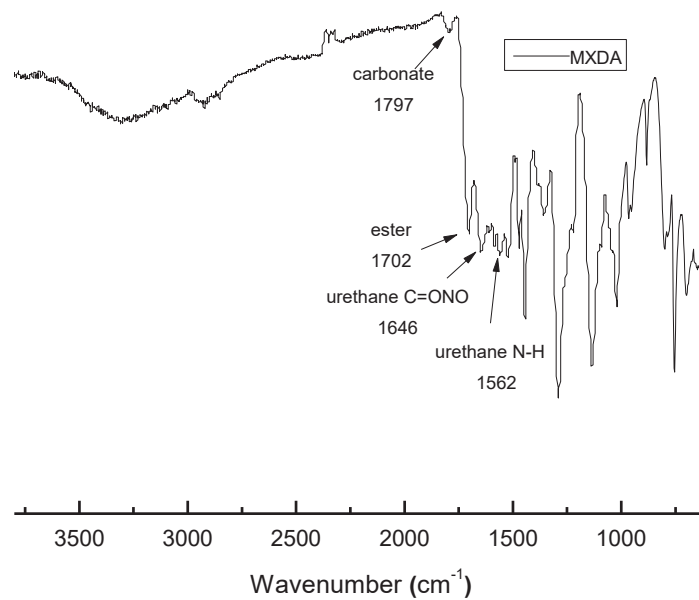


TGA

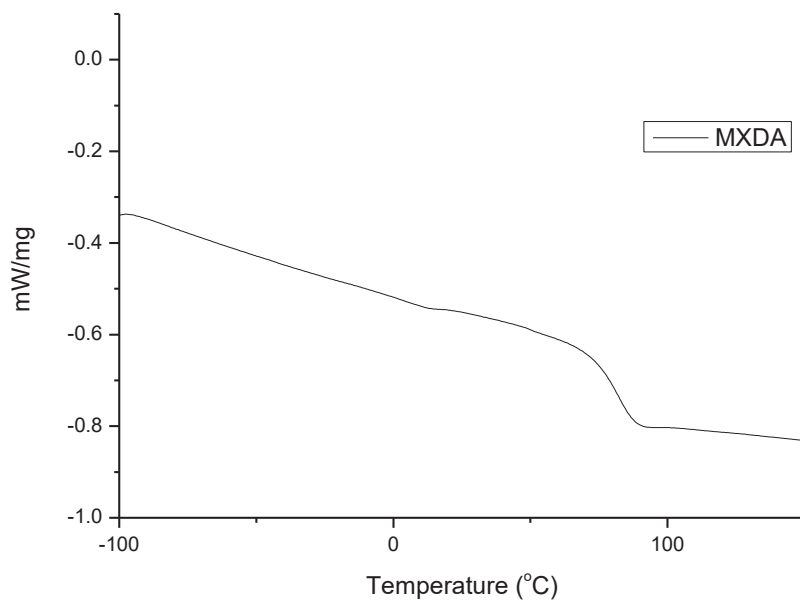


Characterizations of PHUs synthesized from MXDA.

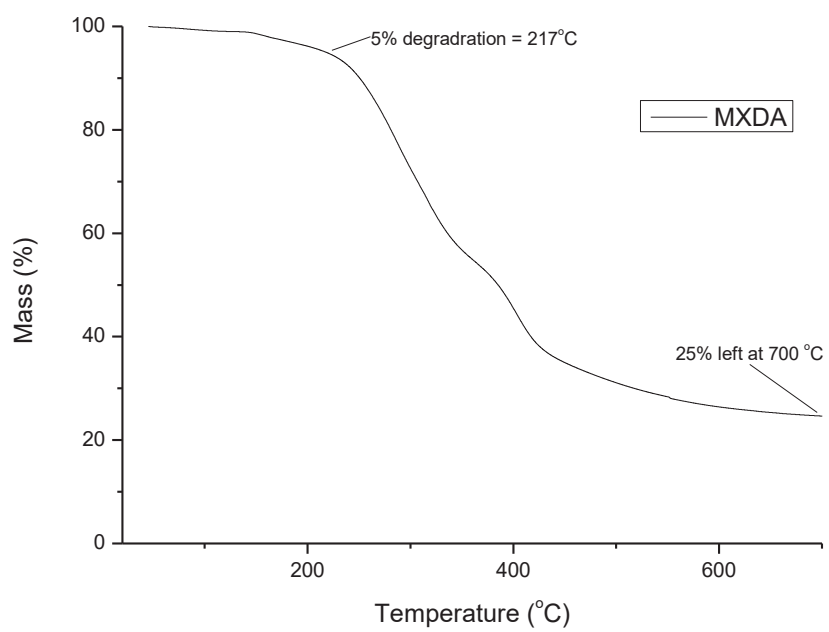
IR analysis



DSC

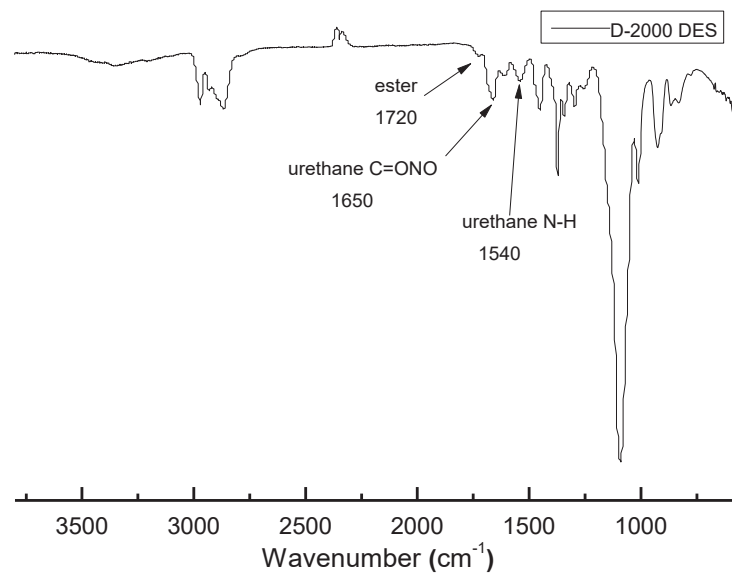


TGA

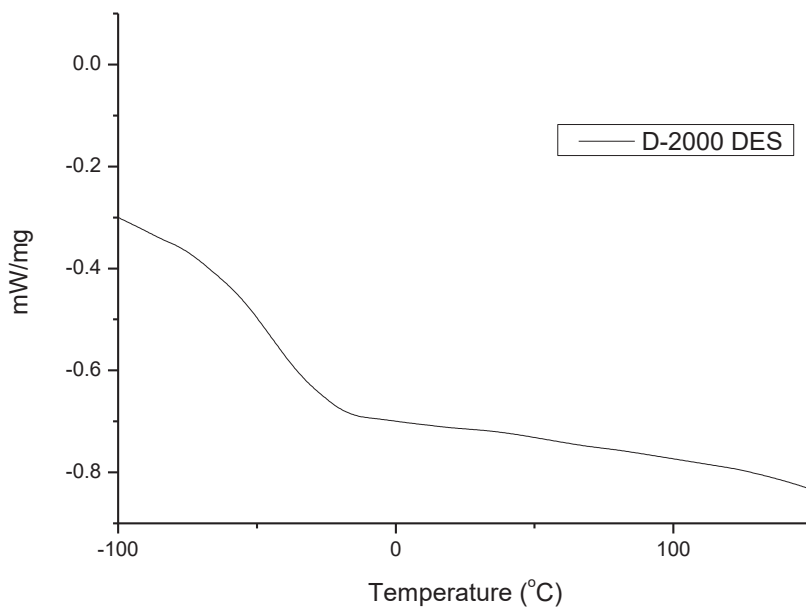


Characterizations of PHUs synthesized from Jeffamine D-2000 in DES.

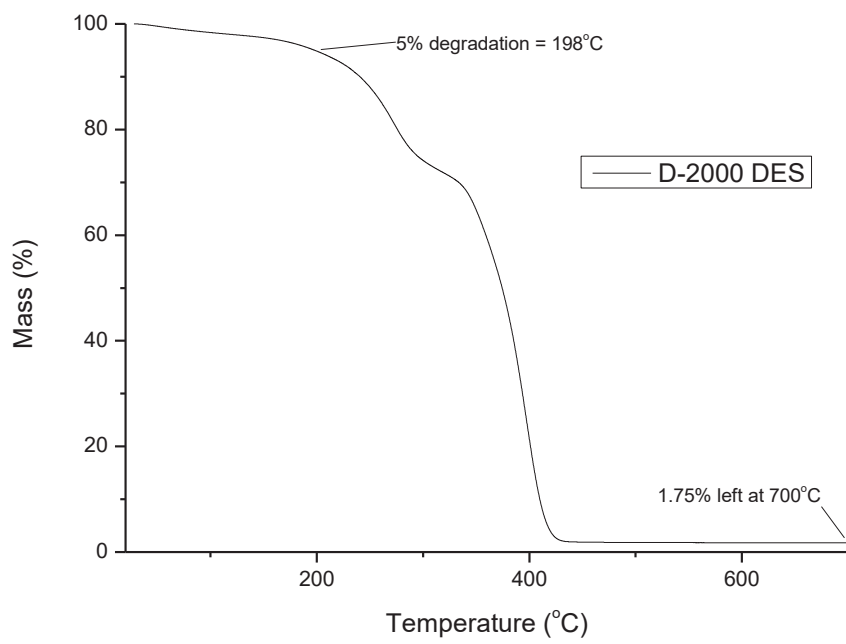
IR analysis



DSC

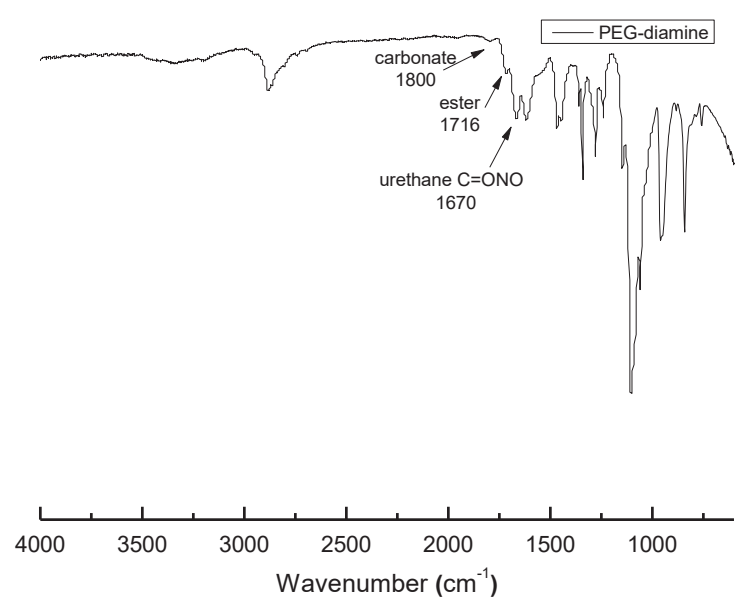


TGA

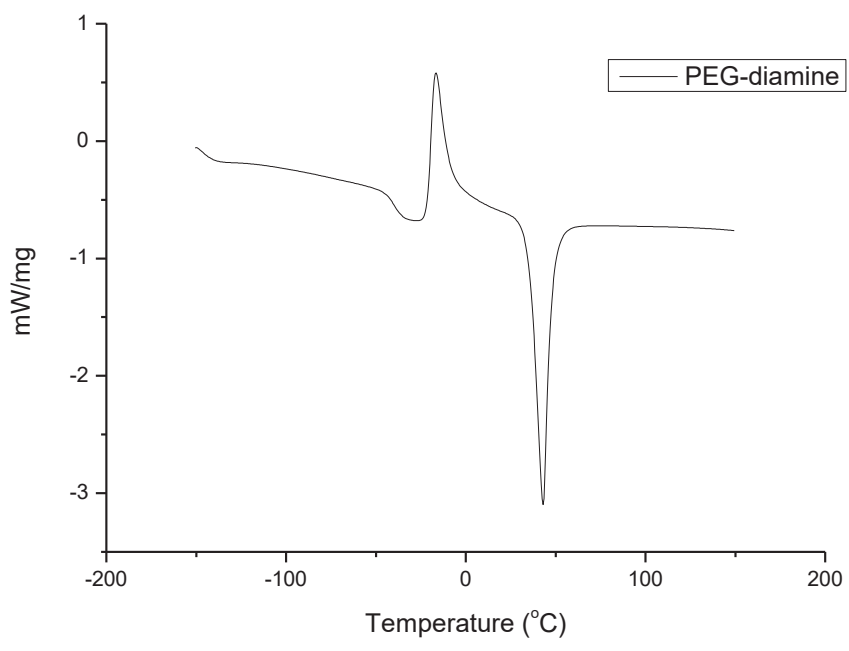


Characterizations of PHUs synthesized from PEG-diamine.

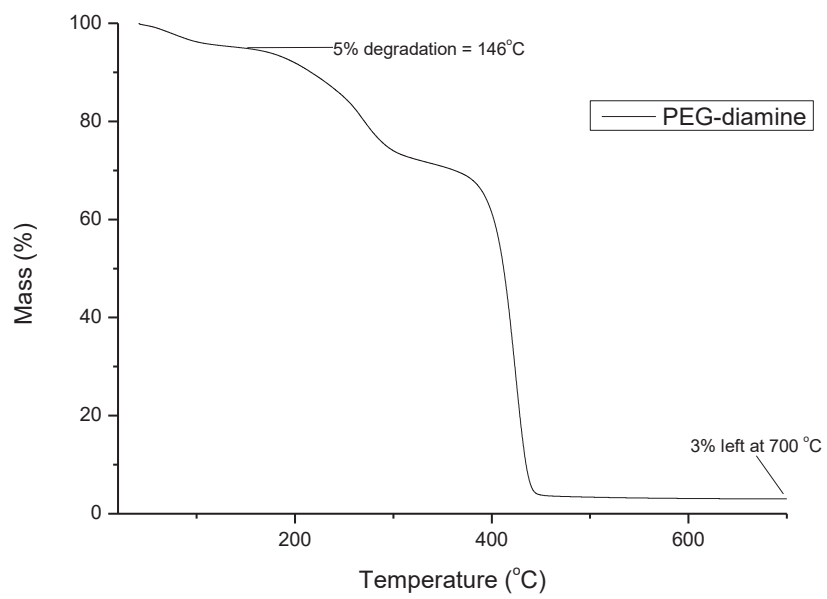
IR analysis



DSC

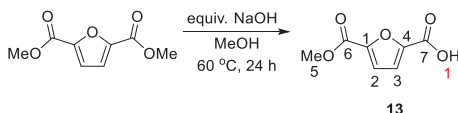


TGA



Chapter 4 Experimental section

Synthesis and characterizations of 5-(methoxycarbonyl)furan-2-carboxylic acid (Me-FDCA) (**13**).



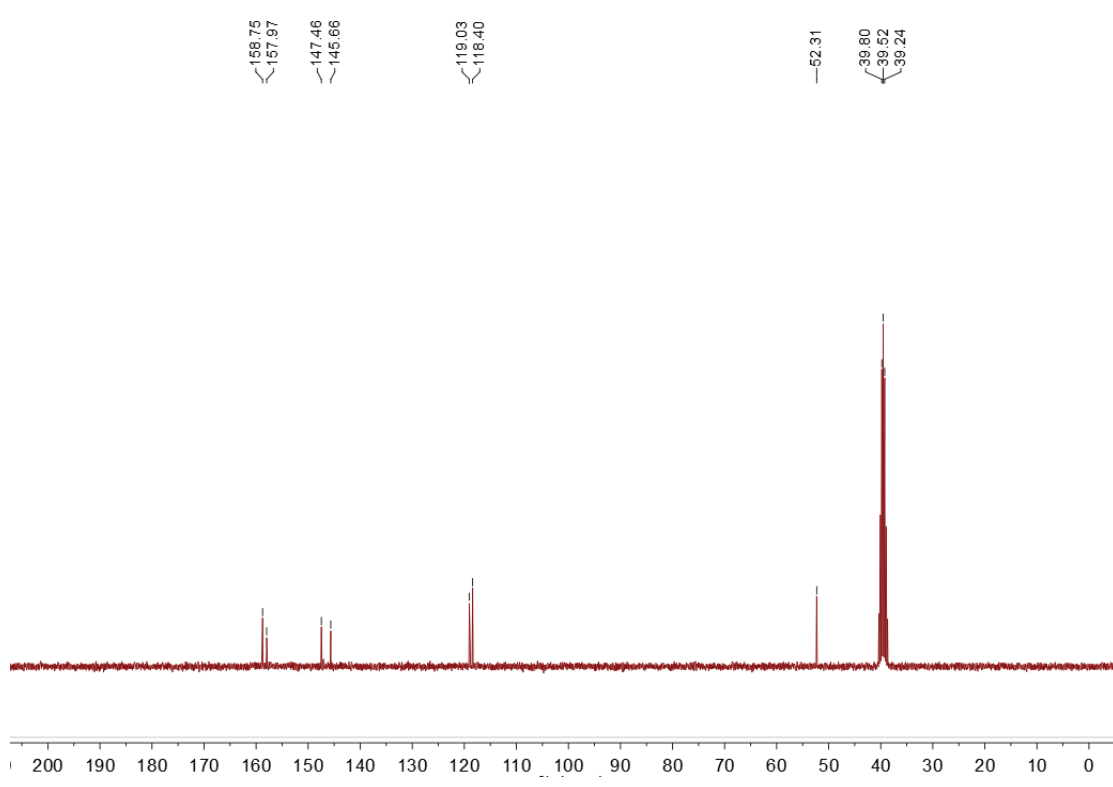
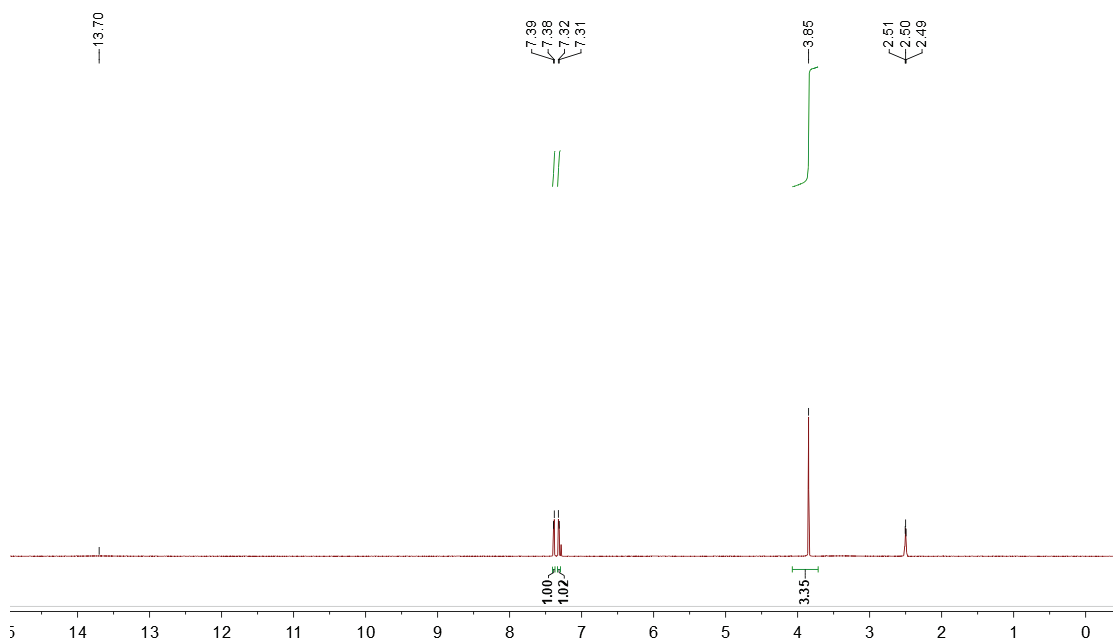
Dimethyl furan-2,5-dicarboxylate (54 mmol, 10 g), anhydrous Na₂SO₄ (5 g), MeOH (120 mL) was added to flask, and then a solution of dry NaOH (54 mmol, 2.16 g) in 30 mL MeOH was dropwise over 6 h. the mixture was stirred at 60°C for 24 h. After concentration, the residue was dissolved in water, and DCM (20 mL x 3) first was used to extract no participating starting material, and then acidified to pH ~ 2 with 12 M HCl. EA/Cyclohexane (6:4, v/v) (30 mL x 5) was used to extract the target product to afford 5-(methoxycarbonyl) furan-2-carboxylic acid (Me-FDCA) in 90% yield (8.3 g) as a off-white solid.

¹H NMR (300 MHz, DMSO) δ 13.70 (s, 1H; O-H₁), 7.39 (d, *J* = 3.7 Hz, 1H; H₃), 7.32 (d, *J* = 3.6 Hz, 1H; H₂), 3.85 (s, 3H; H₅).

¹³C NMR (75 MHz, DMSO) δ 158.8 (s; C₇), 158.0 (s; C₆), 147.5 (s; C₄), 145.7 (s; C₁), 119.0 (s; C₃), 118.4 (s; C₂), 52.3 (s; C₅).

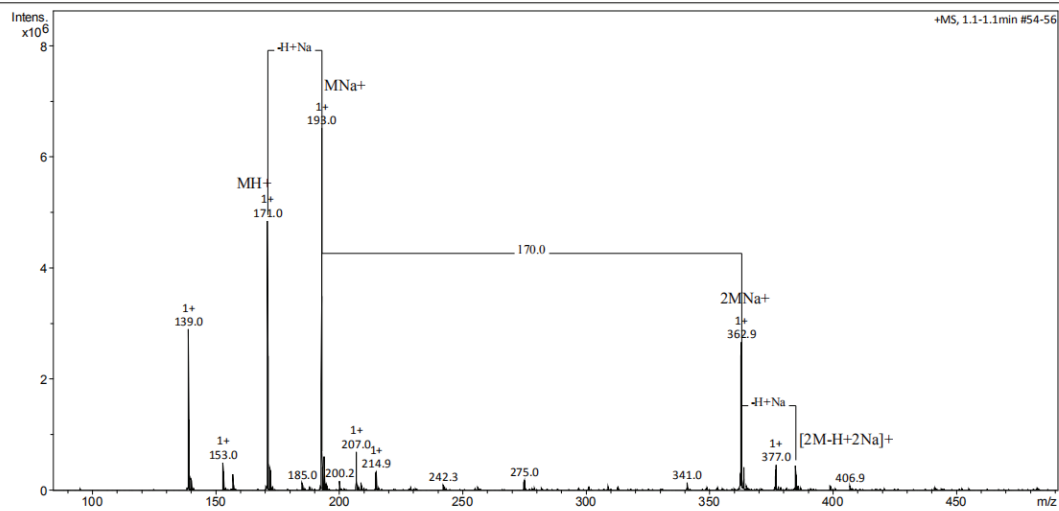
These results are in agreement with the literature. ^[224]

MS: [M+H]⁺ 171.0, [M+Na]⁺ 193.0.

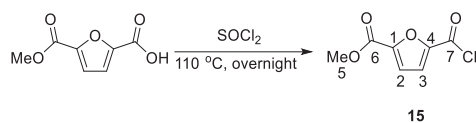


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	439 μ s	RF Level	55 %	Trap Drive	46.3
SPS Target Mass	300 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of 5-(chlorocarbonyl)furan-2-carboxylate (Me-FDCA-Cl) (15).



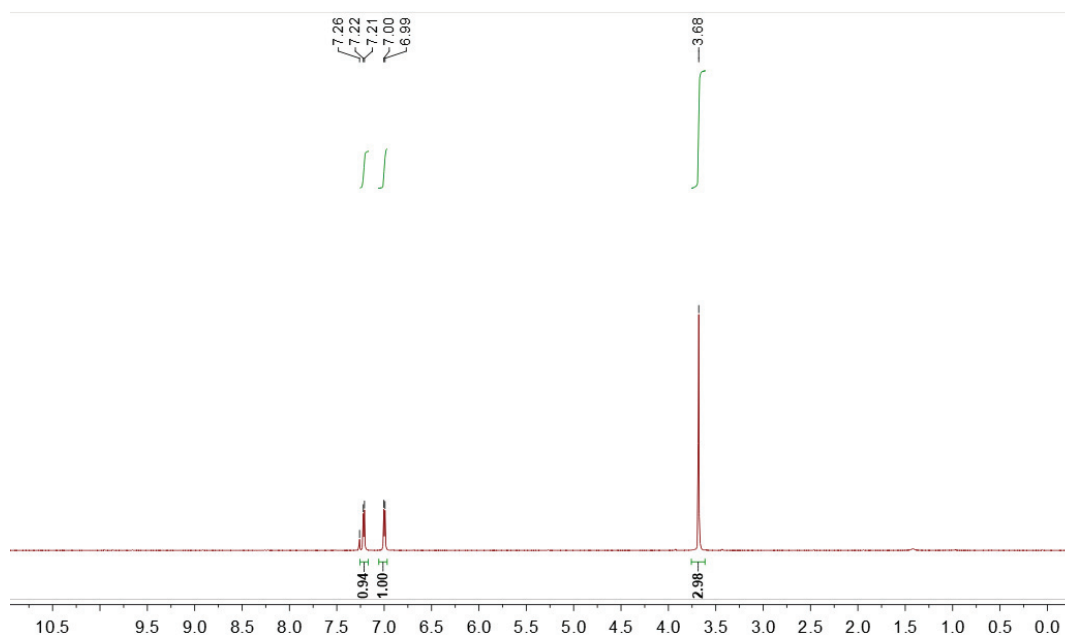
5-(methoxycarbonyl) furan-2-carboxylic acid (Me-FDCA, 40 mmol, 6.8 g) was refluxed with 48 mL thionyl chloride at 110°C overnight. The excess thionyl chloride was removed in vacuum to give methyl 5-(chlorocarbonyl) furan-2-carboxylate (Me-FDCA-Cl) in 100% yield (7.5 g) as a pale-yellow solid.

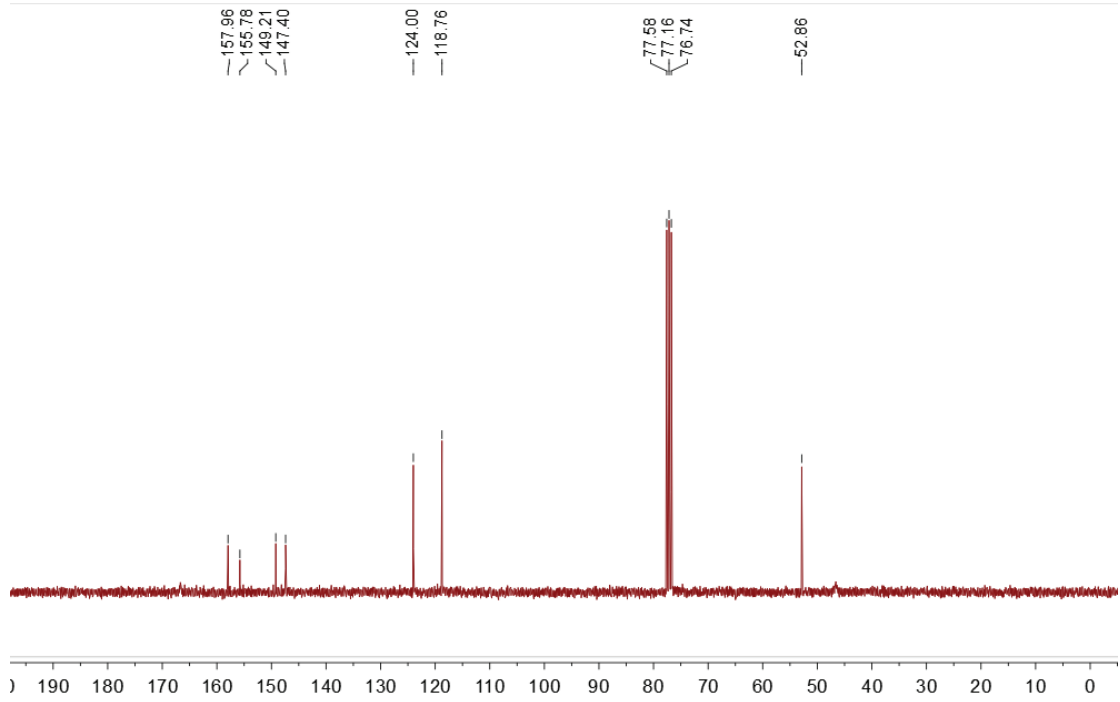
^1H NMR (300 MHz, CDCl_3) δ 7.21 (d, $J = 3.7$ Hz, 1H; H₃), 7.00 (d, $J = 3.8$ Hz, 1H; H₂), 3.68 (s, 3H; H₅).

^{13}C NMR (75 MHz, CDCl_3) δ 158.0 (s; C₆), 156.8 (s; C₇), 149.2 (s; C₄), 147.4 (s; C₁), 124.0 (s; C₃), 118.8 (s; C₂), 52.9 (s; C₅).

These results are in agreement with the literature. ^[224]

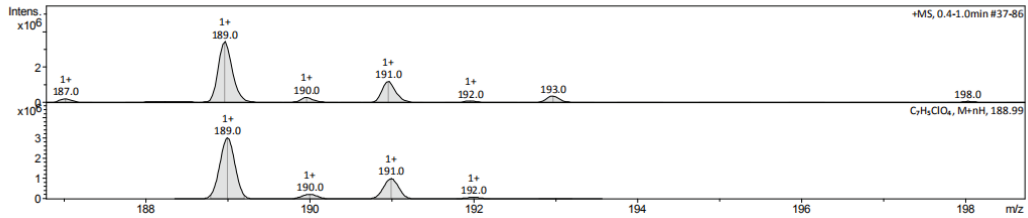
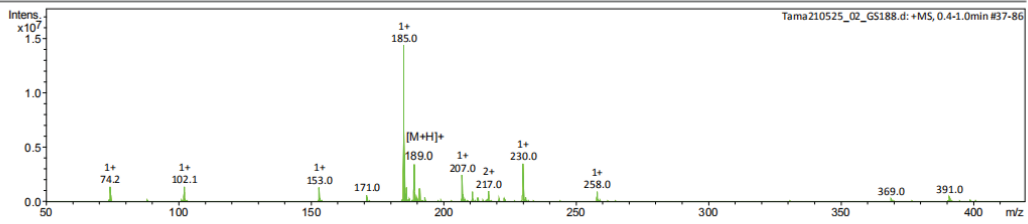
MS: $[\text{M}+\text{H}]^+$ 189.0.



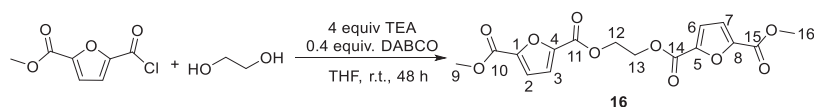


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	300 μ s	RF Level	32 %	Trap Drive	38.0
SPS Target Mass	100 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(ethylene glyceryl) furan-2-carboxylate (Me-EG-FDCA) (**16**).

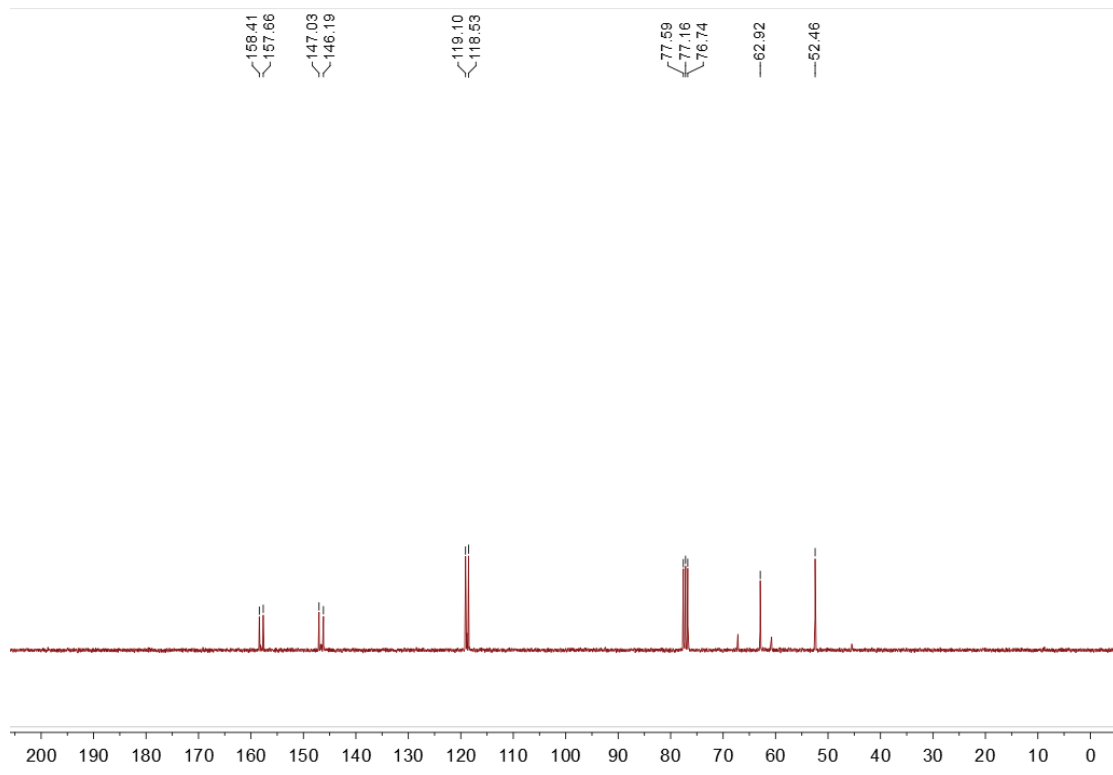
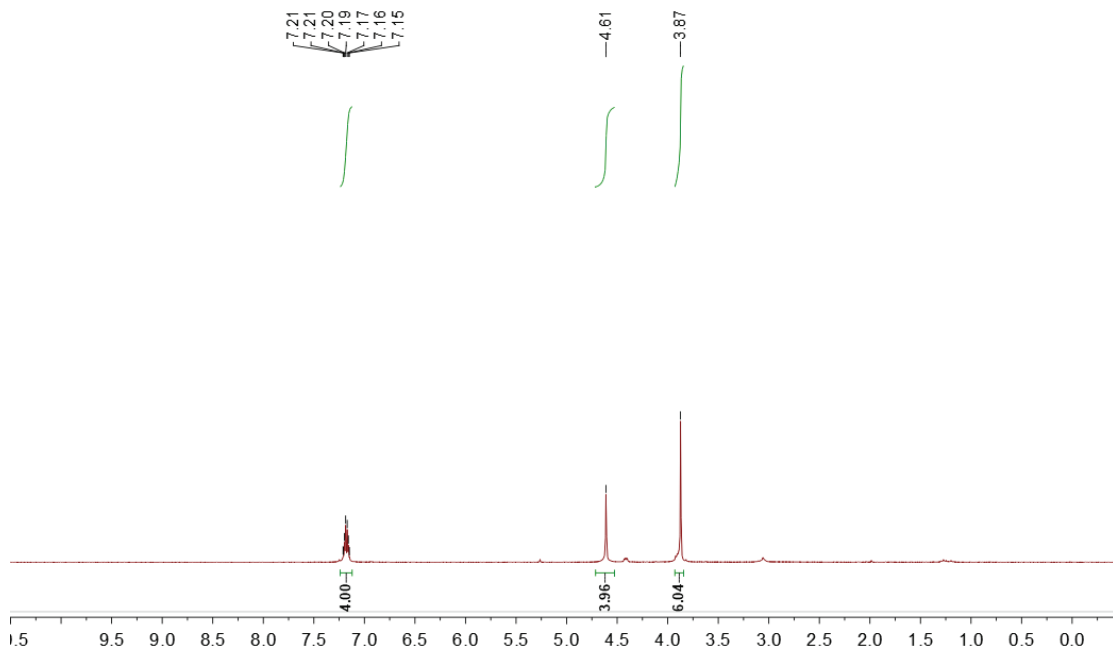


Ethylene glycerol (20 mmol, 1.24 g), triethylamine (TEA, 80 mmol, 8.08 g) and triethylenediamine (DABCO, 8 mmol, 896 mg) were introduced into the flask containing 180 mL THF. A mixture of Me-FDCA-Cl (40 mmol, 7.52 g) and 120 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 48 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (15 mL x 3) and the EA/cyclohexane (3:7, v/v) (10 mL x 3) were used to wash the solid to afford methyl 5-(ethylene glyceryl) furan-2-carboxylate (Me-EG-FDCA) in 86% yield (6.3 g) as a white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.24 – 7.12 (m, 4H; H₂₋₃, H₆₋₇), 4.61 (s, 4H; H₁₂₋₁₃), 3.87 (s, 6H; H₉, H₁₆).

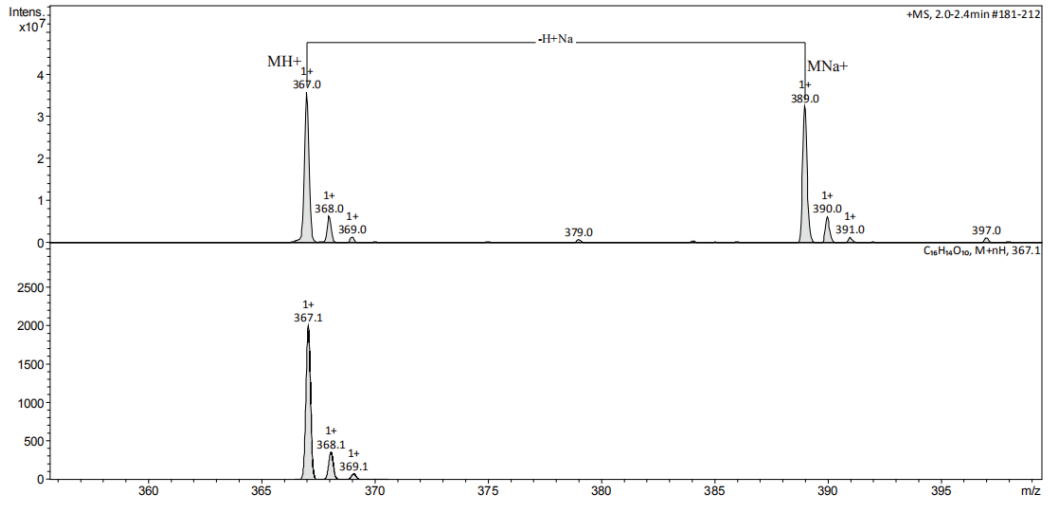
¹³C NMR (75 MHz, CDCl₃) δ 158.4 (s; C₁₀, C₁₅), 157.7 (s; C₁₁, C₁₄), 147.0 (s; C₁, C₈), 146.2 (s; C₄, C₅), 119.1 (s; C₂, C₇), 118.5 (s; C₃, C₆), 62.9 (s; C₁₂, C₁₃), 52.5 (s; C₉, C₁₆).

MS: [M+H]⁺ 367.0, [M+Na]⁺ 389.0.

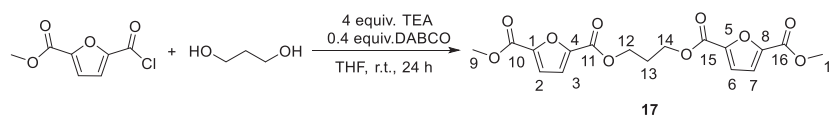


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	404 μ s	RF Level	55 %	Trap Drive	46.3
SPS Target Mass	300 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(propylene glycol) furan-2-carboxylate (Me-PrG-FDCA) (**17**).

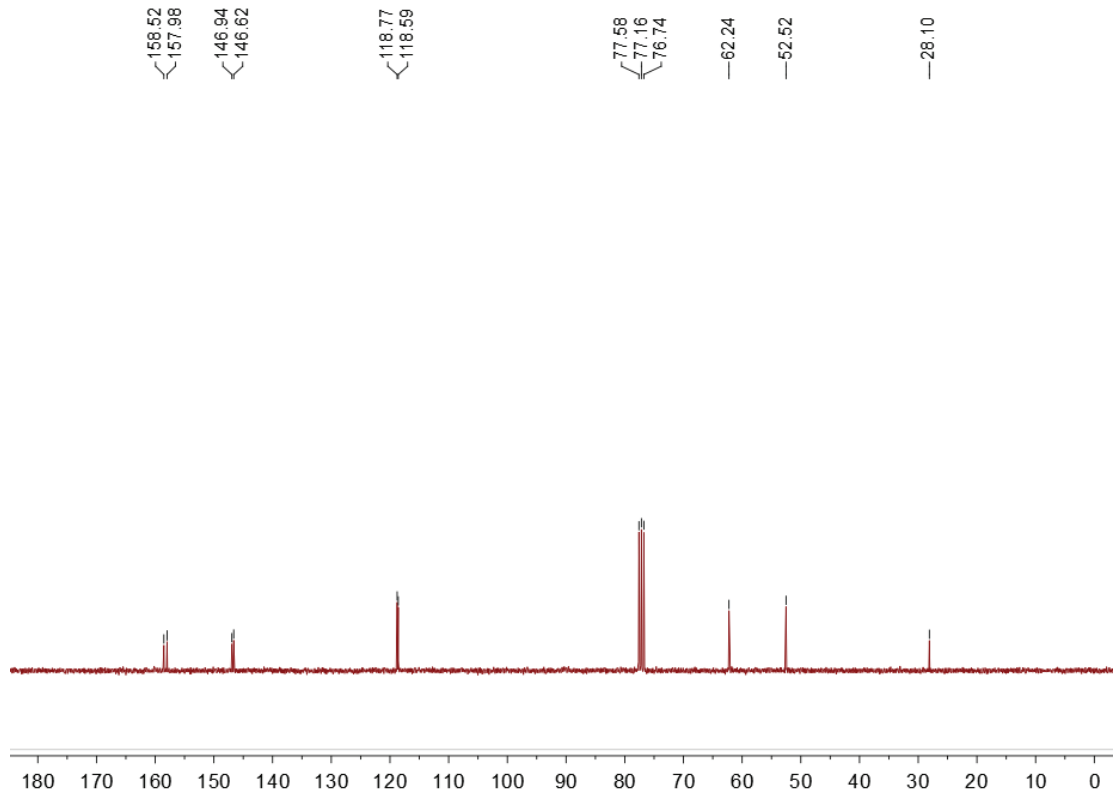
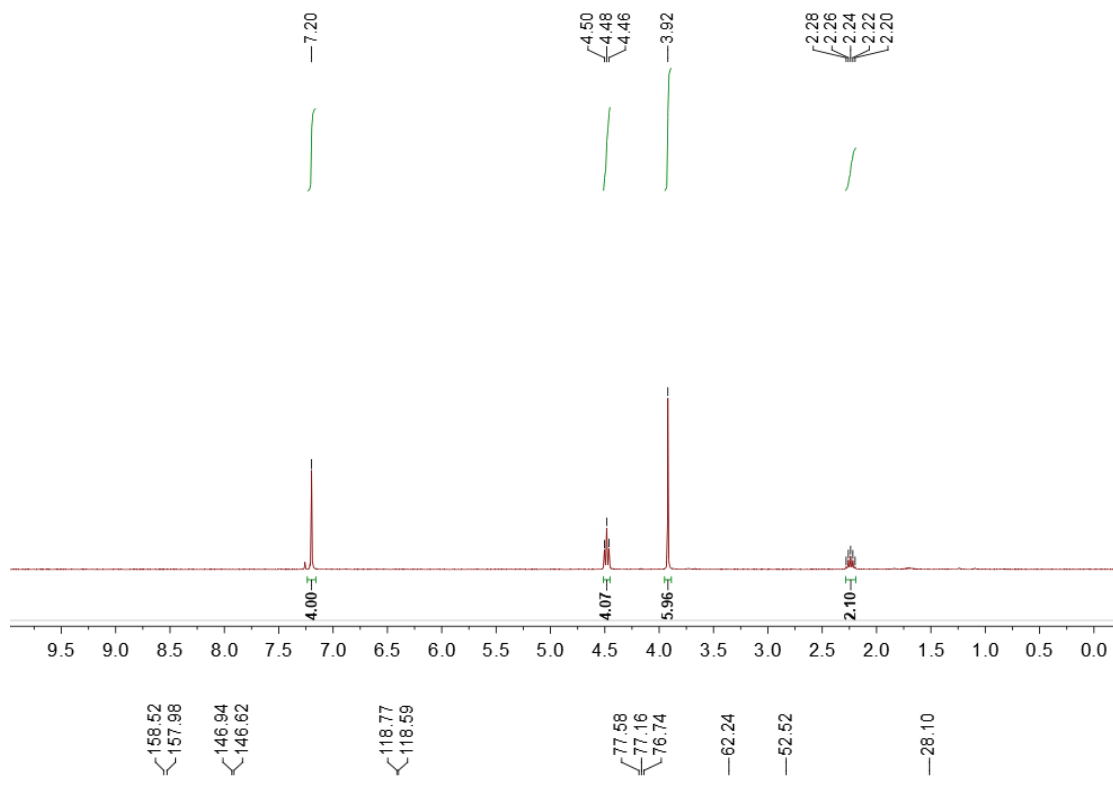


Propylene glycol (5 mmol, 380 mg), triethylamine (TEA, 20 mmol, 2.02 g) and triethylenediamine (DABCO, 2 mmol, 225 mg) were introduced into the flask containing 50 mL THF. A mixture of Me-FDCA-Cl (10 mmol, 1.88 g) and 20 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford methyl 5-(propylene glycol) furan-2-carboxylate (Me-PrG-FDCA) in 98% yield (1.9 g) as a pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.20 (s, 4H; H₂₋₃, H₆₋₇), 4.48 (t, *J* = 6.2 Hz, 4H; H₁₂, H₁₄), 3.92 (s, 6H; H₉, H₁₇), 2.24 (p, *J* = 6.2 Hz, 2H; H₁₃).

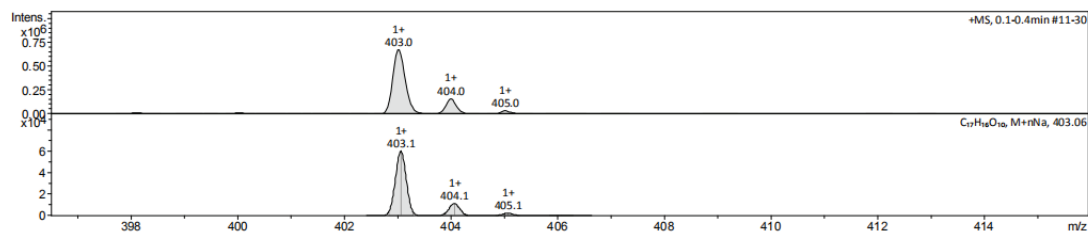
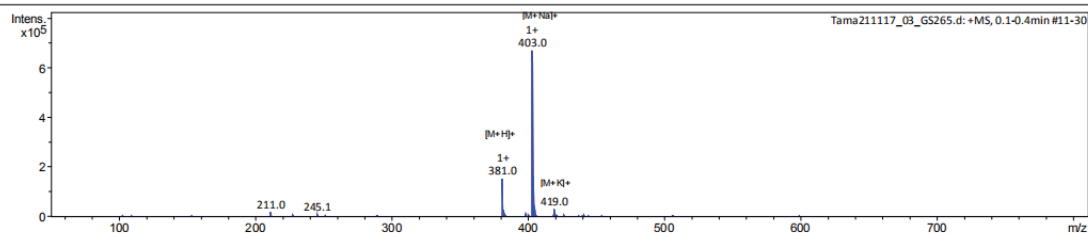
¹³C NMR (75 MHz, CDCl₃) δ 158.5 (s; C₁₀, C₁₆), 158.0 (s; C₁₁, C₁₅), 146.9 (s; C₁, C₈), 146.6 (s; C₄, C₅), 118.8 (s; C₂, C₇), 118.6 (s; C₃, C₆), 62.2 (s; C₁₂, C₁₄), 52.5 (s; C₉, C₁₇), 28.1 (s; C₁₃).

MS: [M+H]⁺ 381.0, [M+Na]⁺ 403.0.

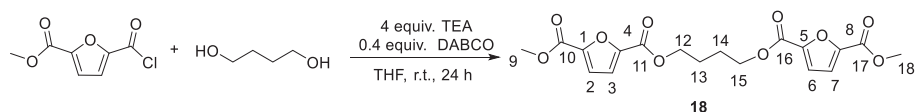


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	4670 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(butylene glycol) furan-2-carboxylate (Me-BG-FDCA) (**18**).

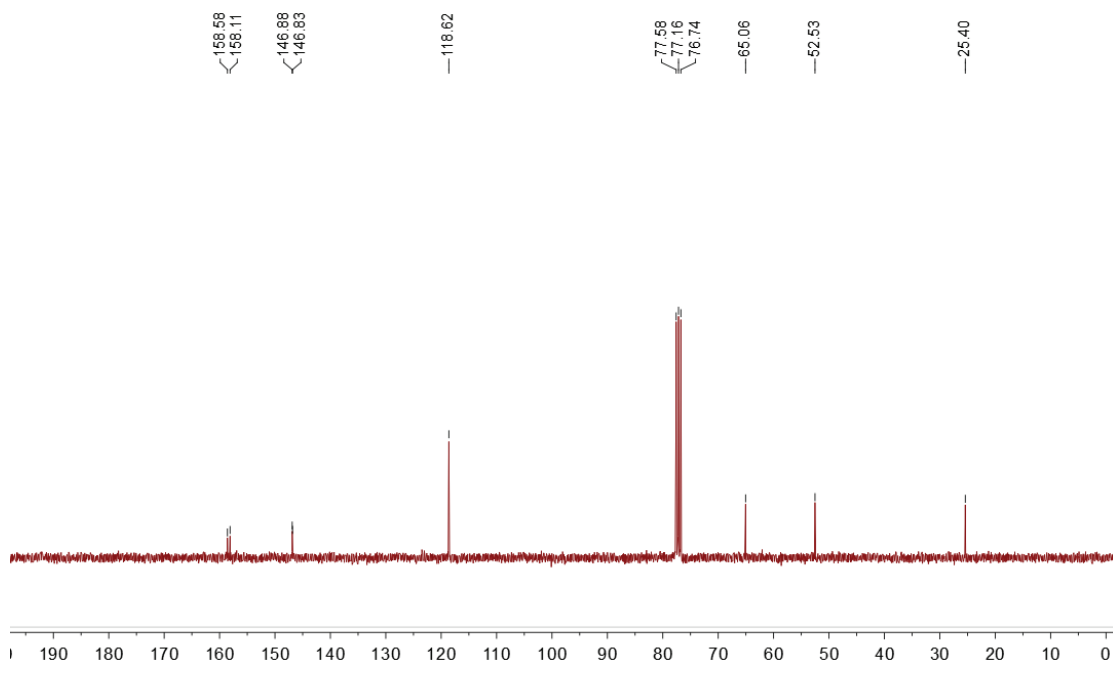
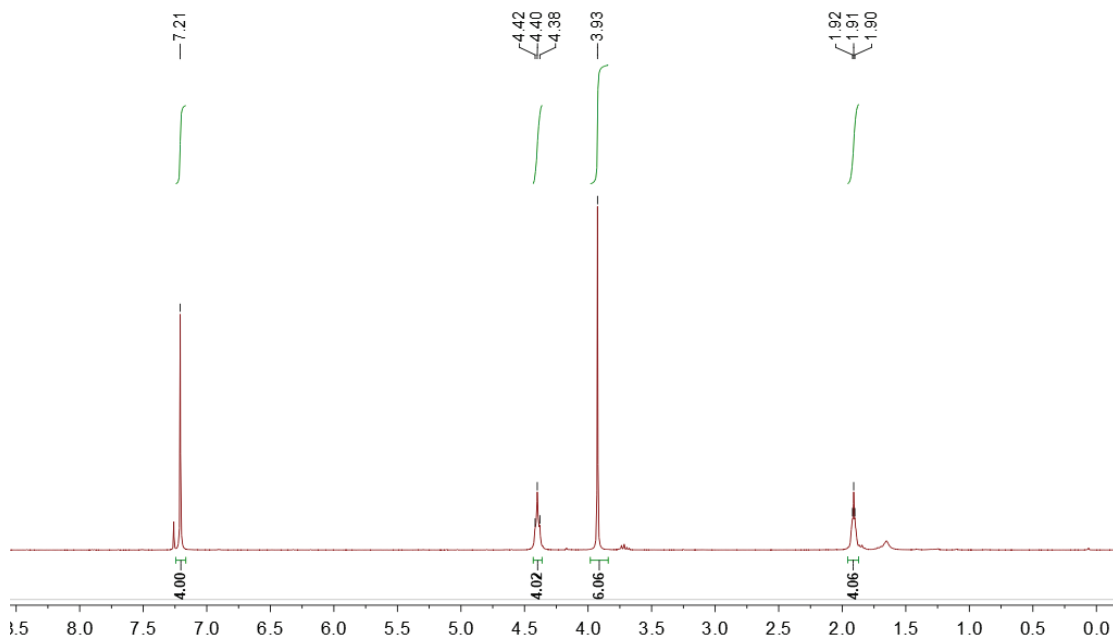


Butylene glycol (2.5 mmol, 225 mg), triethylamine (TEA, 10 mmol, 1.01 g) and triethylenediamine (DABCO, 1 mmol, 113 mg) were introduced into the flask contained 25 mL THF. A mixture of Me-FDCA-Cl (5 mmol, 0.94 g) and 10 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford methyl 5-(butylene glycol) furan-2-carboxylate (Me-BG-FDCA) in 95% yield (0.9 g) as a pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.21 (s, 4H; H₂₋₃, H₆₋₇), 4.40 (t, *J* = 5.6 Hz, 4H; H₁₂, H₁₅), 3.93 (s, 6H, H₉, H₁₈), 1.91 (t, *J* = 2.7 Hz, 4H; H₁₃₋₁₄).

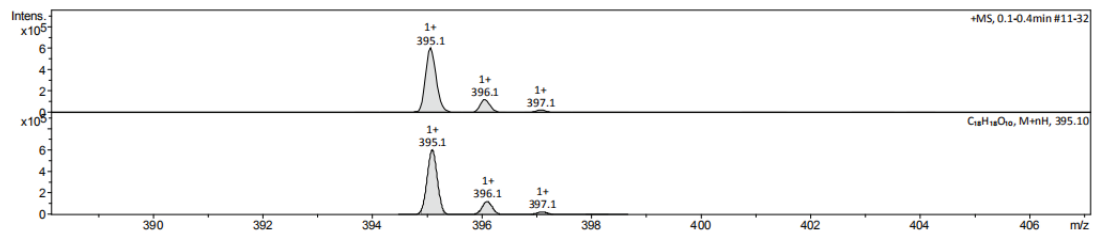
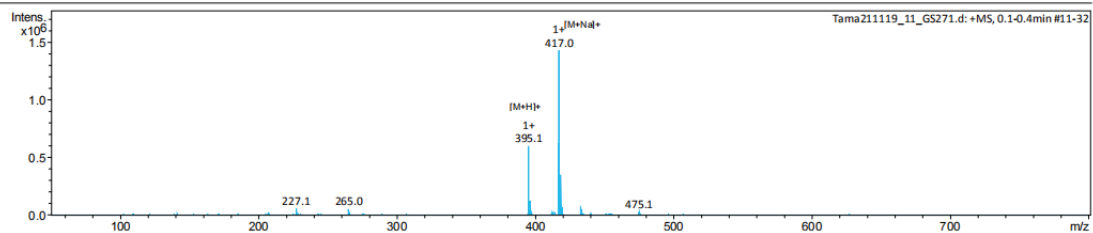
¹³C NMR (75 MHz, CDCl₃) δ 158.6 (s; C₁₀, C₁₇), 158.1 (s; C₁₁, C₁₆), 146.9 (s; C₁, C₈), 146.8 (s; C₄, C₅), 118.6 (s; C₂₋₃, C₆₋₇), 65.1 (s; C₁₂, C₁₅), 52.5 (s; C₉, C₁₈), 25.4 (s; C₁₃, C₁₄).

MS: [M+H]⁺ 395.1, [M+Na]⁺ 417.0.

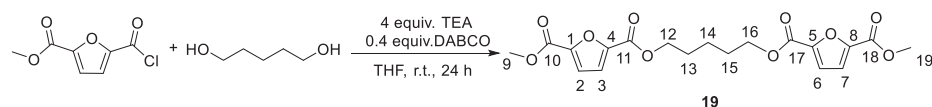


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	1897 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(pentylene glycol) furan-2-carboxylate (Me-PeG-FDCA) (**19**).

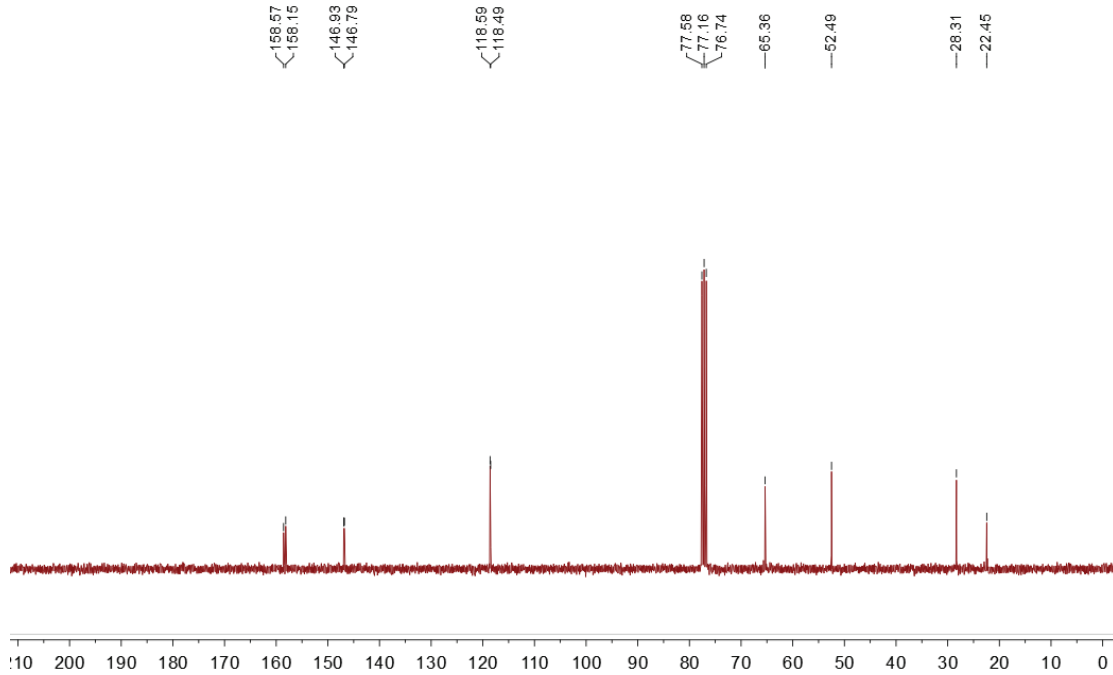
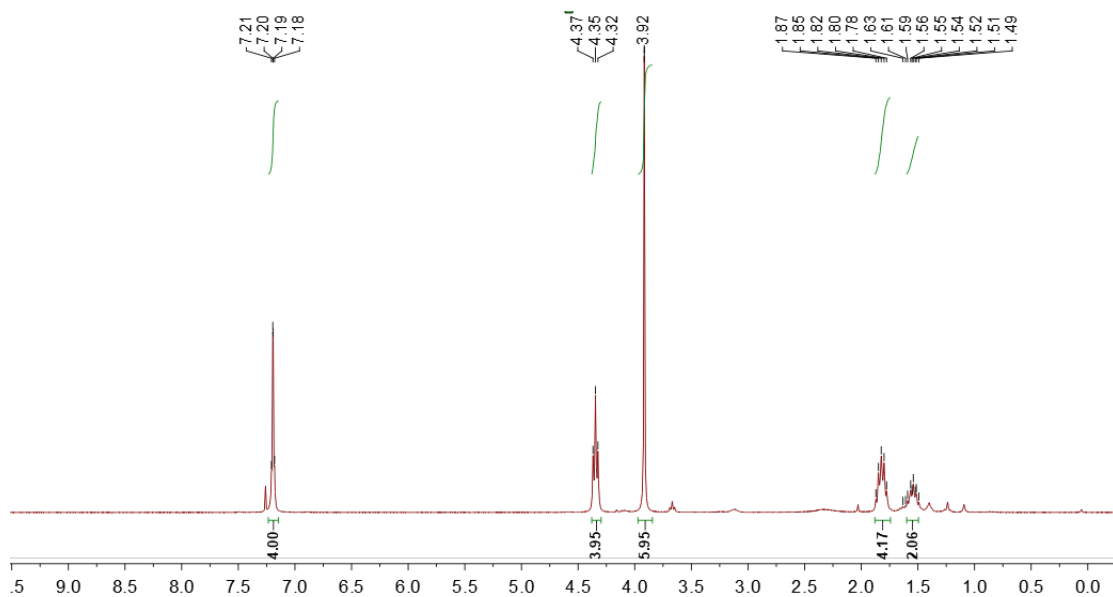


Pentylene glycol (2.5 mmol, 260 mg), triethylamine (TEA, 10 mmol, 1.01 g) and triethylenediamine (DABCO, 1 mmol, 113 mg) were introduced into the flask contained 25 mL THF. A mixture of Me-FDCA-Cl (5 mmol, 0.94 g) and 10 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford powder methyl 5-(pentylene glycol) furan-2-carboxylate (Me-PeG-FDCA) in 96% yield (0.98 g) as a pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.19 (q, *J* = 3.6 Hz, 4H; H₂₋₃, H₆₋₇), 4.35 (t, *J* = 6.5 Hz, 4H; H₁₂, H₁₆), 3.92 (s, 6H; H₉, H₁₉), 1.88 – 1.74 (m, 4H; H₁₃, H₁₅), 1.60 – 1.50 (m, 2H; H₁₄).

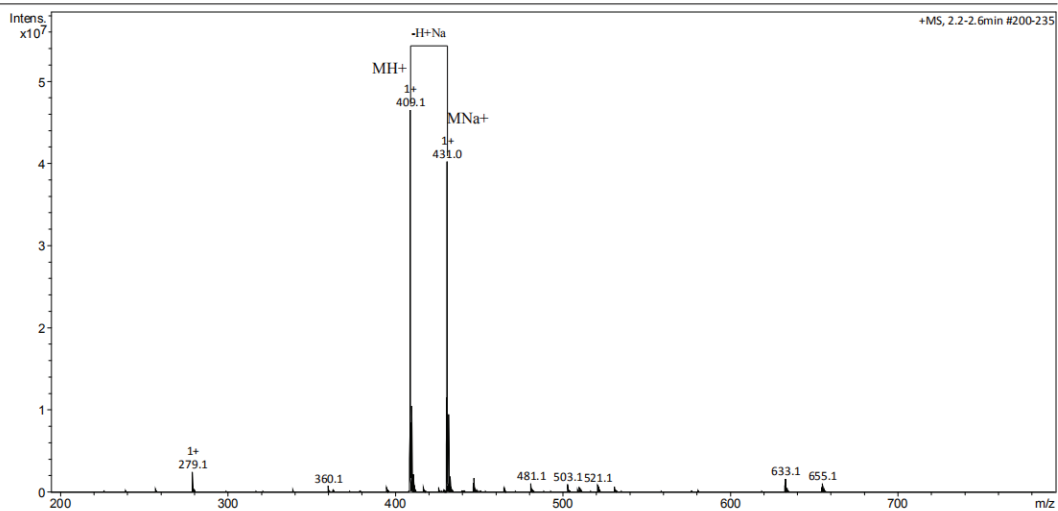
¹³C NMR (75 MHz, CDCl₃) δ 158.6 (s; C₁₀, C₁₈), 158.2 (s; C₁₁, C₁₇), 146.9 (s; C₁, C₈), 146.8 (s; C₄, C₅), 118.6 (s; C₂, C₇), 118.5 (s; C₃, C₆), 65.4 (s; C₁₂, C₁₆), 52.5 (s; C₉, C₁₉), 28.3 (s; C₁₃, C₁₅), 22.4 (s; C₁₄).

MS: [M+H]⁺ 409.1, [M+Na]⁺ 431.0.

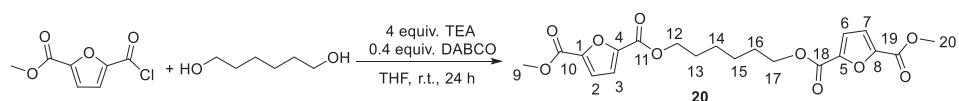


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	77 μ s	RF Level	59 %	Trap Drive	48.4
SPS Target Mass	350 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(hexylene glycol) furan-2-carboxylate (Me-HG-FDCA) (**20**).

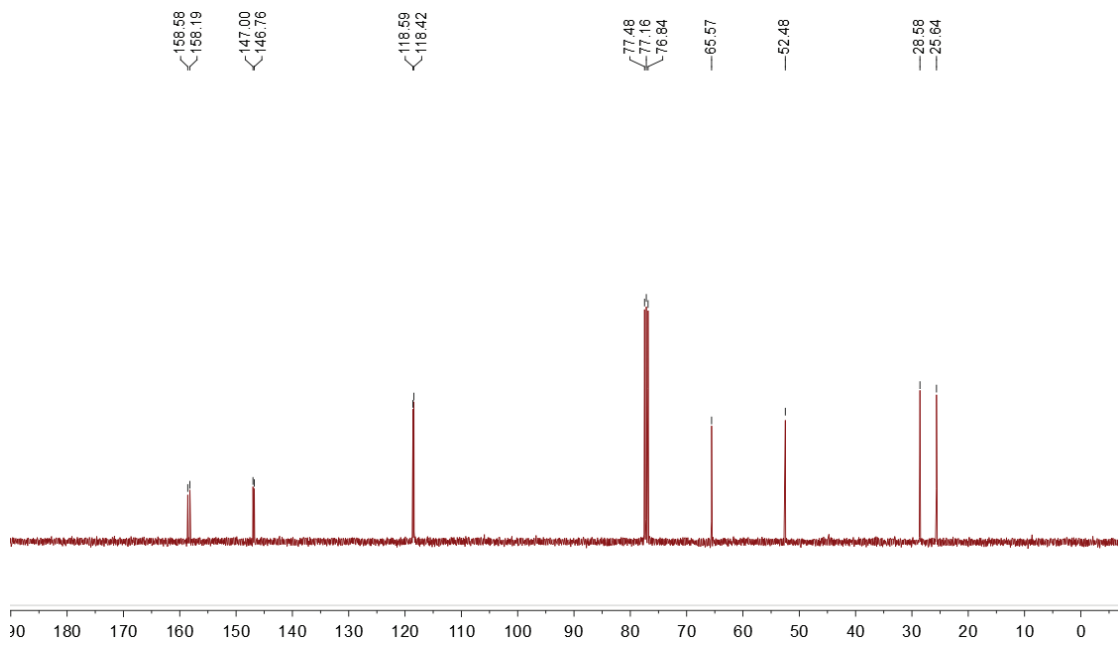
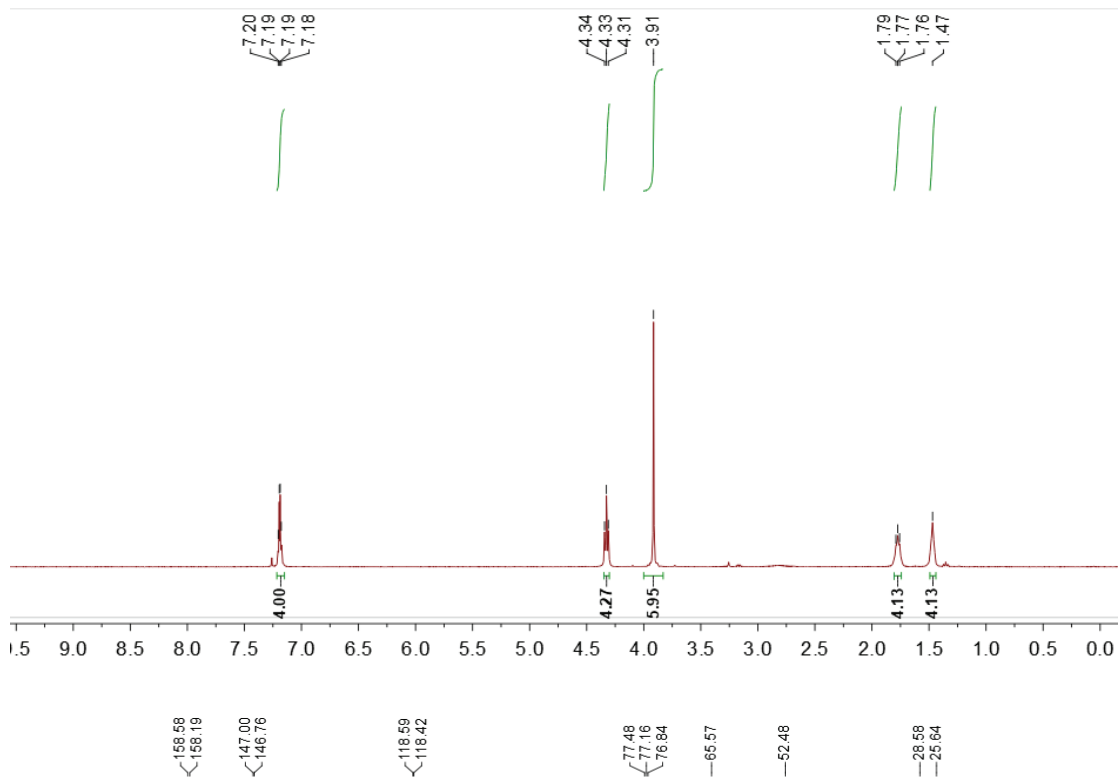


Hexylene glycol (5 mmol, 590 mg), triethylamine (TEA, 20 mmol, 2.02 g) and triethylenediamine (DABCO, 2 mmol, 225 mg) were introduced into the flask contained 50 mL THF. A mixture of Me-FDCA-Cl (10 mmol, 1.88 g) and 20 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford methyl 5-(hexylene glycol) furan-2-carboxylate (Me-HG-FDCA) in 95% yield (2 g) as a pure white powder.

¹H NMR (400 MHz, CDCl₃) δ 7.19 (dd, *J* = 6.9, 3.7 Hz, 4H; H₂₋₃, H₆₋₇), 4.33 (t, *J* = 6.7 Hz, 4H; H₁₂, H₁₇), 3.91 (s, 6H; H₉, H₂₀), 1.81 – 1.74 (m, 4H; H₁₃, H₁₆), 1.47 (s, 4H; H₁₄, H₁₅).

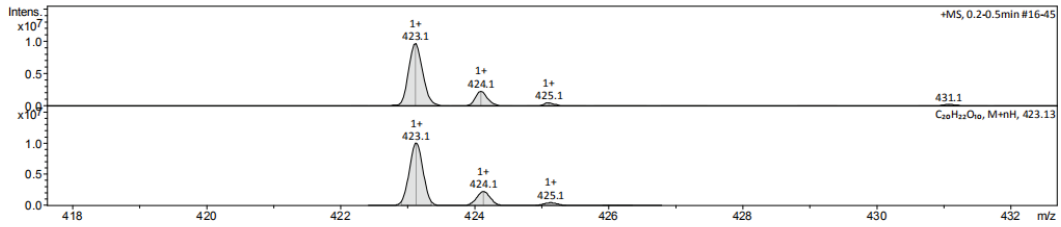
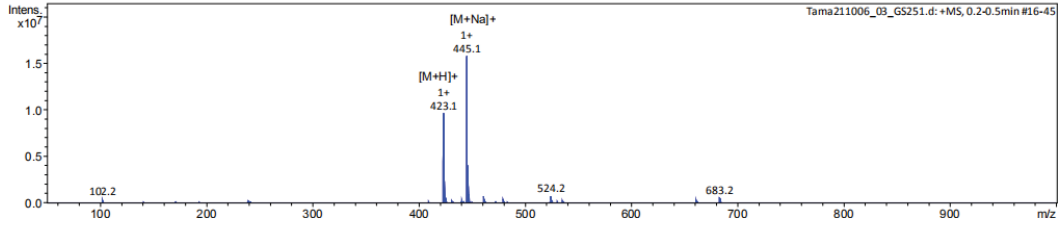
¹³C NMR (101 MHz, CDCl₃) δ 158.6 (s; C₁₀, C₁₉), 158.2 (s; C₁₁, C₁₈), 147.0 (s; C₁, C₈), 146.8 (s; C₄, C₅), 118.6 (s; C₂, C₇), 118.4 (s; C₃, C₆), 65.6 (s; C₁₂, C₁₇), 52.5 (s; C₉, C₂₀), 28.6 (s; C₁₃, C₁₆), 25.6 (s; C₁₄, C₁₅).

MS: [M+H]⁺ 423.1, [M+Na]⁺ 445.1.

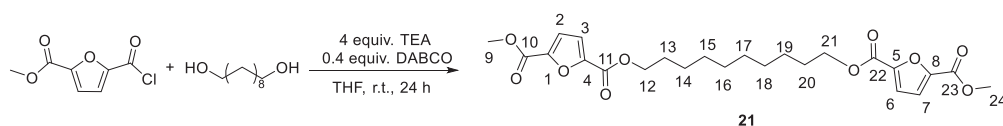


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	188 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-(decene glycol) furan-2-carboxylate (Me-DG-FDCA) (**21**).

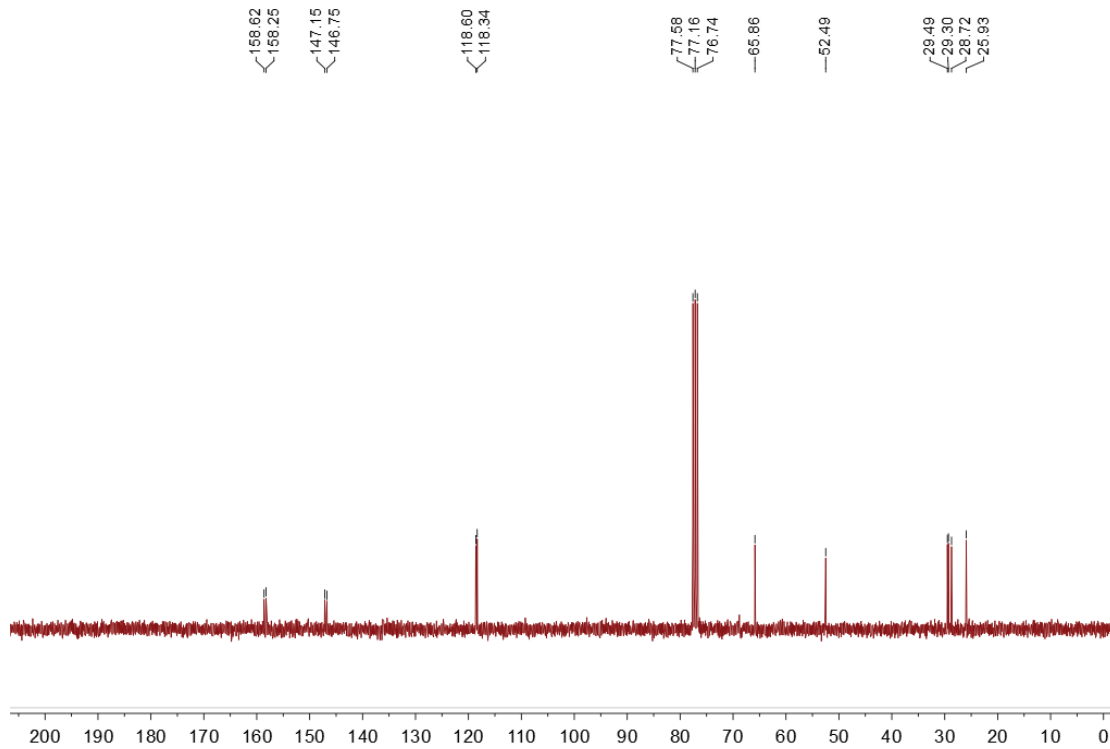
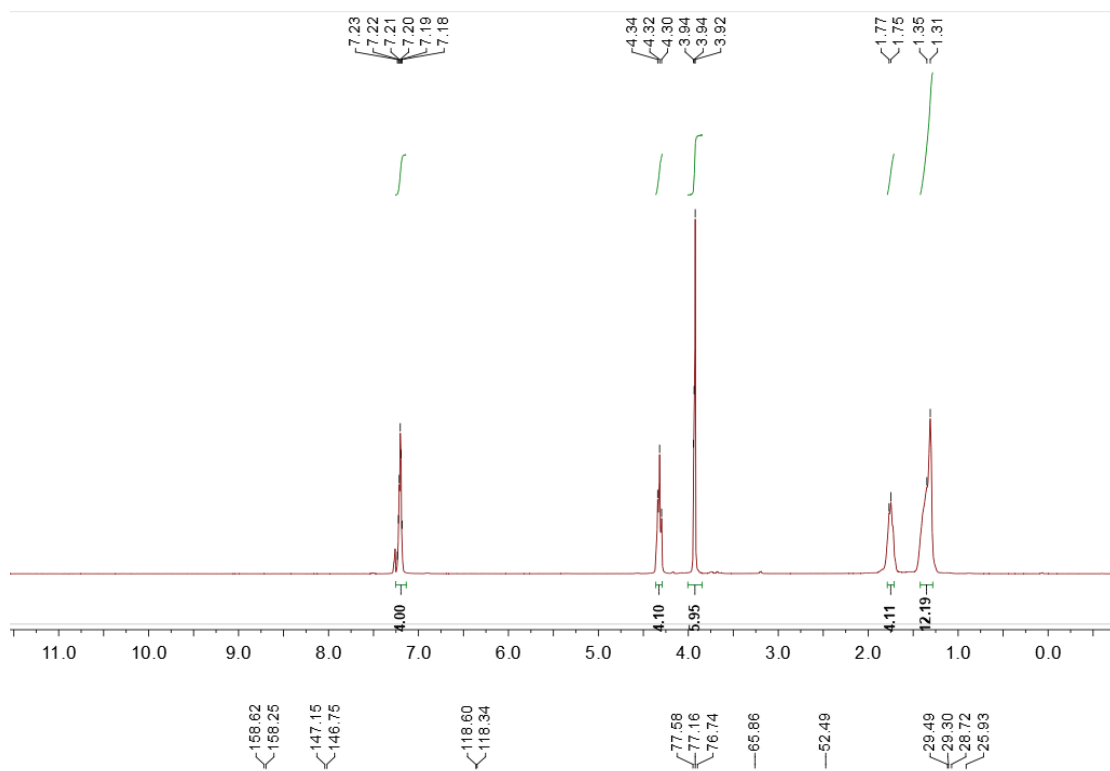


Decene glycol (5 mmol, 870 mg), triethylamine (TEA, 20 mmol, 2.02 g) and triethylenediamine (DABCO, 2 mmol, 225 mg) were introduced into the flask contained 50 mL THF. A mixture of Me-FDCA-Cl (10 mmol, 1.88 g) and 20 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford 5-(decene glycol) furan-2-carboxylate (Me-DG-FDCA) in 94% yield (2.2 g) as a pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.25 – 7.14 (m, 4H; H₂₋₃, H₆₋₇), 4.32 (t, *J* = 6.6 Hz, 4H; H₁₂, H₂₁), 4.01 – 3.85 (m, 6H; H₉, H₂₄), 1.76 (d, *J* = 6.2 Hz, 4H; H₁₃, H₂₀), 1.33 (d, *J* = 11.3 Hz, 12H; H₁₄₋₁₉).

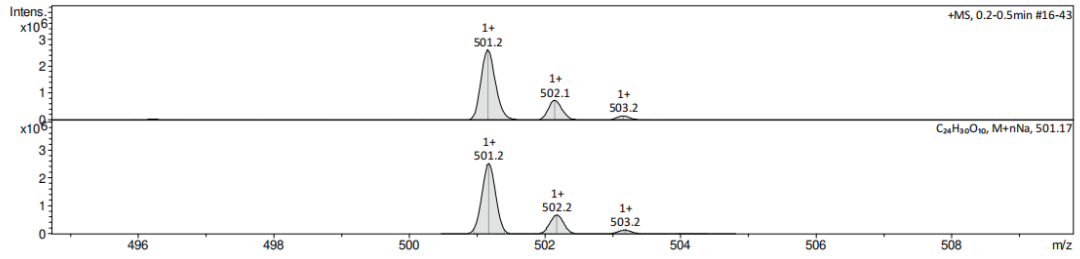
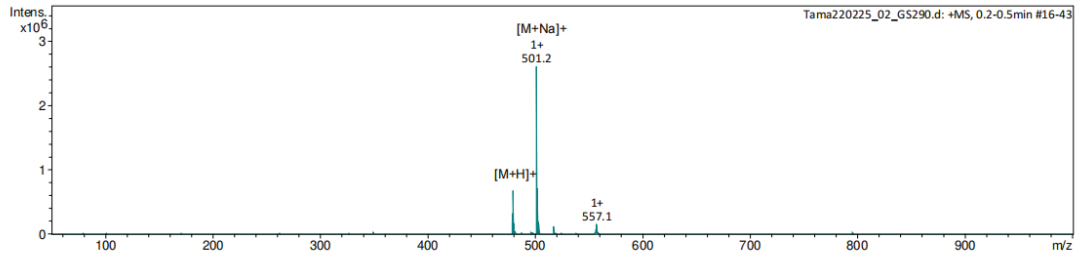
¹³C NMR (75 MHz, CDCl₃) δ 158.6 (s; C₁₀, C₂₃), 158.2 (s; C₁₁, C₂₂), 147.2 (s; C₁, C₈), 146.8 (s; C₄, C₅), 118.6 (s; C₂, C₇), 118.3 (s; C₃, C₆), 65.9 (s; C₁₂, C₂₁), 52.5 (s; C₉, C₂₄), 29.5 (s; C₁₃, C₂₀), 29.3 (s; C₁₄, C₁₉), 28.7 (s; C₁₅, C₁₈), 25.9 (s; C₁₆, C₁₇).

MS: [M+H]⁺ 479.2, [M+Na]⁺ 501.2.

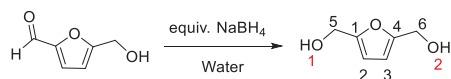


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	468 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of 2,5-furandimethanol (BHMF).



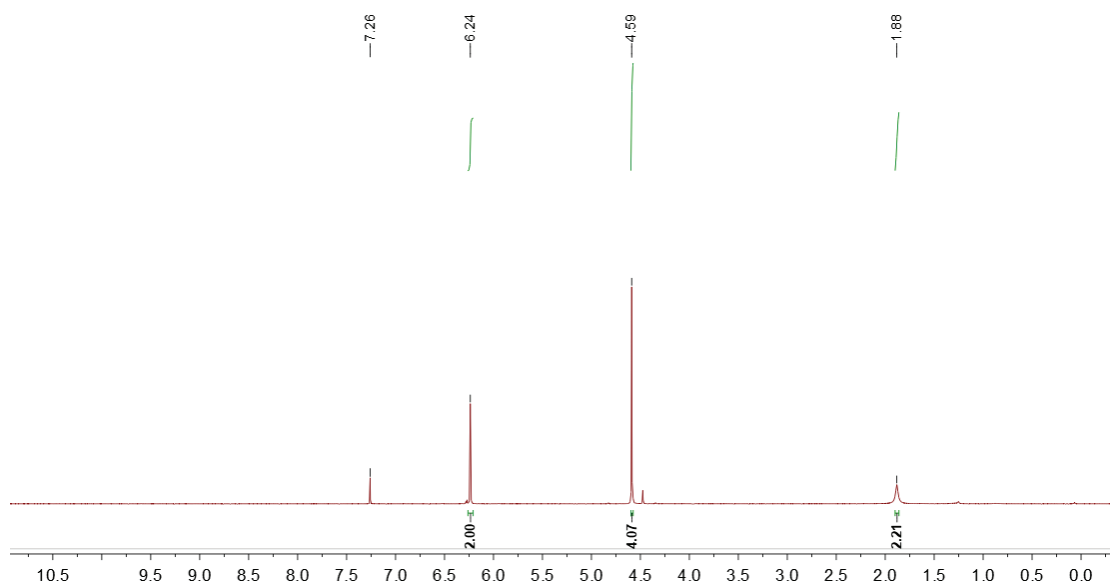
HMF (5 mmol, 0.63 g) was dissolved in 10 mL water, NaBH_4 (5 mmol, 0.19 g) aqueous was added dropwise to the HMF aqueous solution with continuous stirring. Using the TLC monitored the reaction. After the complete reduction, the product (BHMF) was isolated by extracting with ethyl acetate (20 mL x 4). Here the aqueous phase was saturated with NaCl for the quantitative extraction of BHMF. After evaporation of ethyl acetate, BHMF (100% yield, 640 mg) was obtained as white solid product.

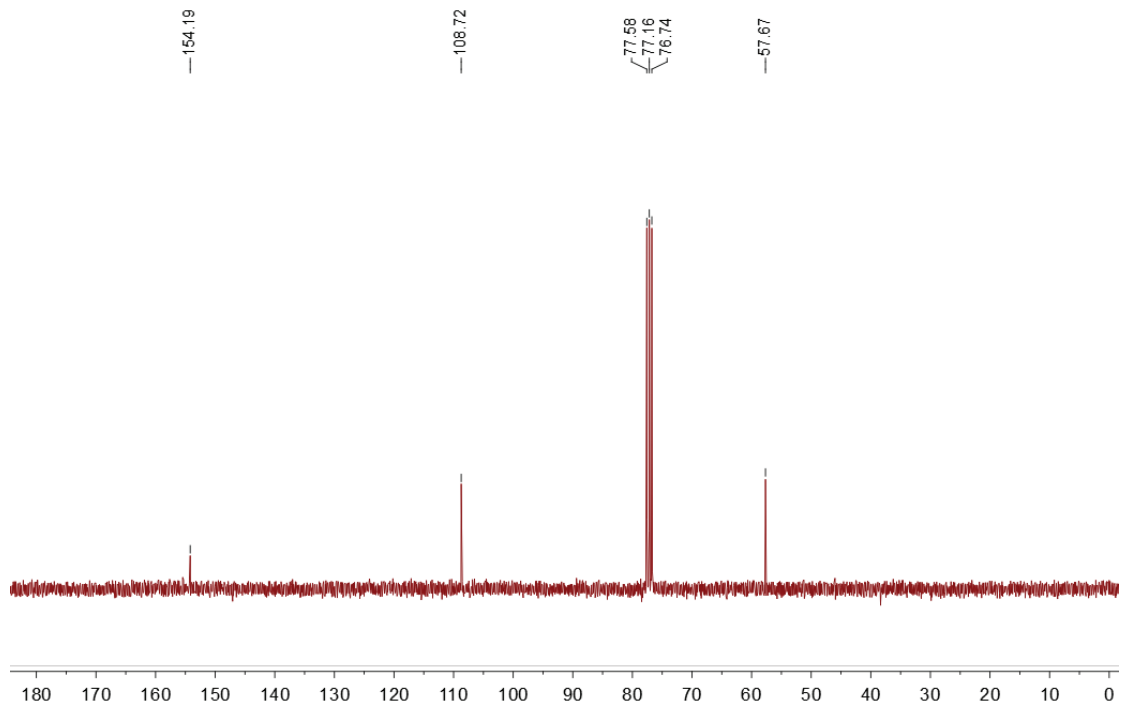
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.24 (s, 2H; H_2 , H_3), 4.59 (s, 4H; H_5 , H_6), 1.88 (s, 2H; O- H_{1-2}).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 154.2 (s; C_1 , C_4), 108.7 (s; C_2 , C_3), 57.7 (s; C_5 , C_6).

These results are in agreement with the literature. ^[230]

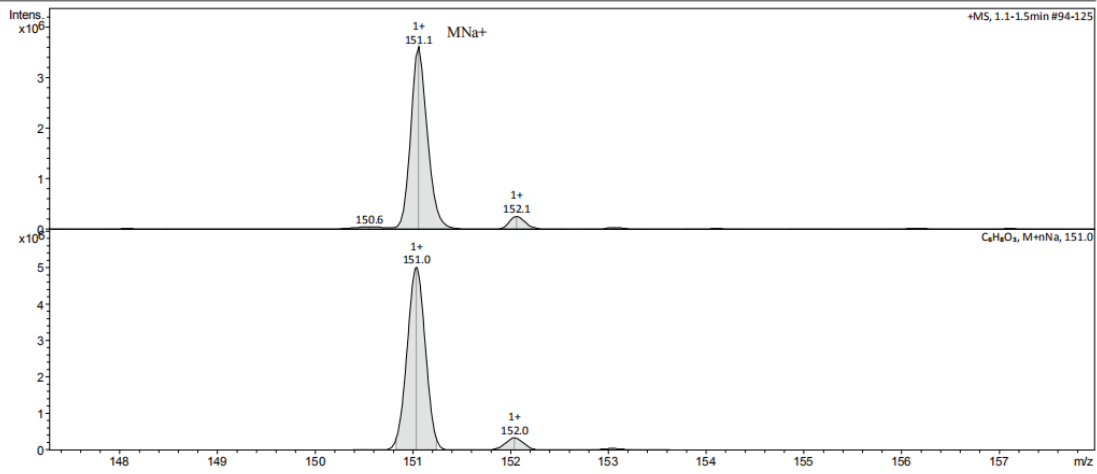
MS: $[\text{M}+\text{Na}]^+$ 151.1.



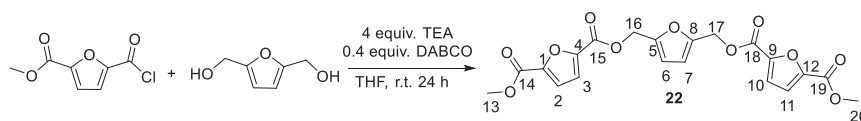


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	1307 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-2,5-furandimethanol furan-2-carboxylate (Me-BHMF-FDCA) (**22**).

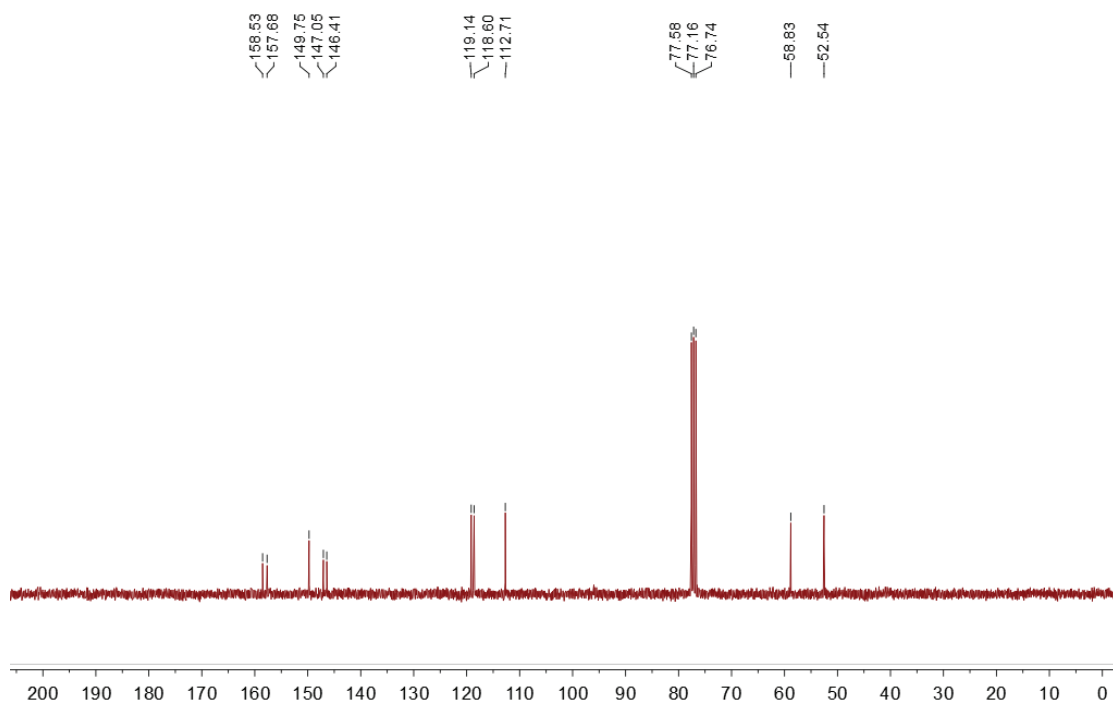
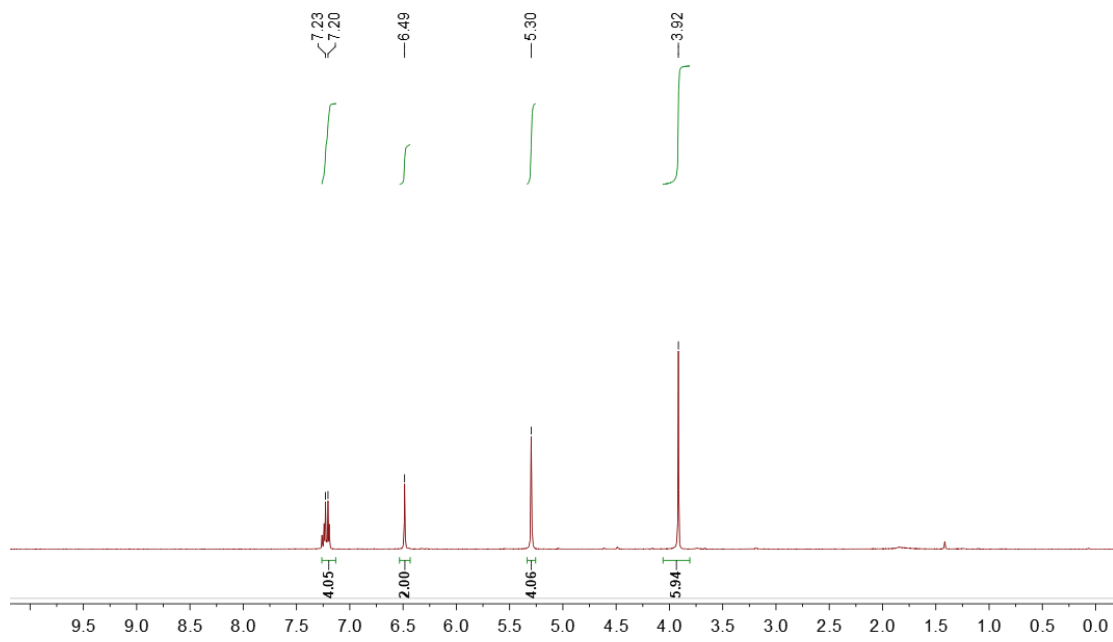


BHMF (2.5 mmol, 320 mg), triethylamine (TEA, 10 mmol, 1.01 g) and triethylenediamine (DABCO, 1 mmol, 113 mg) were introduced into the flask contained 25 mL THF. A mixture of Me-FDCA-Cl (5 mmol, 0.94 g) and 10 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford methyl 5-2,5-furandimethanol furan-2-carboxylate (Me-BHMF-FDCA) in 97% yield (1.0 g) as pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.22 (d, *J* = 7.1 Hz, 4H; H₂₋₃, H₁₀₋₁₁), 6.49 (s, 2H; H₆, H₇), 5.30 (s, 4H; H₁₆, H₁₇), 3.92 (s, 6H; H₁₃, H₂₀).

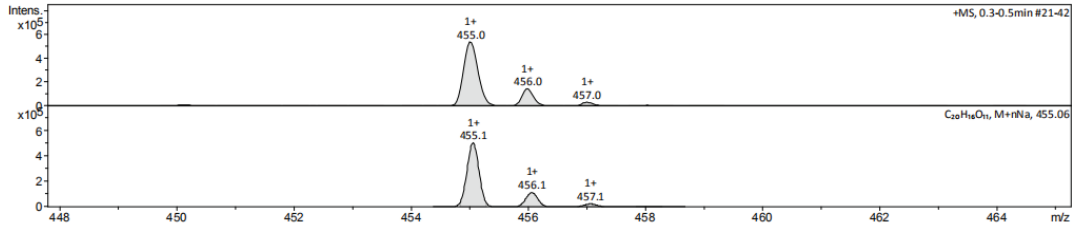
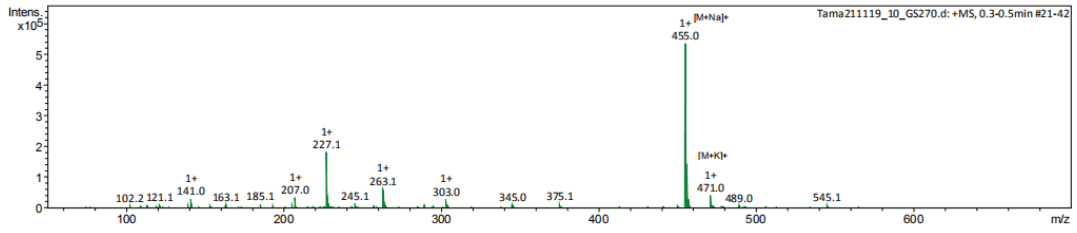
¹³C NMR (75 MHz, CDCl₃) δ 158.5 (s; C₁₄, C₁₉), 157.7 (s; C₁₅, C₁₈), 149.8 (s; C₁, C₁₂), 147.0 (s; C₄, C₉), 146.4 (s; C₂, C₁₁), 119.1 (s; C₃, C₁₀), 118.6 (s; C₅, C₈), 112.7 (s; C₆, C₇), 58.8 (s; C₁₆, C₁₇), 52.5 (s; C₁₃, C₂₀).

MS: [M+Na]⁺ 455.0.

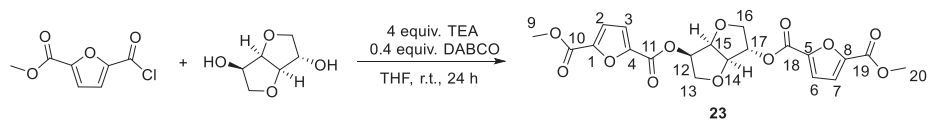


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	4690 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of methyl 5-isosorbide furan-2-carboxylate (Me-Iso-FDCA) (**23**).



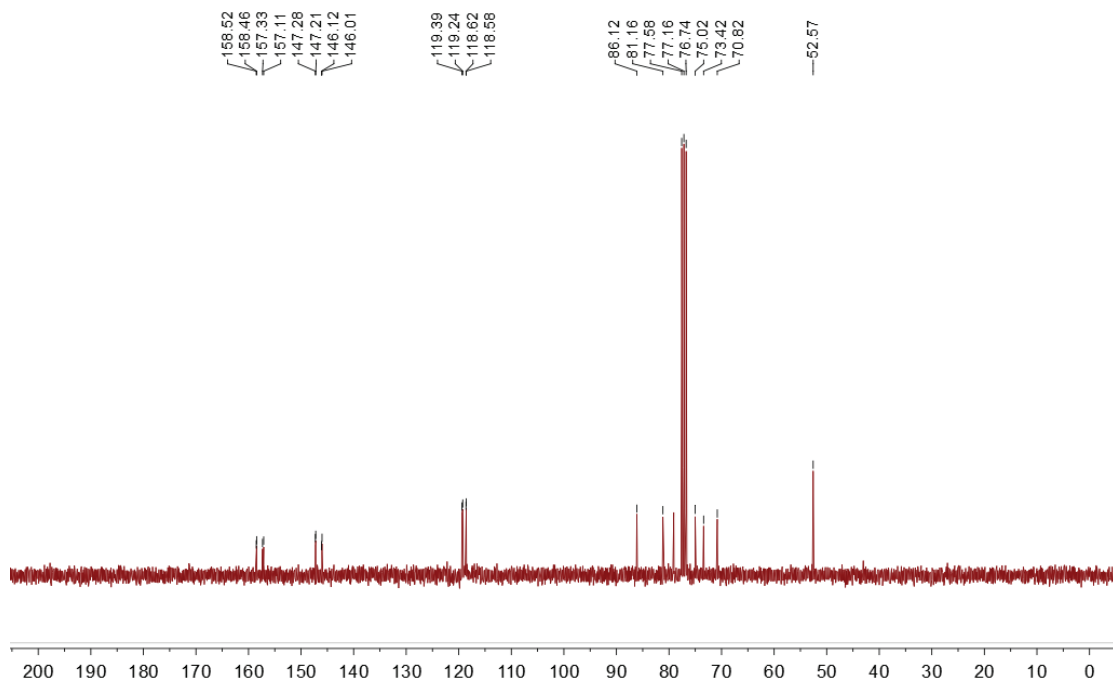
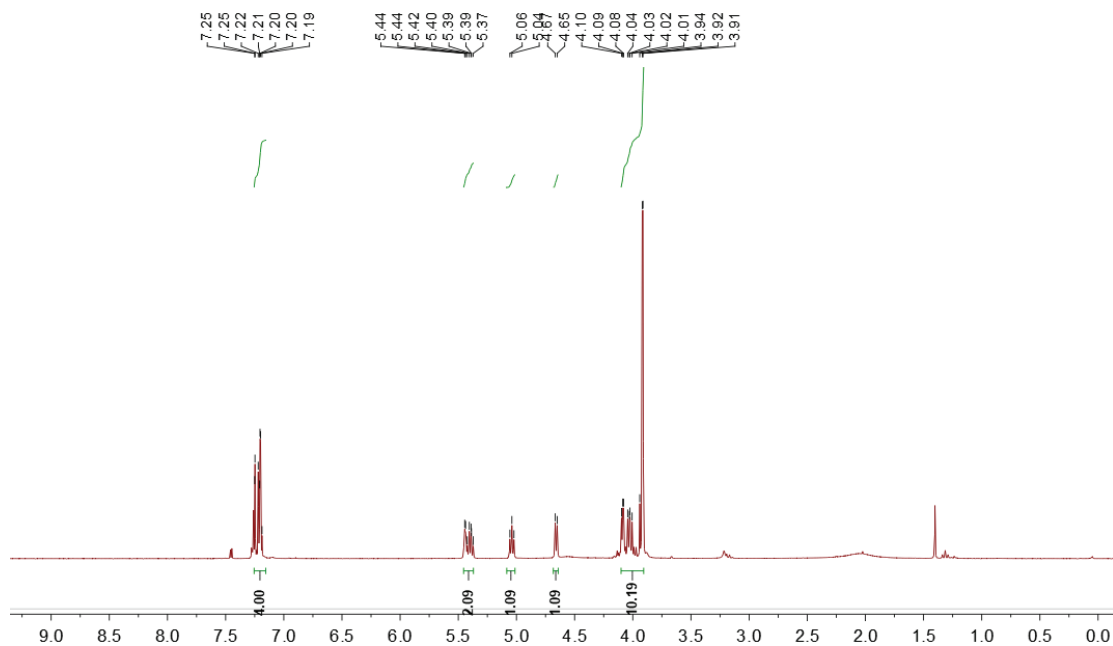
Isosorbide (5 mmol, 730 mg), triethylamine (TEA, 20 mmol, 2.02 g) and triethylenediamine (DABCO, 2 mmol, 225 mg) were introduced into the flask contained 50 mL THF. A mixture of Me-FDCA-Cl (10 mmol, 1.88 g) and 20 ml THF was slowly added to the above solution. The mixture was stirred at r.t. for 24 h. After the reaction, THF was removed in vacuum, and then a saturated aqueous NaHCO₃ solution (10 mL x 3) and the EA/cyclohexane (3:7, v/v) (5 mL x 3) were used to wash the solid to afford methyl 5-isosorbide furan-2-carboxylate (Me-Iso-FDCA) in 96% yield (2.2 g) as a pure white powder.

¹H NMR (300 MHz, CDCl₃) δ 7.26 – 7.15 (m, 4H; H₂₋₃, H₆₋₇), 5.45 – 5.37 (m, 2H; H₁₂, H₁₇), 5.04 (t, *J* = 5.2 Hz, 1H; H₁₄ or H₁₅)*, 4.66 (d, *J* = 4.9 Hz, H₁₄ or H₁₅)*, 4.10 – 3.91 (m, 10H; H₉, H₁₃, H₁₆, H₂₀).

¹³C NMR (75 MHz, CDCl₃) δ 158.5, 158.5 (s; C₁₀, C₁₉)*, 157.3, 157.1 (s; C₁₁, C₁₈)*, 147.3, 147.2 (s; C₁, C₈)*, 146.1, 146.0 (s; C₄, C₅)*, 119.4, 119.2 (s; C₂, C₇)*, 118.6, 118.6 (s; C₃, C₆)*, 86.1, 81.2, 79.1, 75.0, 73.4, 70.8 (s; C₁₂₋₁₇)*, 52.6 (s; C₉, C₂₀).

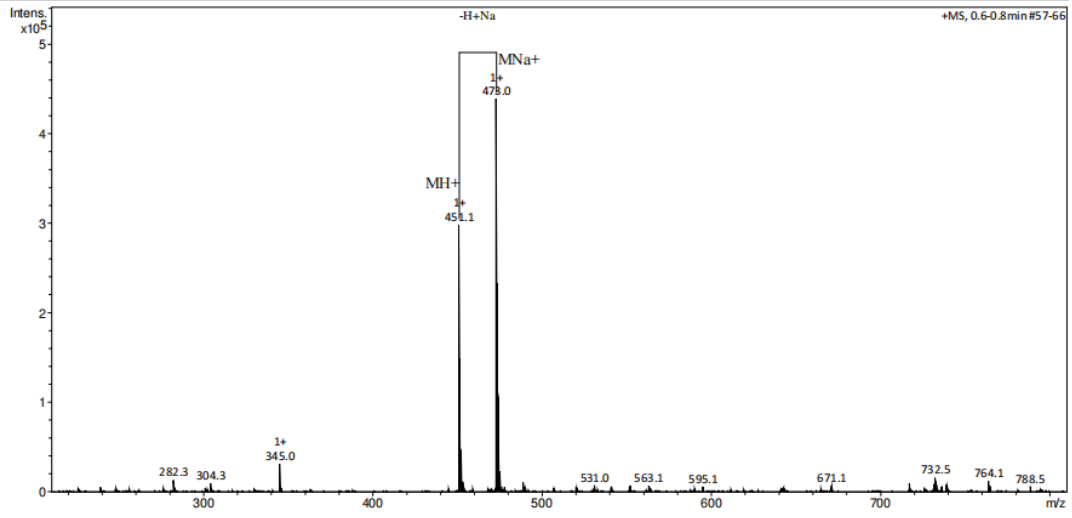
*The compound contains two chiral carbons; thus, some peaks can't be assigned exactly.

MS: [M+H]⁺ 451.1, [M+Na]⁺ 473.0.

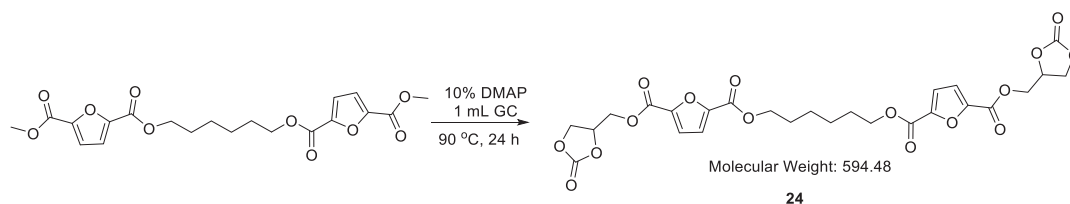


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	322 μ s	RF Level	59 %	Trap Drive	48.4
SPS Target Mass	350 m/z	Averages	5 Spectra	n/a	n/a



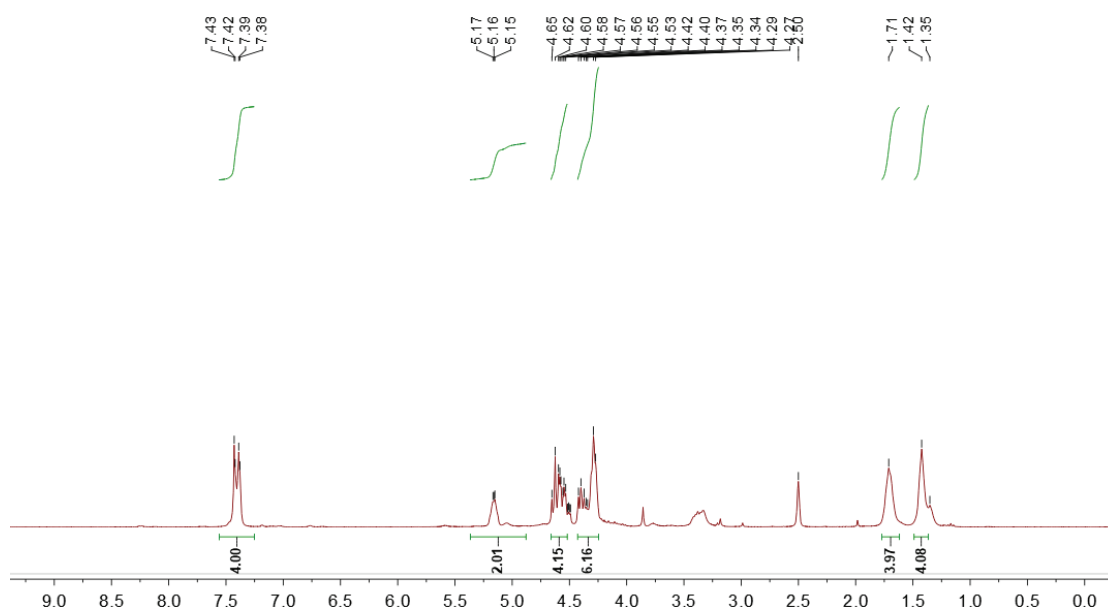
Synthesis and characterizations of glycerol carbonate 5-(hexylene glycol) furan-2-carboxylate (GC-HG-FDCA) (**24**).

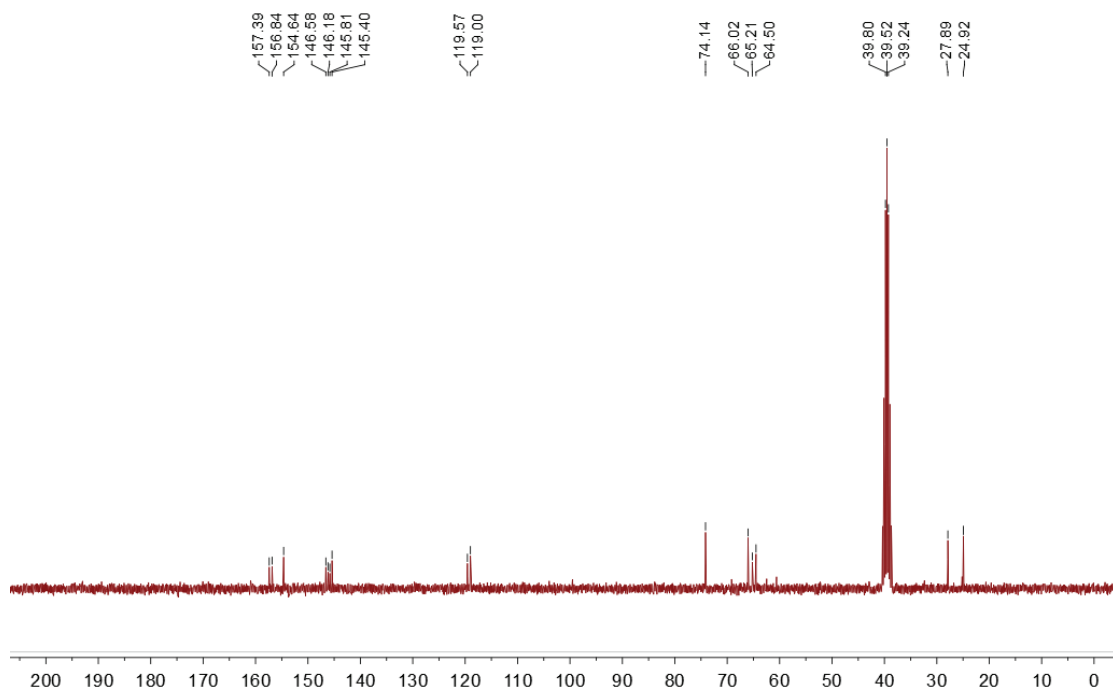


Me-HG-FDCA (0.5 mmol, 211 mg), DMAP (10%, 6 mg), and 1 mL GC as solvent were introduced into in flask. The flask was kept open and was heated at 90°C for 24 h. After the reaction, water (5 mL x 3) and the EA/cyclohexane (7:3, v/v) (10 mL x 3) were used to wash the solid to afford an impure glycerol carbonate 5-(hexylene glycol) furan-2-carboxylate (GC-HG-FDCA) in 35% yield (104.2 mg) as a pure white powder.

The product contains traces by-product; thus, the NMR can't totally match the product (**24**).

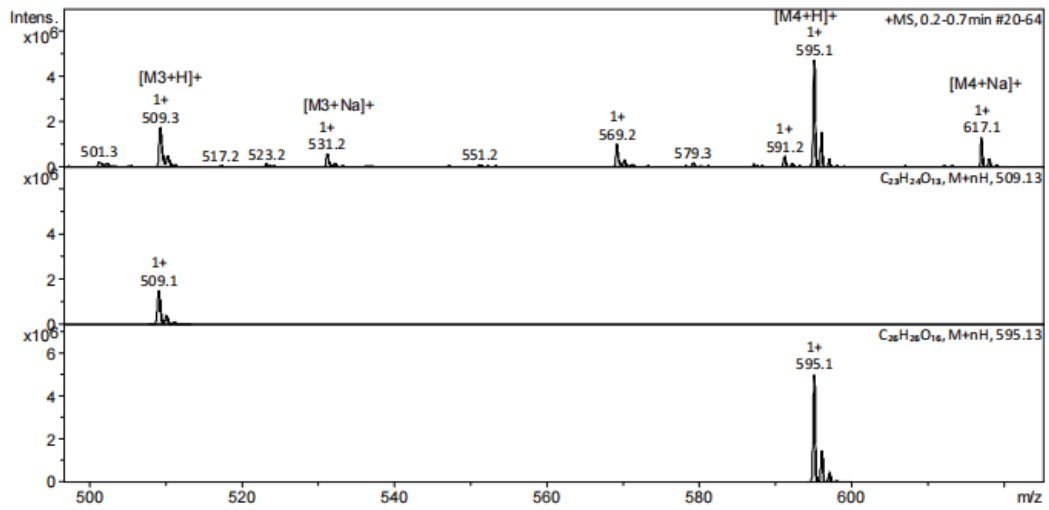
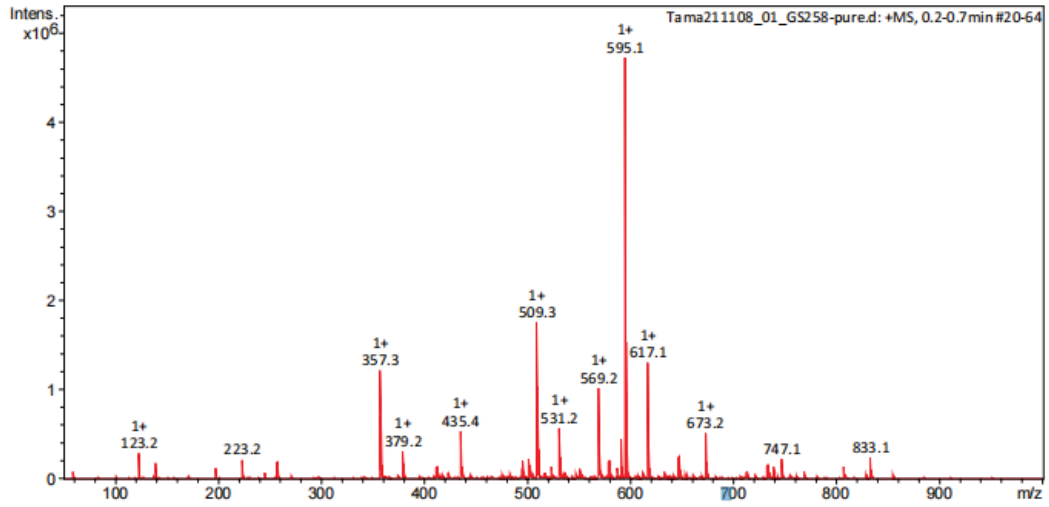
MS: $[M+H]^+$ 595.1, $[M+Na]^+$ 617.1.



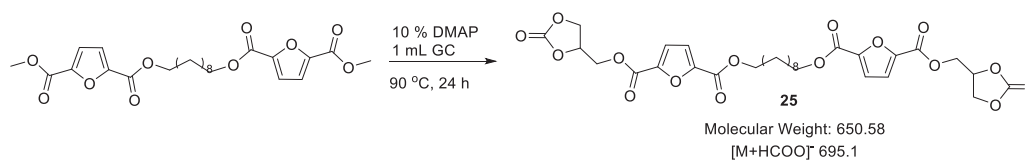


Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	470 μ s	RF Level	50 %	Trap Drive	44.2
SPS Target Mass	250 m/z	Averages	5 Spectra	n/a	n/a



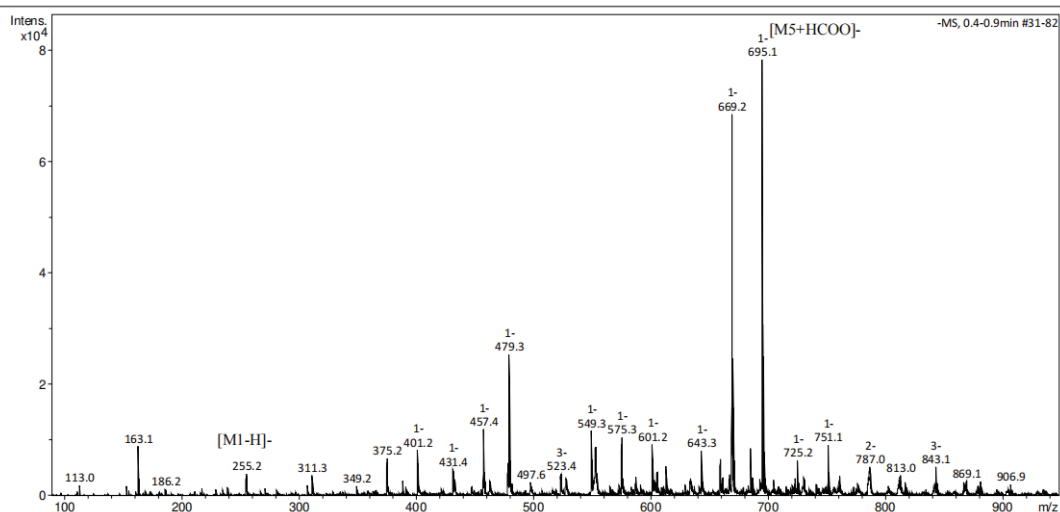
Synthesis and characterizations of glycerol carbonate 5-(decene glycol) furan-2-carboxylate (GC-DG-FDCA) (**25**).



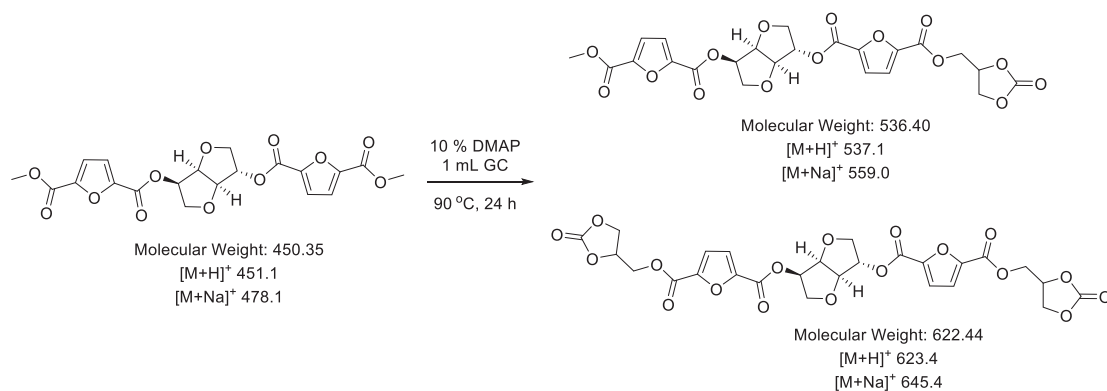
Me-GD-FDCA (0.5 mmol, 239 mg), DMAP (10%, 6 mg), and 1 mL GC as solvent were introduced into in flask. The flask kept open and was heated at 90°C for 24 h. After the reaction, using the water (5 mL x 3) and the EA/cyclohexane (7:3, v/v) (10 mL x 3) to wash the solid to obtain mixture white powder glycerol carbonate 5-(decene glycol) furan-2-carboxylate (GC-DG-FDCA).

Acquisition Parameter

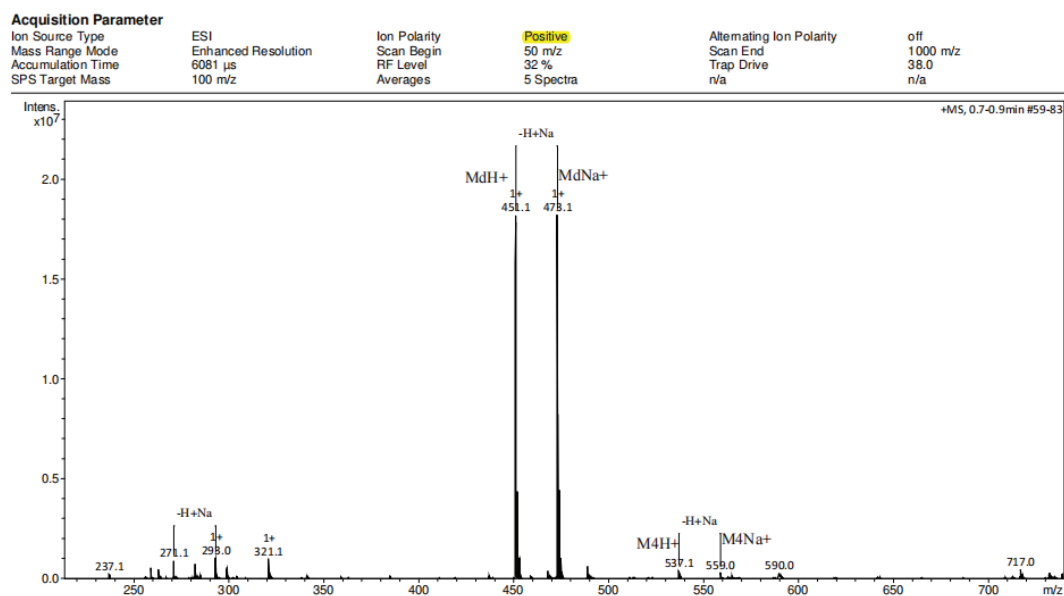
Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	50 m/z	Scan End	1000 m/z
Accumulation Time	1468 μ s	RF Level	59 %	Trap Drive	48.7
SPS Target Mass	350 m/z	Averages	5 Spectra	n/a	n/a



Synthesis and characterizations of glycerol carbonate 5-isosorbide furan-2-carboxylate (GC-Iso-FDCA).



Me-Iso-FDCA (0.5 mmol, 225 mg), DMAP (10%, 6 mg), and 1 mL GC as solvent were introduced into in flask. The flask kept open and was heated at 90°C for 24 h.



Abstract

The traditionally fossil based plastics have resulted in serious troubles in energy and natural ecosystems. PUs 6th among all polymers on the European market, thus, the researchers reached a consensus on exploring non-toxic intermediates and more sustainable process to produce renewable PHUs. We first synthesized fully bio-based bis-cyclocarbonate from 2,5-Furandicarboxylic acid, 2,2-bifuryl-5,5-dicarboxylic acid, glycerol, and diols, avoiding the toxic chemicals, and then launched the aminolysis reaction in green and renewable solvent DES (ChCl/Urea) to obtain the polymers. The DES (ChCl/Urea) also play a catalyst role in aminolysis, achieving wide scope of diamines, even the α -methyl primary amine in a relative ambient condition.

Résumé

Les plastiques traditionnels d'origine fossile ont entraîné de graves problèmes d'énergie et d'écosystèmes naturels. Les PU sont au sixième rang des polymères sur le marché européen. Les chercheurs sont donc parvenus à un consensus sur l'exploration d'intermédiaires non toxiques et d'un processus plus durable pour produire des PHU renouvelables. Nous avons d'abord synthétisé un bis-cyclocarbonate entièrement biobase à partir d'acide 2,5-furandicarboxylique, d'acide 2,2-bifuryl-5,5-dicarboxylique, de glycérol et de diols, en évitant les produits toxiques. Nous avons ensuite lancé la réaction d'aminolyse dans le solvant vert et renouvelable DES (ChCl/Urée) pour obtenir les polymères. Le DES (ChCl/Urée) joue également un rôle de catalyseur dans l'aminolyse, permettant d'obtenir un large éventail de diamines, même le α -méthylamine primaire dans des conditions ambiantes relatives.