出國報告（出國類別：開會）

赴德國參加高分子雙年會
「GDCh Makro 2024 – Polymers for a Sustainable Future」

服務機關：台灣中油股份有限公司煉製研究所
姓名職稱：黃麟強　化學工程師
派赴國家/地區：德國
出國期間：113年9月14日至113年9月21日
報告日期：113年10月21日

摘要

本次赴德國參與德勒斯登工業大學主辦之高分子雙年會「GDCh Makro 2024 – Polymers for a Sustainable Future」，與德國化學學會高分子領域會員年度大會 (GDCh-Fachgruppe Makromolekulare Chemie)。本次會議匯集了來自德國為主的產學研界高分子研究開發人員一同聚集分享及交流專業領域的知識及想法，聚焦綠色永續的高分子研究開發與應用。從聚合物原料單體、高分子合成生產、新型塑材應用、各式回收技術開發及以廢塑為料源再製材料，成為一個完整的閉環循環系統，勾勒出未來淨零環境下循環高分子經濟的樣貌。目前材料經濟仍以線型為主，由石化原料生產到使用完畢的掩埋或高碳排焚化，於本次會議當中眾多德國及西歐等國高分子研究開發者投入心力對於相當多的研究議題及開發方向，由再生資源為主的料源以更綠色環保的方式設計製成高分子材料，經過產業應用與市場使用後以先進技術妥善地回收與再製造新材料回用而不是直接掩埋焚燒，期以將高分子的經濟路線轉為綠色圓型的循環，達到淨零永續的目標。

目次

赴德國參加高分子雙年會「GDCh Makro 2024 – Polymers for a Sustainable Future」

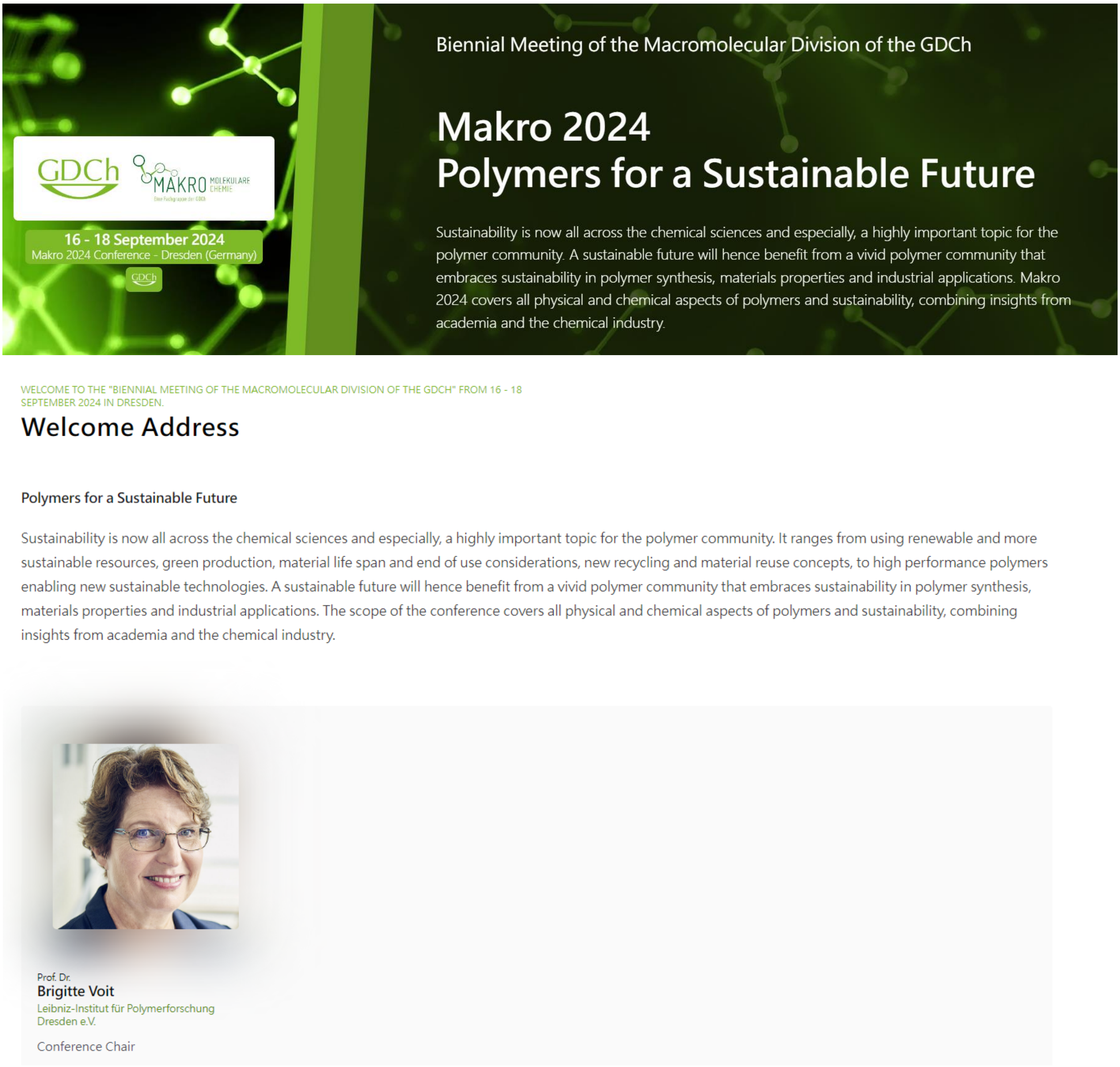
1. 目的

永續發展已經成為當今人類社會的最大共同訴求，人類必須真正將其經濟轉向永續發展和循環經濟。GDCh Makro2024 德國高分子2024雙年會會議訂於113年9月16日至18日於德國德勒斯登理工大學舉行。本次會議強調永續性，永續的議題現在已遍及整個化學科學領域，在高分子及聚合物領域更是一個非常重要的主題，人類永續的未來必將受益於一個充滿活力的高分子聚合物領域，該領域涵蓋了聚合物合成、材料性能和工業應用的可持續性等。本次德國 Makro 2024 會議涵蓋了聚合物和永續性的所有物理和化學方面，結合了學術界和化學工業的見解，讓來自產學研各界與會者互相交流，並能夠激發出有創造性的永續發展動力。會議包含聚合物的電子應用、永續功能、廢塑因應、自組裝結構、生質材料、綠色化學、控制合成、及永續性研究等領域多個專題演講以及海報展示。與會者主要來自德國尖端研究型大學、研究單位以及德國強勢的化工行業如 BASF、Covestro、Evonik 等，亦有荷蘭、比利時、瑞士等歐美國家研究者與會。派遣人員黃麟強為台灣中油煉製研究所石化產品組高分子聚合物開發相關研究人員，亦為德國化學學會會員，本次會議亦為與德國相關領域人員進行經濟及技術等資訊交流，共重要的是更深層的社群關係建立。本次會議所彙整的資訊會對於台灣中油公司於淨零轉型期間有所裨益。

2. 過程

起迄日期	到達地點	詳細工作內容
113.9.14	台灣-法蘭克福	搭乘飛機啟程
113.9.15	法蘭克福-德勒斯登	抵達法蘭克福並移動至會場舉辦城市
113.9.16	德勒斯登	參加 GDCh Makro 2024大會。
113.9.17	德勒斯登	1. 參加 GDCh Makro 2024大會。 2. 參加德國化學學會高分子分會會員大會
113.9.18	德勒斯登	參加 GDCh Makro 2024大會。
113.9.19	德勒斯登-法蘭克福	返回法蘭克福機場
113.9.20~21	法蘭克福-台北	搭乘返程飛機

會議於德國德勒斯登工業大學(TU Dresden)舉行



16 - 18 September 2024
Makro 2024 Conference - Dresden (Germany)

Biennial Meeting of the Macromolecular Division of the GDCh

Makro 2024
Polymers for a Sustainable Future

Sustainability is now all across the chemical sciences and especially, a highly important topic for the polymer community. A sustainable future will hence benefit from a vivid polymer community that embraces sustainability in polymer synthesis, materials properties and industrial applications. Makro 2024 covers all physical and chemical aspects of polymers and sustainability, combining insights from academia and the chemical industry.

WELCOME TO THE "BIENNIAL MEETING OF THE MACROMOLECULAR DIVISION OF THE GDCH" FROM 16 - 18 SEPTEMBER 2024 IN DRESDEN.

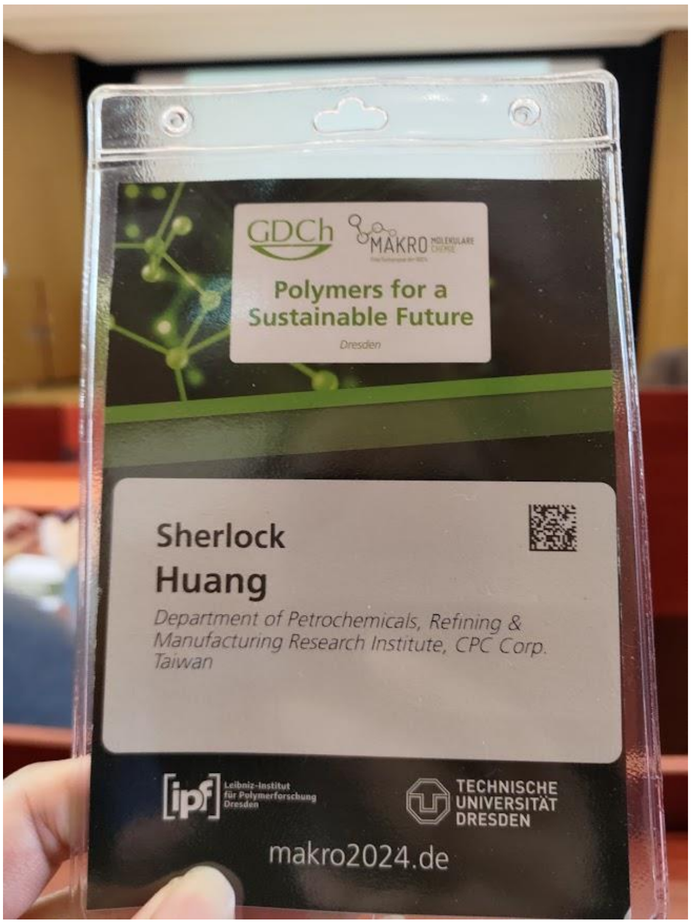
Welcome Address

Polymers for a Sustainable Future

Sustainability is now all across the chemical sciences and especially, a highly important topic for the polymer community. It ranges from using renewable and more sustainable resources, green production, material life span and end of use considerations, new recycling and material reuse concepts, to high performance polymers enabling new sustainable technologies. A sustainable future will hence benefit from a vivid polymer community that embraces sustainability in polymer synthesis, materials properties and industrial applications. The scope of the conference covers all physical and chemical aspects of polymers and sustainability, combining insights from academia and the chemical industry.

Prof. Dr.
Brigitte Voit
Leibniz-Institut für Polymerforschung Dresden e.V.

Conference Chair

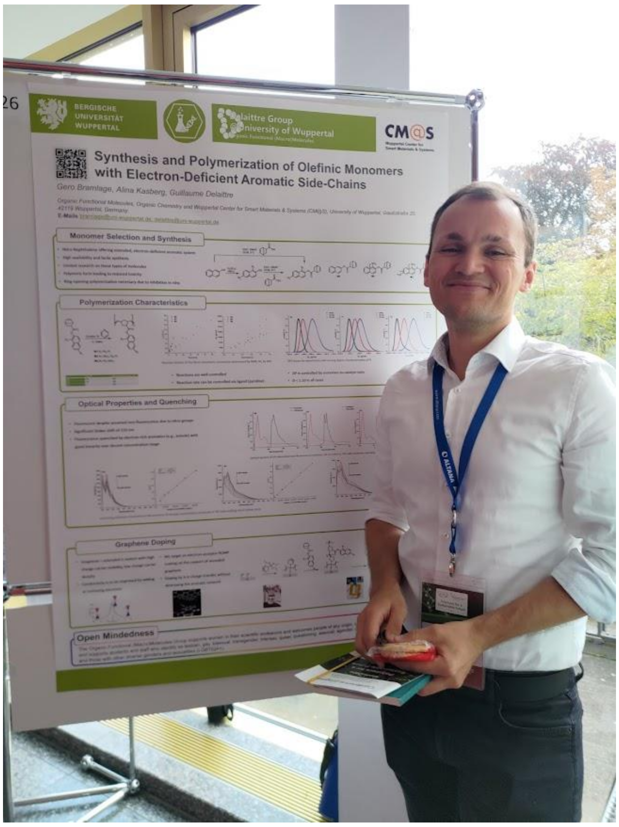


與會人員黃麟強的會議識別證

大會主會場開會情形

3. 具體成效

參與化工領域強勢的德國舉辦之國際會議 Makro2024與與會者進行研討交流增加台灣中油公司在高分子及聚合物開發等領域之能見度，並於現場資訊交流中更深層地了解綠色永續高分子化學在德國產學研界的發展狀況及最新趨勢，特別是BASF、Covestro、Evonik等德國化工標竿企業對於永續材料的發展策略及因應作為，對於中油公司開發新型聚合物、特用化學品開發以及發展策略擬定等會有所助益。在淨零減碳的趨勢下，本次會議蒐集德國化工行業發展經驗、產學合作資訊以及與學研單位互動分享所專注之焦點技術等可以作為中油公司未來發展之參考。



出國人員黃麟強在德國前老闆兼導師 Guillaume Delaittre 教授實驗團隊的成員 Gero Bramlage 於會議會場照相留影

4. 會議研討內容及心得建議彙整

4.1. 材料的永續循環發展

2021年德國自然保護協會 (Naturschutzbund Deutschland, NABU) 表示德國每年開採約10億噸初級原料，另有7億噸原料、半成品和製成品進口。扣除4億出口，德國消耗原料約13億噸。這相當於每年人均消費量 16 噸。如果不僅考慮進口重量，還考慮國外生產進口商品（上游鏈）的原料消耗，每年消耗量甚至達到17噸。從圖1中可以看出，只有一小部分原料被回收。德國的經濟仍然是線性結構而不是循環結構，循環材料利用率 (CMU) 在2017年僅 12%，雖然當時德國為世界廢棄物資源回收成效第一名的佼佼者。其中石化來源的循環使用率僅有2.5%，石化資源除了作為能源外大部分被用為塑膠及高分子材料應用。

圖1、德國的2017年度材料流動量圖示。圓圈中的圓點代表資源種類由上而下依序為礦物質、金屬、石化以及生物資源。來源：德國自然保護協會 NABU 委託海德堡能源環境研究所 ifeu 彙整報告於2021發表 https://www.nabu.de/umwelt-undressourcen/abfall-und-recycling/kreislaufwirtschaft/29818.html)

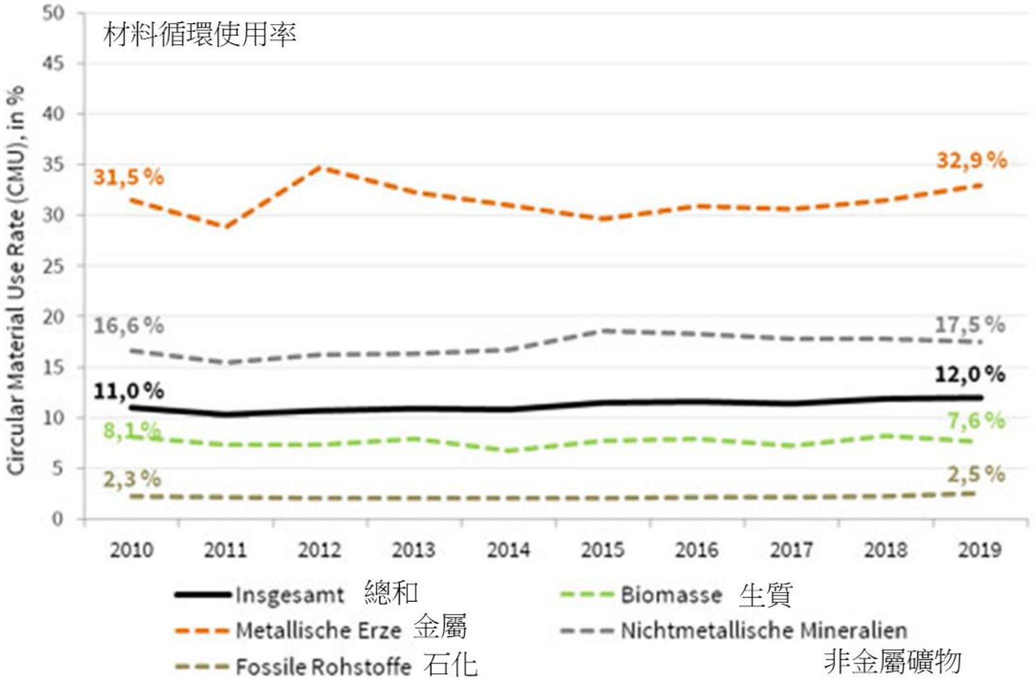


圖2、2010至2019年德國各種原料的 CMU（循環材料使用率），最低的為石化原料區塊。來源：ifeu (2021)

圖3為歐洲塑膠產業聯盟 (PlasticsEurope)於2024年繪出的塑膠循環經濟圖，為了實現「塑膠轉型」路線圖當中設定的 2050 年淨零排放和循環利用目標，加快系統性變革對於產業加速轉型至關重要。其中循環經濟是一個回收或捕捉塑膠作為主要的資源價值之系統，防止塑膠使用完畢後最終被掩埋、焚燒或污染我們的海洋以對人類生活環境和地球產生正面影響。循環利用目前為減少塑膠系統廢棄及碳排放最快、有效且可靠的方法之一，由從生產商到回收整個塑膠價值鏈必須進行合作及創新，將用完即拋棄之線性的塑膠系統轉變為再利用的循環系統。因此產業鏈相關業者需要採取多種行動如從改善塑膠廢棄物收集和分類、更具創新性的回收利用，到生態設計和增加包括生物質和二氧化碳利用在內的循環原料的使用。圖3中數據顯示截至2022年，歐洲共生產五千八百八十萬左右之各類高分子塑膠，整體數據比較2018年的消長呈現循環性提高的正面趨勢，廢塑收集及分類量上升、循環性塑膠產量增加、能源回收效益增

加及直接掩埋量降低等。

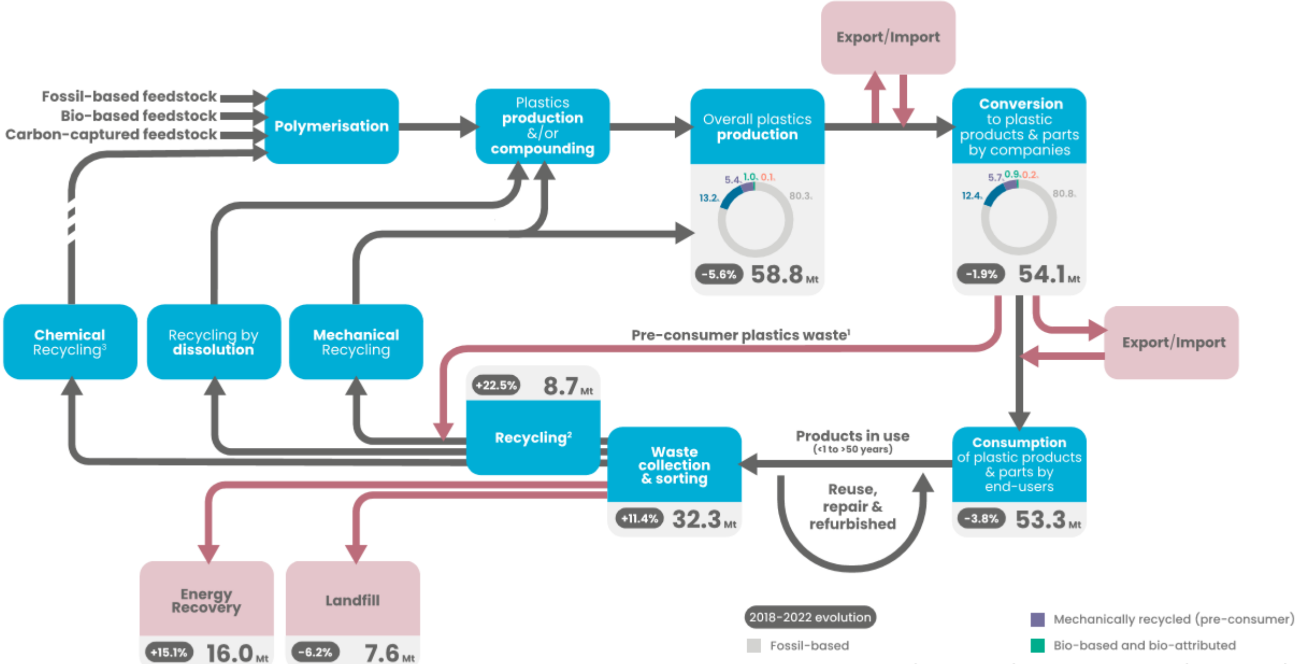


圖3、塑膠循環經濟圖及2018至2022年產量變化概略。來源：Plastics Europe 2024

由2022年歐洲生產高分子材料種類來看(圖4)，有19.6%的占比為循環型材料(含回收塑料、生質材料)，其他均為石油基的塑膠材料，其中聚丙烯(PP)和聚乙烯(PE)佔據重要比率約為37%。

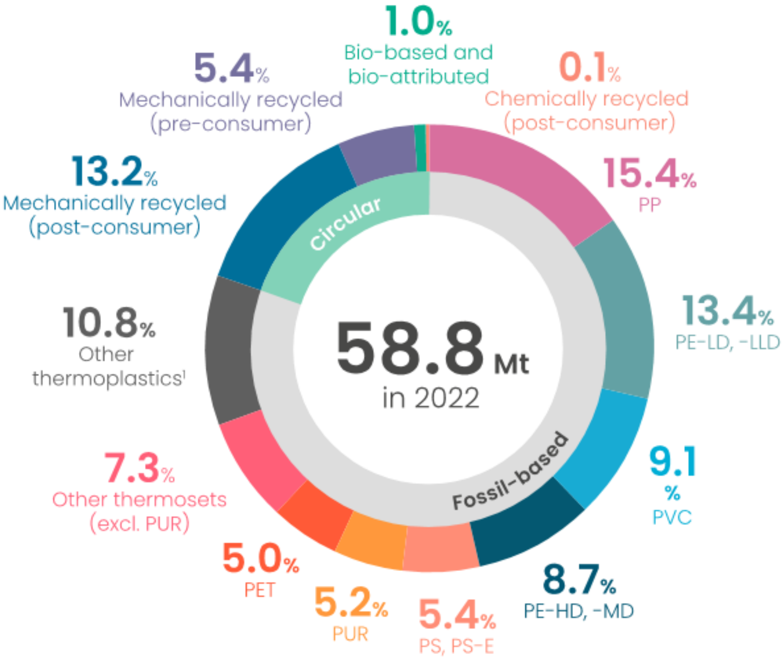


圖4、2022年歐洲塑膠/高分子生產分布狀況。來源：Plastics Europe 2024

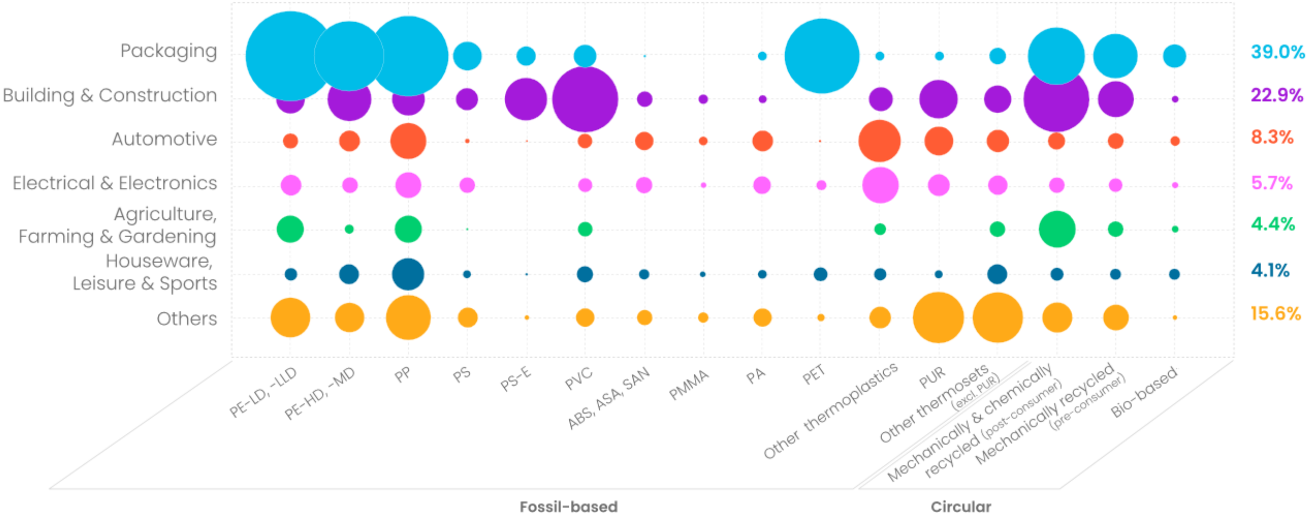


圖5、2022年歐洲依應用分類的塑膠/高分子。來源：Plastics Europe 2024

不同的高分子聚合物依據其特定性能被用於各自的應用中 (圖 5)。一次性或短壽命的包裝應用以聚烯烴 PE、PP 和 PET 聚酯為主，這些材料使用完畢並回收，在完善的廢棄物收集分類之基礎設施下通常可在一年內進行盡可能的回收。另一方面預期有較長壽命的材料例如建築中占主導地位的聚合物聚氯乙烯 (PVC)等，通常在其應用中會有數十年的使用時間，理論上甚至可以再次回收作為原料使用。根據歐洲塑膠產業聯盟，歐洲整體在2022年以農業應用的塑膠循環利用程度最高 (41.7%循環率)，其次為建築應用(29.9%循環率)及包裝(17.3%循環率)，循環利用程度最低的則為電子應用(6.4%)。發展循環經濟下，短壽命應用如包裝除了使用大量的回收材料外，亦有使用生物質材料及生物可分解材料取代現行石油基一次性材料的趨勢，而需要耐用耐侯性質的長壽命高分子材料則會以發展環境友善可回收使用的高分子材料，以及藉由創新賦予更優異特性如自我修復等。這對於建立聚合物循環經濟有兩個重要後果：隨著過去幾十年聚合物使用量呈指數級增長，當今可用廢棄塑膠流的成分偏向於短期應用中使用的材料類型，因此從創新的角度來看，使用時間延長也意味著包裝行業以外的材料必須重新設計，特別在干預措施如強制性循環相關政策實施生效下。

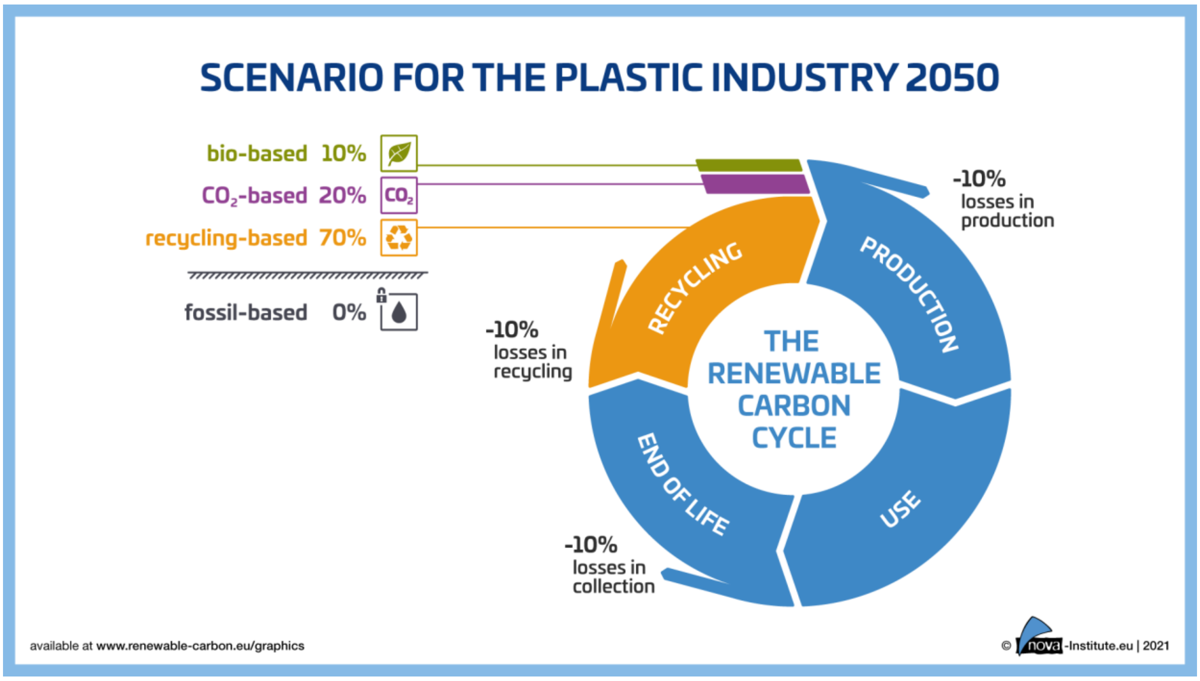


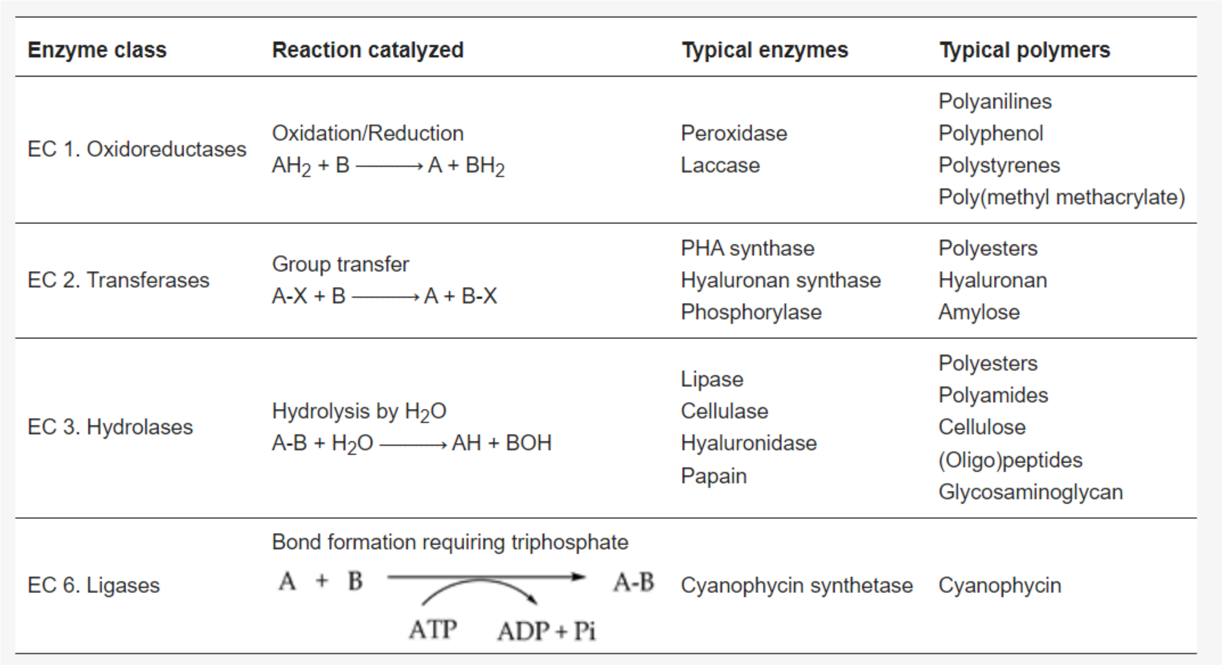
圖6、淨零理想下非石油基的高分子塑膠產業碳循環

4.2. 石化替代料源—生物質高分子發展

4.2.1. 生物酵素催化聚合反應

Katja Loos 女士為荷蘭格羅寧根大學(University of Groningen)澤尼克先進材料研究所教授並擔任高分子化學和新型高分子材料系主任，同時也是歐洲高分子聯盟(European Polymer Federation)現任盟主，她在本次年會闡述了以生物的方式進行高分子合成。

自德國化學家赫曼・施陶丁格(Hermann Staudinger，1953年諾貝爾化學獎得主) 引入高分子概念的時代以來，合成高分子已成為每個人日常使用的不可或缺的材料，從包裝中的塑料，到汽車和航空領域的輕質高性能材料，或作為生物醫學應用的材料等等，但如果不適當地丟棄和回收，龐大數量塑膠的生產和散佈在地球上將使合成大分子成為全球環境威脅。大多數合成聚合物和塑膠是透過化學方法生產的，而天然存在的聚合物如纖維素、多醣、蛋白質等是透過細胞的酵素生化機制合成的，酵素可以催化聚合反應由低分子量單體連接成高分子量大分子，使用酵素或整個細胞作為聚合催化透過生物催化途徑合成聚合物是可行的。使用天然催化劑進行聚合最令人注目的好處及潛力為大多數酵素無毒且具有生物相容性，或者它們可以生產具有立體化學或區域選擇性的聚合物。現在許多非天然聚合反應也可以由酵素催化，例如表 XX 的氧化還原酶(Oxidoreductase)、轉移酶 (Transferase)、水解酶 (Hydrolase) 和連接酶(Ligase)[200]。其中，聚酯(Polyester, 如 PET 等)是酵素聚合研究最廣泛的聚合物；脂肪酶(Lipase)是聚酯酶聚合最有效的生物催化劑。



Enzyme class	Reaction catalyzed	Typical enzymes	Typical polymers
EC 1. Oxidoreductases	Oxidation/Reduction $AH_2 + B \longrightarrow A + BH_2$	Peroxidase Laccase	Polyanilines Polyphenol Polystyrenes Poly(methyl methacrylate)
EC 2. Transferases	Group transfer $A\text{-}X + B \longrightarrow A + B\text{-}X$	PHA synthase Hyaluronan synthase Phosphorylase	Polyesters Hyaluronan Amylose
EC 3. Hydrolases	Hydrolysis by H_2O $A\text{-}B + H_2O \longrightarrow AH + BOH$	Lipase Cellulase Hyaluronidase Papain	Polyesters Polyamides Cellulose (Oligo)peptides Glycosaminoglycan
EC 6. Ligases	Bond formation requiring triphosphate $A + B \xrightarrow[\text{ATP} \rightarrow \text{ADP + Pi}]{} A\text{-}B$	Cyanophycin synthetase	Cyanophycin

表7、Katja Loos 教授提到可應用於高分子聚合之生物酵素種類。來源：doi.org/10.3390/polym8070243

一般來說，脂肪酶(Lipase)催化聚酯合成可以進行三種聚合模式 (圖8)：(1) 逐步增長縮聚 (Step-growth polycondensation)； (2)開環聚合 (Ring-opening polymerization)；(3)開環聚合和縮聚的組合(開環加成縮合聚合)。其中，縮聚和開環聚合是生物催化聚酯合成最常使用的方法。

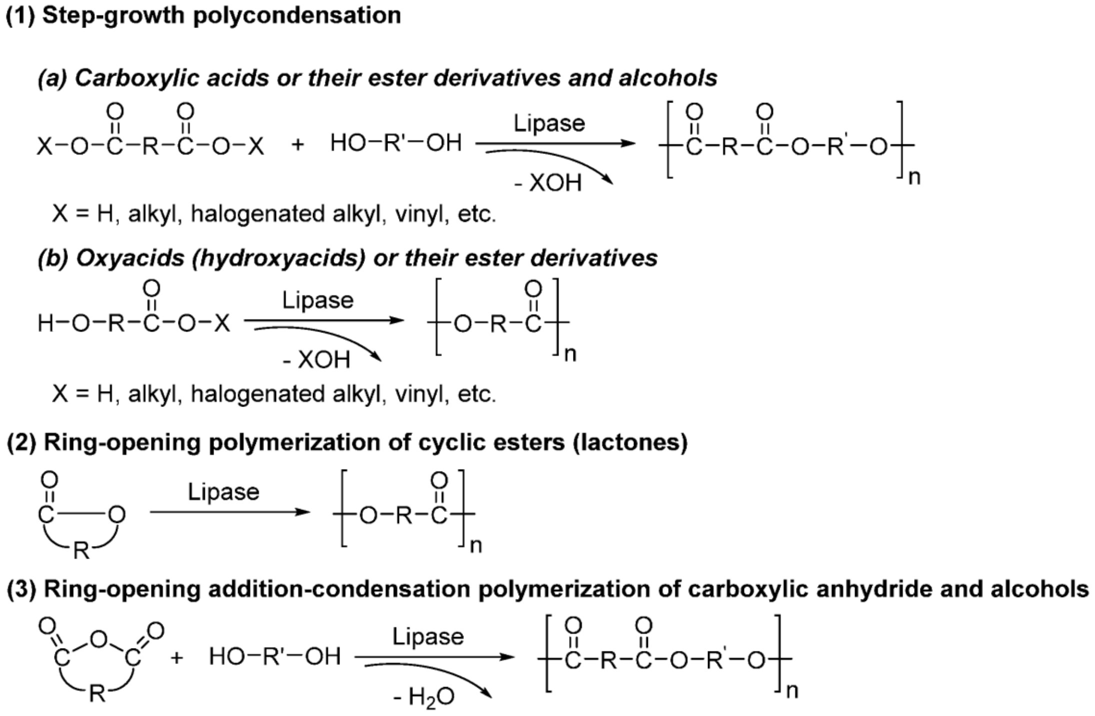


圖8、脂肪酶催化合成聚酯的主要反應模式。來源： doi.org/10.3390/polym8070243

Katja Loos 教授實驗團隊近期致力於以生質化學品呋喃單體透過酵素脂肪酶進行聚酯合成研究(圖9)，反應採用之單體以及酵素均為生物來源，期以發展對環境更永續的綠色高分子材料合成技術。

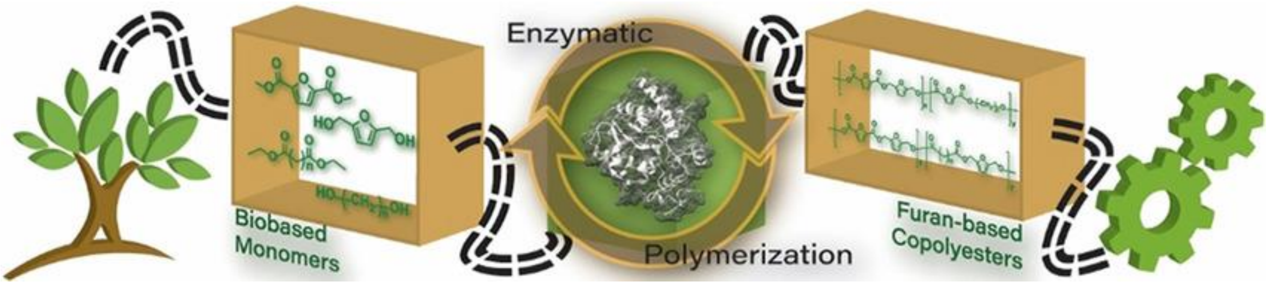


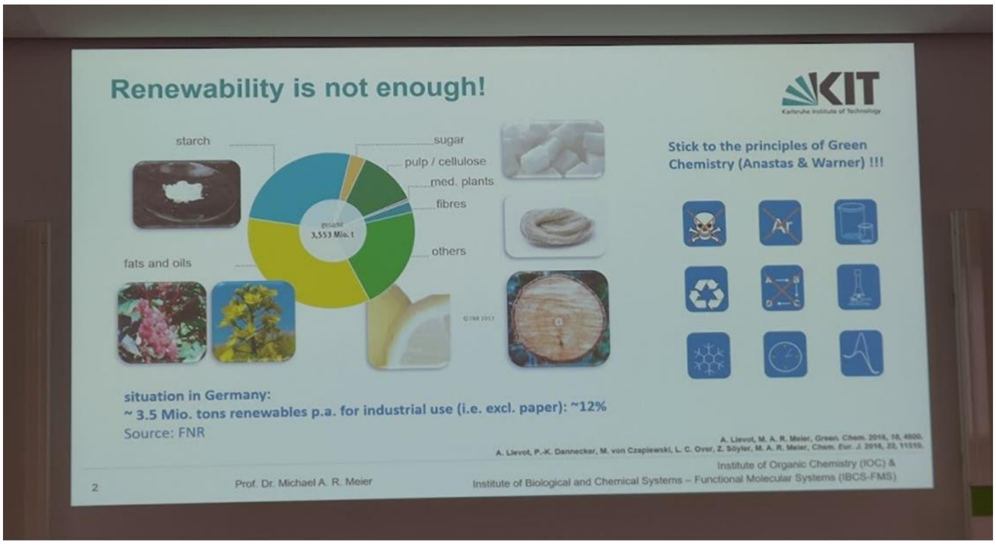
圖9、Katja Loos 教授研究團隊近期致力於利用酵素及生物質單體合成綠色生物聚酯材料。來源：doi.org/10.1002/cssc.201802867

圖10、Katja Loos 教授於會場的演講

4.2.2. 生質高分子/化學品發展

卡魯理工學院 (Karlsruher Institut für Technologie)的 Michael Meier 教授實驗團隊致力於以天然物作為綠色材料開發，於本次會議以自然界最豐富的纖維素及木質素為主要原料進行綠色化學品/材料合成開發。木質素和纖維素約佔為地球上第二及第一豐富的生物聚合物。其中木質素具獨特的多酚結構和一系列特殊功能如抗菌功能、生物降解性、抗氧化等等，在過去幾十年中在各個領域引起了人們的關注，直到今天木質素的潛力並未真正的發揮。木質素是芳香族化合物的唯一重要天然來源，可以轉化為高附加價值化學物質，但木質素目前通常為造紙工業的廢棄物或副產品，總產量當中只有非常小的部分用於材料應用，其餘大部分被作燃料；Michael Meier 教授表示每年木質素的生產約為1億噸，但只有2%被回收用於材料利用，目前將功能化木質素用作聚合物合成的巨單體(macromonomer)已在天然聚合物應用成為一個顯學之一，木質素上的羥基加上其脂肪族和芳香族結構的豐富性使得木質素適合進行化學改質以設計綠色材料的應用。

本次會議當中 Meier 團隊的 Celeste Libretti 女士分享了近期改質木質素進行 NIPU (non-isocyanate polyurethanes)材料的研究，以木質素及赤藻糖醇(Erythritol)的環碳酸酯衍生物與葵花油二胺衍生物進行反應合成木質素修飾之 NIPU 作為綠色生質熱固材料開發(圖11)。Michael Meier 教授表示大家熟知的聚氨酯(polyurethanes, PU)是一類最重要的聚合物，全球產量超過每年1000萬噸，且在汽車、建築業、醫療應用、紡織業、家具和電子產品等等領域有多種應用，這和 PU 在分子和宏觀層面上多樣化和可調節的特性有關，例如其卓越的硬度、機械強度和延展性。1937年德國化學家奧托·拜爾(Otto Bayer)在德國 I.G. Farben 公司的實驗室首次使用了脂肪族結構的二異氰酸酯(diisocyanate)和甘油合成了聚氨酯，在當期已知的其他塑料相比，這些新材料在靈活性和塗層效率方面提供了優勢。在聚異氰酸酯 (polyisocyanates) 商業化後，聚氨酯的重要性進一步上升，然而在工業上聚氨酯的製造使用異氰酸酯(isocyanate)，其本身不僅有毒，還需要危險和有毒的光氣來進行合成，才會有後續 NIPU(非異氰酸酯的聚氨酯)材料的開發。以環碳酸酯與胺反應從合成 NIPU 技術正變得越來越成熟，特別是使用來自生物資源的環碳酸酯和胺方法更受到矚目，與工業上使用的異氰酸酯相比，環碳酸酯顯示出較低的毒性，然而環碳酸酯比異氰酸酯較低的反應性通常需要使用催化劑。NIPU 材料對於台灣中油公司並不陌生，本公司煉研所對於綠色材料 NIPU 正進行前期開發當中。



Renewability is not enough!

Stick to the principles of Green Chemistry (Anastas & Warner) !!!

situation in Germany:
~ 3.5 Mio. tons renewables p.a. for industrial use (i.e. excl. paper): ~12%
Source: FNR

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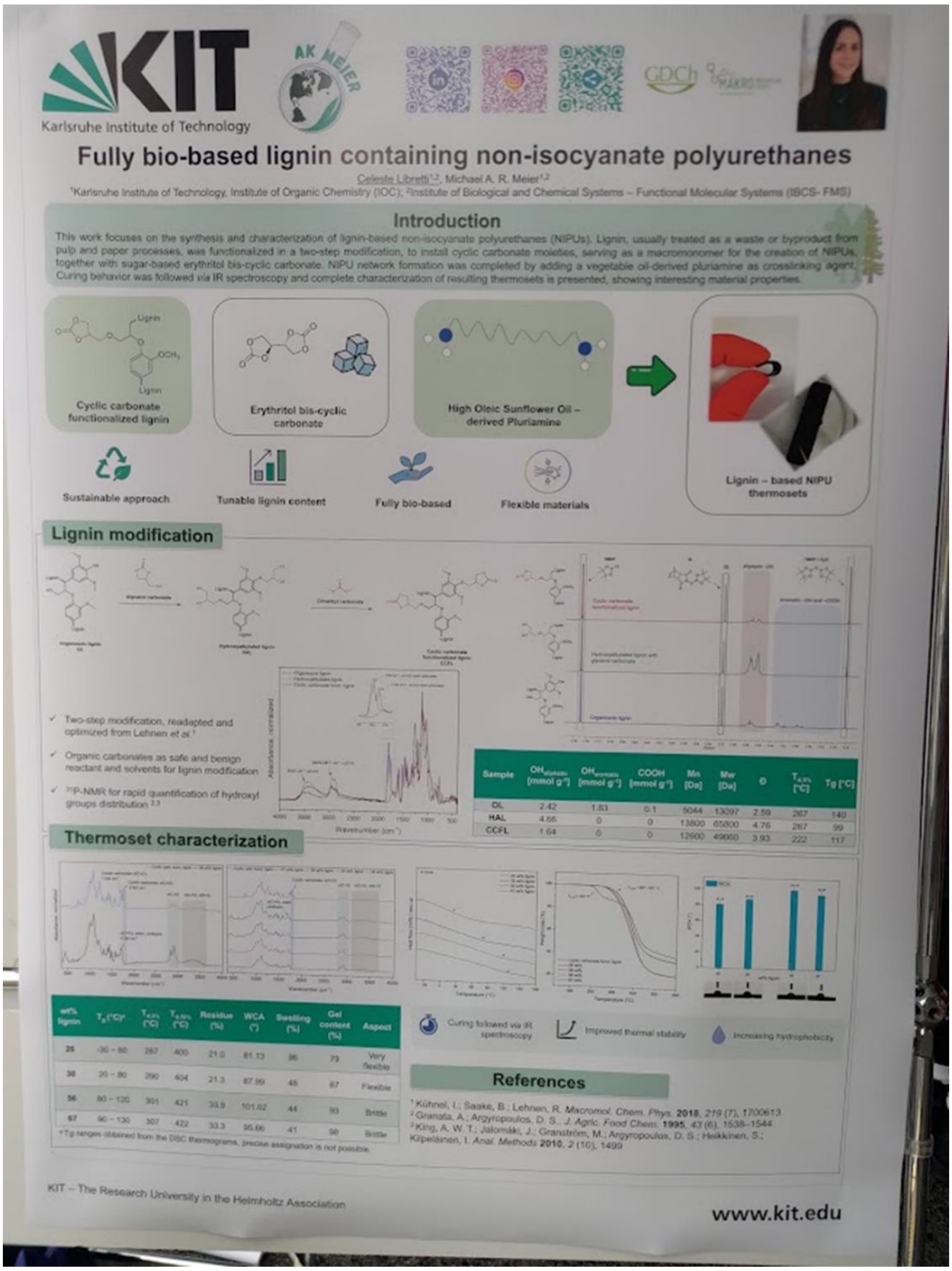
2 Prof. Dr. Michael A. R. Meier Institute of Organic Chemistry (IOC) & Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS)



Fully bio-based lignin containing non-isocyanate polyurethanes

Celeste Libretti[1,2], Michael A. R. Meier[1,2]
[1]Karlsruhe Institute of Technology, Institute of Organic Chemistry (IOC); [2]Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS- FMS)

Introduction

This work focuses on the synthesis and characterization of lignin-based non-isocyanate polyurethanes (NIPUs). Lignin, usually treated as a waste or byproduct from pulp and paper processes, was functionalized in a two-step modification, to install cyclic carbonate moieties, serving as a macromonomer for the creation of NIPUs, together with sugar-based erythritol bis-cyclic carbonate. NIPU network formation was completed by adding a vegetable oil-derived pluriamine as crosslinking agent. Curing behavior was followed *via* IR spectroscopy and complete characterization of resulting thermosets is presented, showing interesting material properties.

Cyclic carbonate functionalized lignin

Erythritol bis-cyclic carbonate

High Oleic Sunflower Oil – derived Pluriamine

Lignin – based NIPU thermosets

Sustainable approach

Tunable lignin content

Fully bio-based

Flexible materials

Lignin modification

- ✓ Two-step modification, readapted and optimized from Lehnen *et al.*[1]
- ✓ Organic carbonates as safe and benign reactant and solvents for lignin modification
- ✓ ^{31}P-NMR for rapid quantification of hydroxyl groups distribution [2,3]

Sample	$OH_{aliphatic}$ [mmol g⁻¹]	$OH_{aromatic}$ [mmol g⁻¹]	COOH [mmol g⁻¹]	Mn [Da]	Mw [Da]	Đ	$T_{d,5\%}$ [°C]	Tg [°C]
OL	2.42	1.83	0.1	5044	13097	2.59	267	140
HAL	4.66	0	0	13800	65800	4.76	267	99
CCFL	1.64	0	0	12600	49660	3.93	222	117

Thermoset characterization

wt% lignin	T_g (°C)*	$T_{d,5\%}$ (°C)	$T_{d,50\%}$ (°C)	Residue (%)	WCA (°)	Swelling (%)	Gel content (%)	Aspect
25	-30 – 60	287	400	21.0	81.13	56	79	Very flexible
38	20 – 80	290	404	21.3	87.99	48	87	Flexible
56	80 – 120	301	421	33.9	101.02	44	93	Brittle
67	90 – 130	307	422	33.3	95.66	41	98	Brittle

*Tg ranges obtained from the DSC thermograms, precise assignation is not possible.

Curing followed via IR spectroscopy

Improved thermal stability

Increasing hydrophobicity

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圖11、Michael Meier 教授實驗團隊發展綠色材料及合成技術於本次會議之展示

4.2.2. 生質材料產業發展—生物精煉廠(Biorefinery)

荷蘭 Avantium 生質化學品公司副總 Heleen Goorissen 博士於本次會議介紹該公司主要的生物精煉化學品業務。Avantium 在2000年由殼牌石油衍生(Spin off)出來，一開始以高通量(high-throughput)催化劑測試系統等的觸媒技術起家，藉由此技術優勢從可再生來源如植物來源的醣類和二氧化碳，用來生產基礎材料及高分子單體，目標為替代石化來源材料。

圖12、Avantium 生質化學品公司副總 Heleen Goorissen 博士於本次會議的生質化學品 FDCA 產業化演講

Avantium 公司製造生質 PEF 核心技術第一個為該公司取名的 YXY®技術 (圖13)，該技術主要為催化植物來源糖轉化成 FDCA (2,5-Furandicarboxylic acid,呋喃二羧酸)，供作為 PEF (polyethylene furanoate)高分子的主要組成，PEF 為一種100%植物來源且完全可回收的塑料材料，相對於市場主流石油基 PET 具有顯著的性能優勢且碳足跡更低(圖14)。Avantium 第二項核心技術是 Ray Technology™主要為一步催化將糖轉化為乙二醇(glycol)單體 plantMEG™以及丙二醇單體 plantMPG™，做為 PEF 和 PET 的重要單體也可以功能性流體使用 (如除冰、熱傳導等)。Avantium 第三項技術是 Dawn Technology™，該技術可將非食品用途的木質纖維素生物質轉化為工業用糖和木質素，將化學品和材料料源轉為非石化及食品資源，利用非食品生物質作為料源的概念對於未來產業發展較可以永續推動。Avantium 除了發展使用植物碳源之生物精煉廠外，亦開發以二氧化

碳（CO2）作為再生碳源的原料 (圖17)，Avantium 的 Volta Technology 是一個重要的碳捕集與利用（CCU）技術步驟，以電催化之電化學技術平台做為基礎，將 CO_2轉化為化學前驅物、單體和高價化學品如草酸 (oxalic acid) 和羥基乙酸 (glycolic acid)等可作為聚酯單體等的化學品。

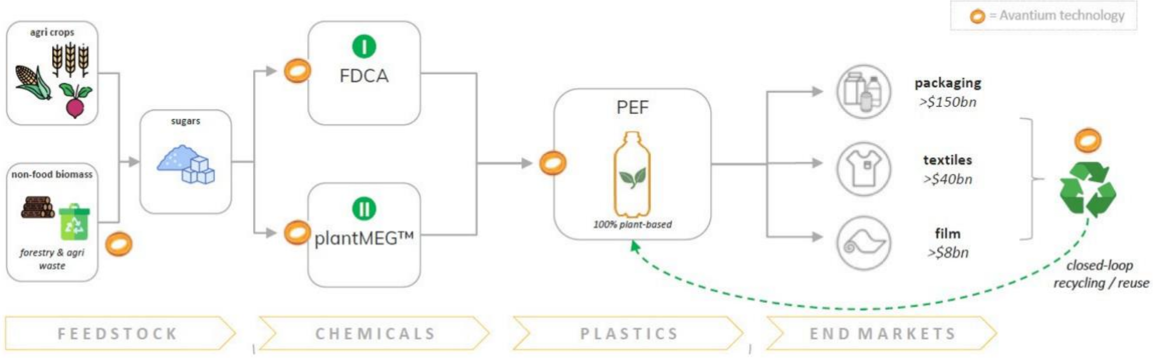


圖13、YXY® 技術價值鏈概述，從生質原料到 FDCA 和 PEF，以及工業用糖的 Dawn Technology^{TM} 和使用植物料源的 plantMEG^{TM} 的 Ray® Technology^{TM}。來源：Avantium

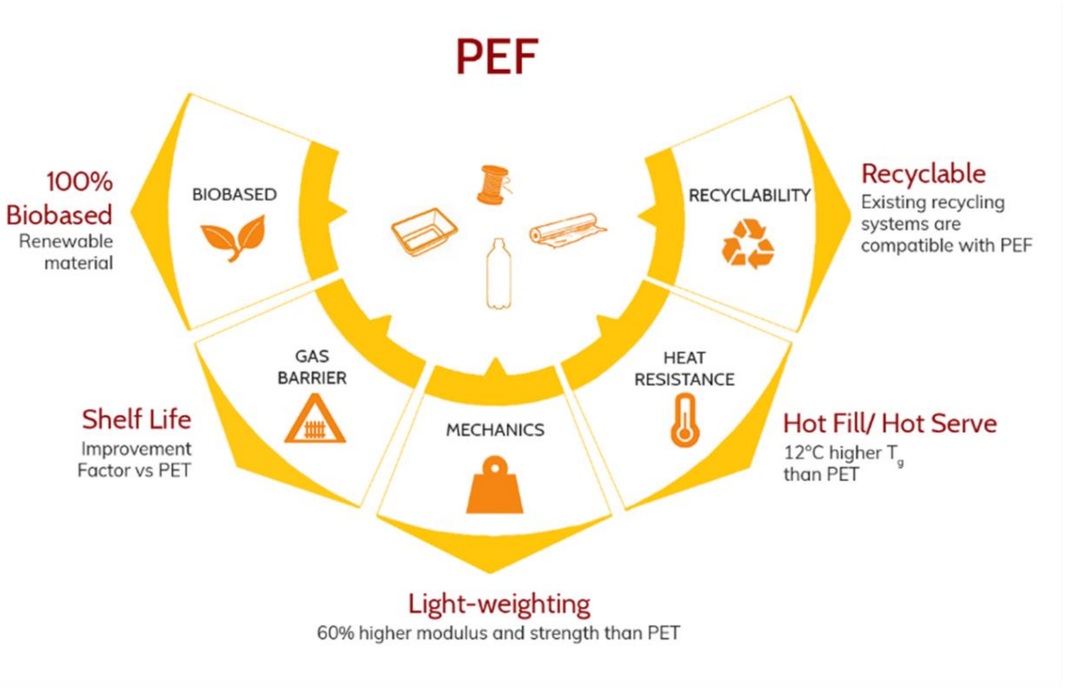


圖14、生質 PEF 的優勢面向。來源：Avantium

Avantium 於2024年中旬完工的旗艦 PEF 工廠(圖15)，荷蘭麥克西瑪王后(Koningin Máxima der Nederlanden)於10月22日主持開幕儀式。Avantium 在 PEF 的開發上已經努力了超過18年，最初在阿姆斯特丹的實驗室進行研究，在2011年在荷蘭 Geleen 建立試驗工廠(pilot plant)中持續推進，該公司已經優化了 FDCA/PEF 技術，並與全球多個合作

夥伴廣泛測試 FDCA 和 PEF 的應用， PEF 瓶子和包裝已經生產出來同時也生產了用於服裝、室內和工業應用的 PEF 纖維，Avantium 並與合作夥伴及下游廠商建立堅實重要的合作價值鏈(圖16)。

Avantium's first-of-a-kind FDCA plant on stream in 2024

avantium

Prove Technology at **5 kt/a scale**

Selling PEF & FDCA **at commercial scale**

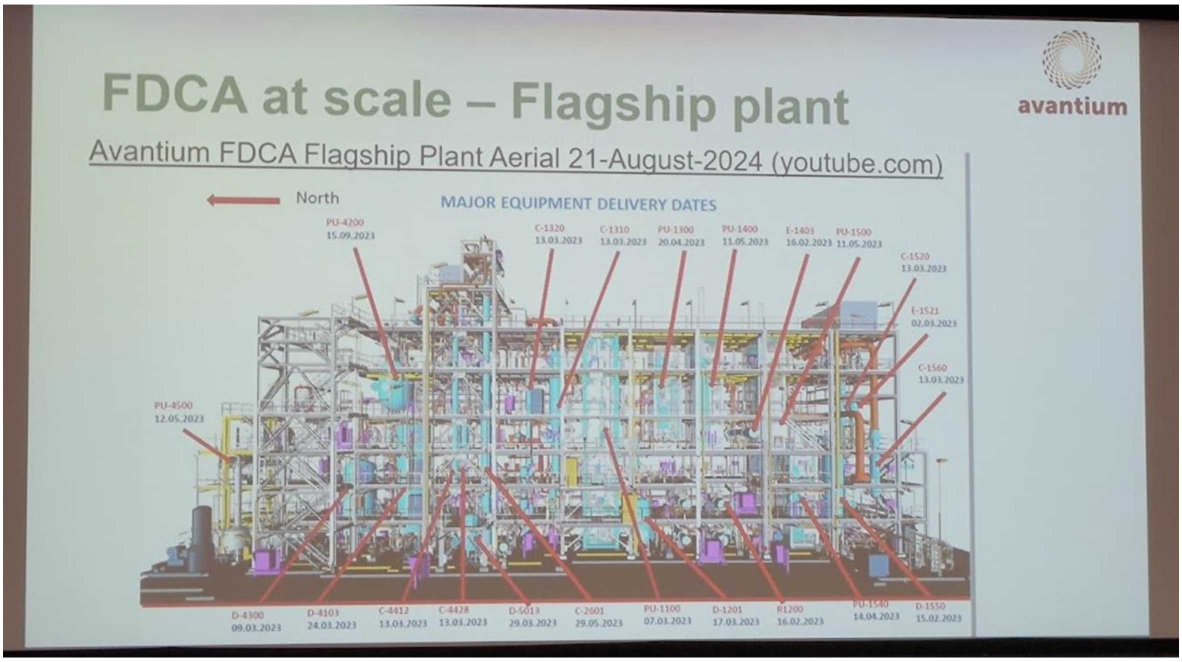
Further **accelerate licensing deployment**

NETHERLANDS

Chemie Park Delfzijl

Progress

- **15** offtake agreements **signed**
- First **commissioning activities** have started in **Q1 2024** and we are close to start up
- **FDCA production** expected on stream in **H2 2024**

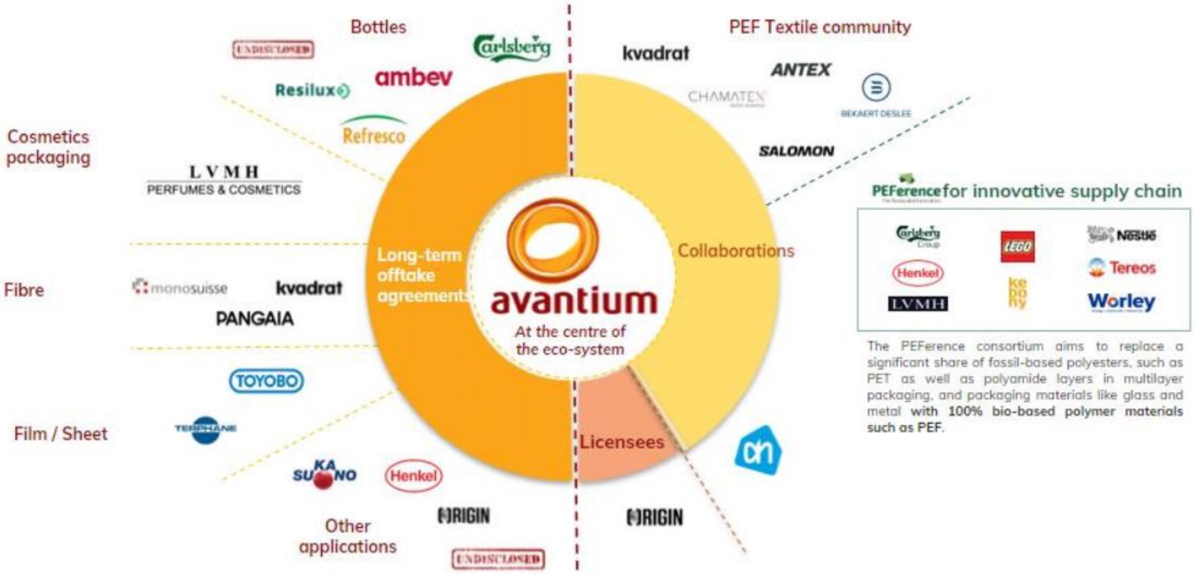


FDCA at scale – Flagship plant

avantium

Avantium FDCA Flagship Plant Aerial 21-August-2024 (youtube.com)

圖15、本次會議展示關於 Avantium 2024年中旬完工的旗艦 PEF 工廠的簡報。



The PEFerence consortium aims to replace a significant share of fossil-based polyesters, such as PET as well as polyamide layers in multilayer packaging, and packaging materials like glass and metal with 100% bio-based polymer materials such as PEF.

圖16、Avantium 的產業鏈及合作夥伴建立。來源：Avantium

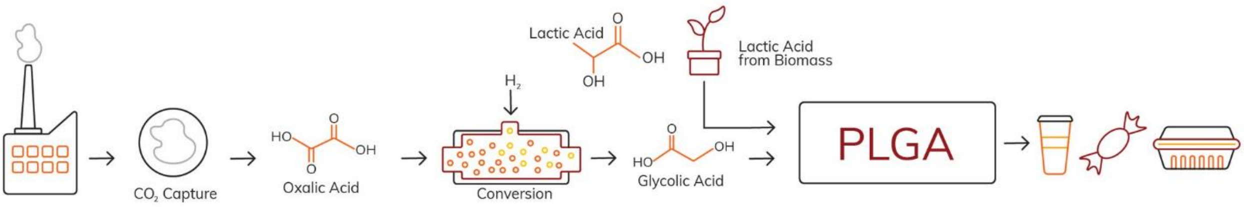
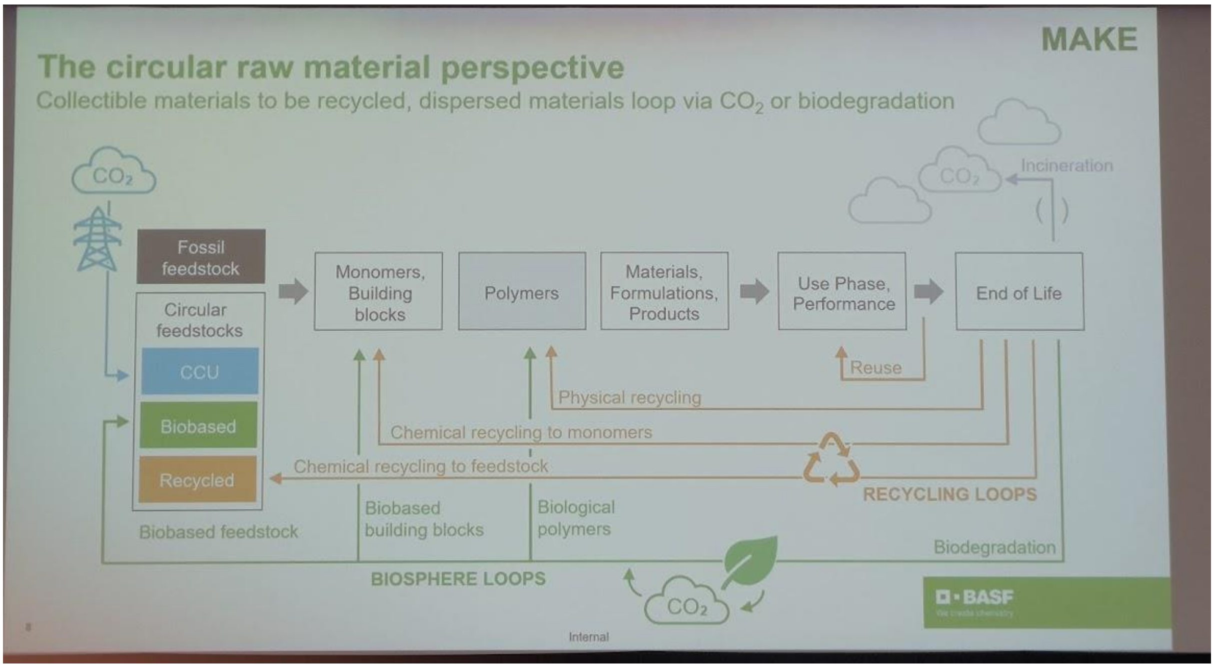


圖17、Avantium 和 SCGC 合作將二氧化碳基聚合物帶入試驗階段。來源：Avantium

另外讓我們也有興趣的是 Avantium 的 CCU(碳利用)相關技術平台之一為他們所謂的 Volta 技術，利用電化學將二氧化碳轉化為高價值產品和包括乙醇酸在內的化學構件。透過將乙醇酸與乳酸結合，Avantium 可以進一步生產聚乳酸-乙醇酸共聚物(PLGA)，具有出色的氧氣和濕氣阻隔性、良好的機械性能、可回收利用以及家庭可堆肥和海洋可降解，為一種優秀的負碳聚合物，這可以使 PLGA 成為不可降解的石化基聚合物等更永續和成本效益的替代品。自 2023 年初以來，Avantium 和 泰國皇象水泥集團旗下的化學公司 SCGC 一直在合作進一步評估 PLGA 的生產。雙方現已簽署聯合開發協議。根據該協議，在未來兩年內將乙醇酸單體和 PLGA 聚酯的生產規模擴大到試驗工廠。

4.3. 高分子回收永續利用

高分子塑膠材料使用的增加在過去幾十年中促進了許多經濟體的快速經濟增長，歸功於塑料輕便、性能容易調整且易於成型，因此能應用於人類食衣住行各個領域如汽車、包裝和住房等。然而高分子塑膠的耐用性使其成為環境日益嚴重的問題，與各種形式的生物質如木質素和幾丁質等相比，塑膠不易被微生物分解導致環境污染。塑膠的替代品不一定對環境產生積極的正面影響，由於替代包裝材料如玻璃或金屬容器重量較重會讓運輸過程中會增加二氧化碳排放。每年產生數百萬噸塑料廢料在釋放到環境中時對環境及生態系統造成損害，並且焚燒過程中會釋放大量二氧化碳，荷蘭烏特勒支大學 Ina Vollmer 教授在會議中表示二氧化碳排放的質量約為焚燒塑膠質量的三倍，因此，廢棄塑料代表著潛在的二氧化碳排放，占比相當於當前全球碳排放的2%。在過去幾十年中，高分子塑料價格低廉且缺乏回收的經濟激勵，且中國等國最近已開始拒絕來自國外的塑料廢料。關於目前立法對回收的鼓勵，歐盟的一項具有法律約束力的指令規定，所有塑料包裝到2030年應以具成本效益的方式可回收或可重用，並旨在使回收對企業有利可圖。這些法律驅動將促使政府機構和行業解決塑料回收問題，理想情況下以循環的方式實現價值創造。其他倡議包括國家和歐洲的塑料公約、終止塑料廢物聯盟以及艾倫·麥克阿瑟基金會的新的塑料經濟，呼籲減少、增加再利用和回收措施以應對全球挑戰，邁向循環高分子塑膠材料經濟。圖18為德國化工巨擘BASF 循環高分子部門的 Bernhard von Vacano 博士在本次會議展示的高分子聚合物價值鏈及生命週期，橘色為各式回收路線，綠色為生物路線，藍色為 CCU 碳利用路線，灰色為直接碳排放的開放路線。



MAKE

The circular raw material perspective

Collectible materials to be recycled, dispersed materials loop via CO_2 or biodegradation

圖18、德國 BASF 於本次會議中展示的循環高分子價值鏈。

荷蘭烏特勒支大學 Bert Weckhuysen 教授表示所有替代焚燒的處理方式都能將處置結束塑膠材料壽命 (End of Life, EoL) 時的二氧化碳排放降低，主要是避免了新資源的生產，圖19為不同塑料在結束使用時(EoL)各式處置方式的碳排量比較排名，以未回收能源的焚燒作為基準(100%)。廢棄塑料使用掩埋處理雖然碳幾乎不會釋放，但掩埋這個方式並不符合循環經濟的理念，且需要大量土地面積且還有可能會有有毒物質滲入土壤和地下水，除非採取昂貴的預防措施。在圖 xx 最右側的溶解/沉澱措施碳排最低，因其不需要打破或重新形成化學鍵，其次為溶劑解聚 (solvolysis)措施可有效地轉化為高價值的再生材料如 PET 再生材，而含添加劑的混合塑料進行機械回收由於再生材料品質較差會有較前兩種措施高的碳排放，熱解(Pyrolysis)產物可替代燃油和天然氣以降低焚燒過程中的碳排。

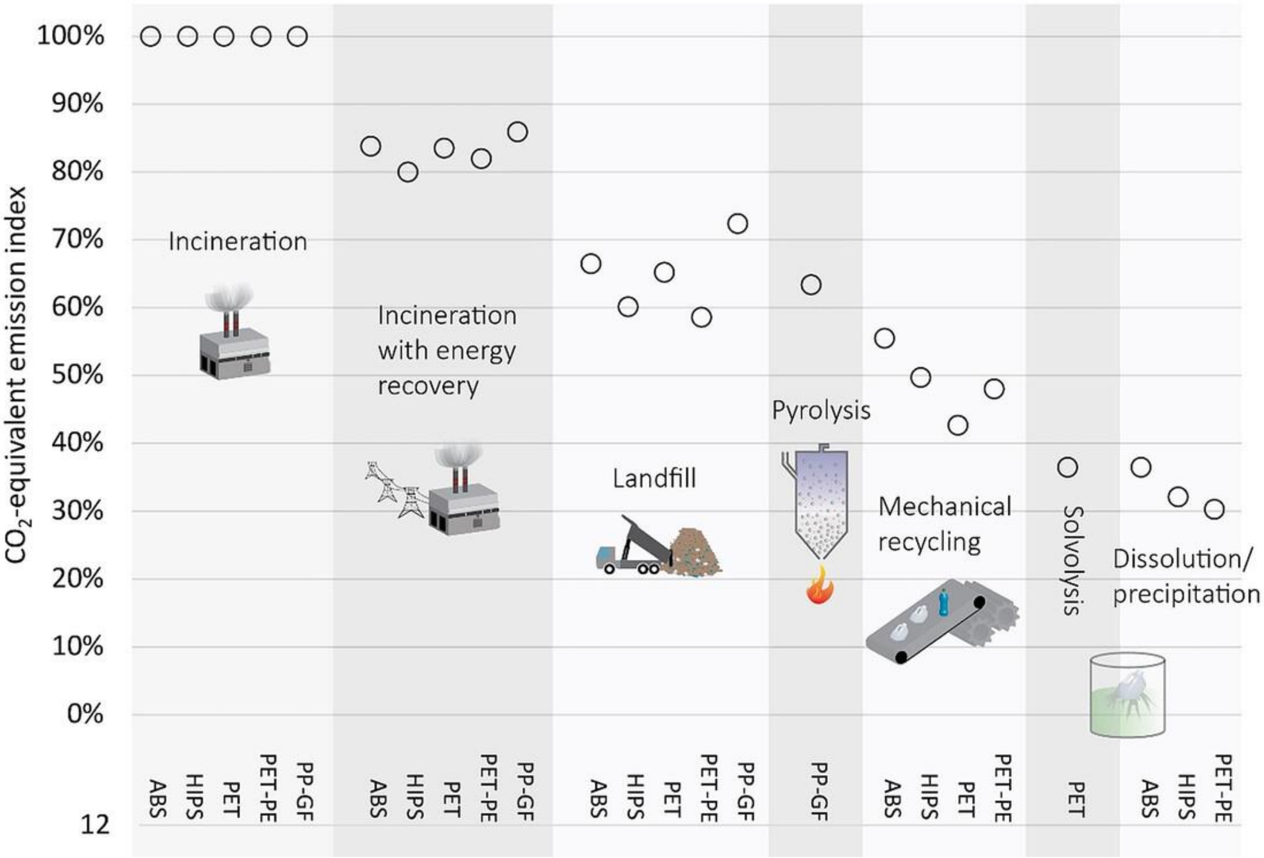


圖19、不同塑料在結束使用時(EoL)各式處置方式的碳排量比較排名。來源: doi.org/10.1002/anie.201915651

以減碳的觀點來看，再利用的措施在所有回收路徑中具有優勢，因其避免塑料處理再造、熱解及能源的消耗，但藉由再生能源供應對這些過程進行電氣化可助於降低對石化料源及能源的依賴。未來的聚合物生產可能會尋求可持續的單體來源途徑，例

如利用二氧化碳衍生的甲醇或生物質料源等，進一步減少產品的碳排放。

4.3.1.循環聚乙烯的化學回收發展

德國康士坦茲大學 Stefan Mecking 教授於會議介紹聚乙烯材料當前概況及未來關鍵的聚乙烯化學回收。聚乙烯是世界上生產量最大的合成聚合物，年產量超過一億噸，僅聚乙烯就佔整體塑料生產的約三分之一。與其他塑料相比，每生產一公斤聚乙烯的溫室氣體排放量相對較低，從原料原油開始到以能源回收的焚燒結束的整個生命週期會產生每公斤聚乙烯4.4公斤的二氧化碳當量。不同類型的聚乙烯由於生產過程及共聚物的成分含量造成其微觀結構有所不同，常見的高密度聚乙烯 (HDPE)、低密度聚乙烯 (LDPE) 和線性低密度聚乙烯 (LLDPE) 各自有許多不同的等級，其他衍生產物包括蠟和超高分子量聚乙烯 (UHMWPE)，雖然體積較小但仍然產量達到數百萬噸。聚乙烯的應用範圍非常廣由食品、紡織、包裝、繩材到建築等等，其生命週期也依應用不同而有寬廣的範圍，從一次性包裝級的短期使用時間到超過50年的建材應用。

聚乙烯的物理性機械回收相較於大多數其他塑膠材料 (除了 PET 外) 已相對成熟，但 Stefan Mecking 教授表示收集的廢棄聚乙烯材料目前仍然幾乎無法利用回收材來生產可達到相同應用材料以滿足理想的閉環循環回收系統，主要的原因如反覆加工和使用會導致聚合物性能的劣化，以及回收材帶有不同分子量分佈、不同穩定劑、不同助劑等等會讓機械回收變得相當複雜等。為了在我們永續的地球的環境需要建立可持續循環的高分子塑材經濟，必需建立現有聚合物的其他化學回收技術，以及設計可助益回收程序的大宗聚合物。

Stefan Mecking 教授提到聚乙烯化學回收技術門檻在於聚乙烯中飽和碳氫鏈的化學惰性和 C–C 鍵的一致性使其難以分解回乙烯單體，且飽和碳氫鏈轉化為烯烴單體在動力學上受到抑制，使得該類型反應在熱力學角度上不易實行。另外透過石化業熟知的熱解 (Pyrolysis) 生成液態碳氫化合物及其蒸汽裂解 (Steam Craking)以生成烯烴的兩個步驟均需要高達800°C 的高溫會消耗大量能源，且在目前在實際操作下乙烯的產量/回收率限制在約一到二成左右。為求降低反應溫度(約300˚C)以減少能耗，聚乙烯的催化裂解相關技術亦受到關注。 Stefan Mecking 教授在本次會議展示的聚乙烯及類聚合物的化學回收概念則在較溫和條件下進行(約低於200°C)，並可理想地避免高吸熱反應(見圖20)，從廢棄材料、天然植物油即可再生來源等資源獲取並製造聚乙烯類材料，透過聚乙烯鏈中的低密度鏈內功能基團如酯基來增益並實現化學回收，而生物降解則作為一種保護措施，防止不當管理的廢棄塑料在環境中累積。

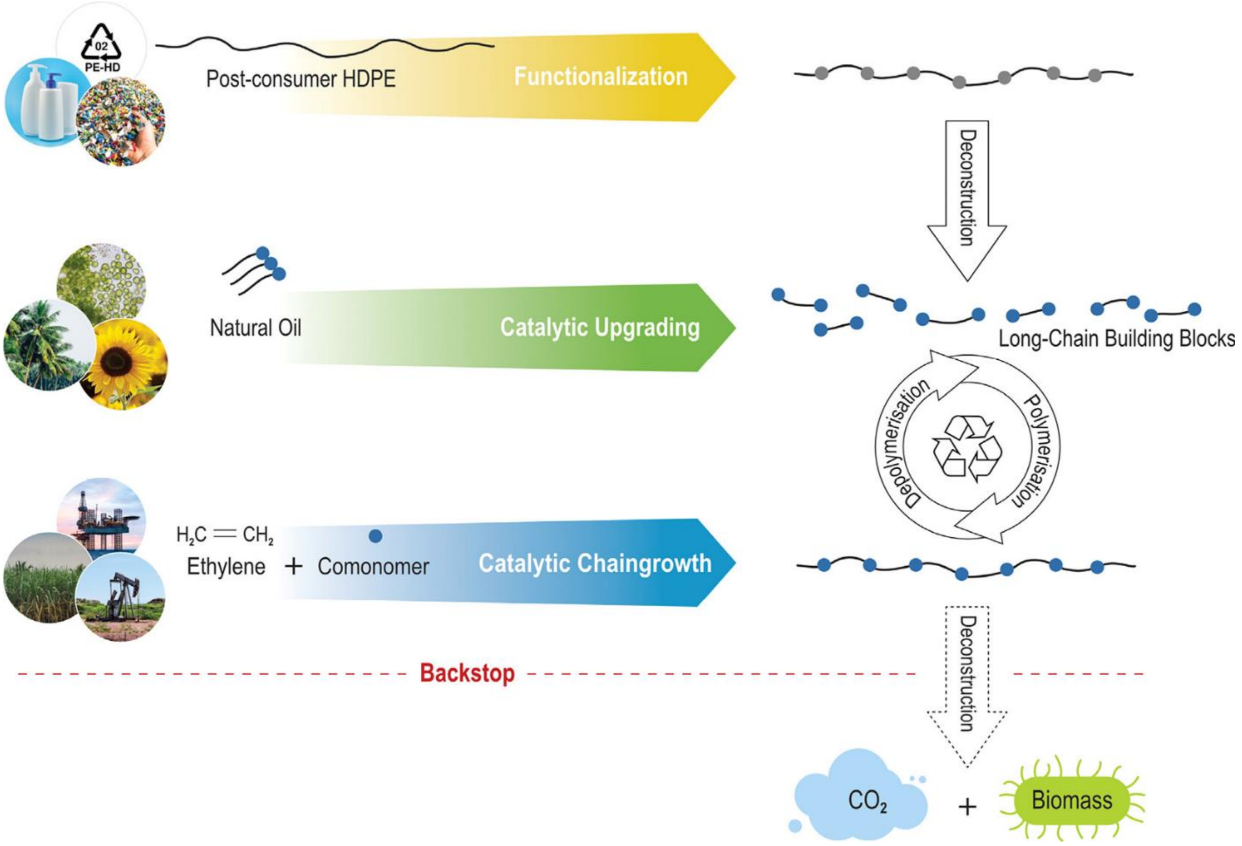
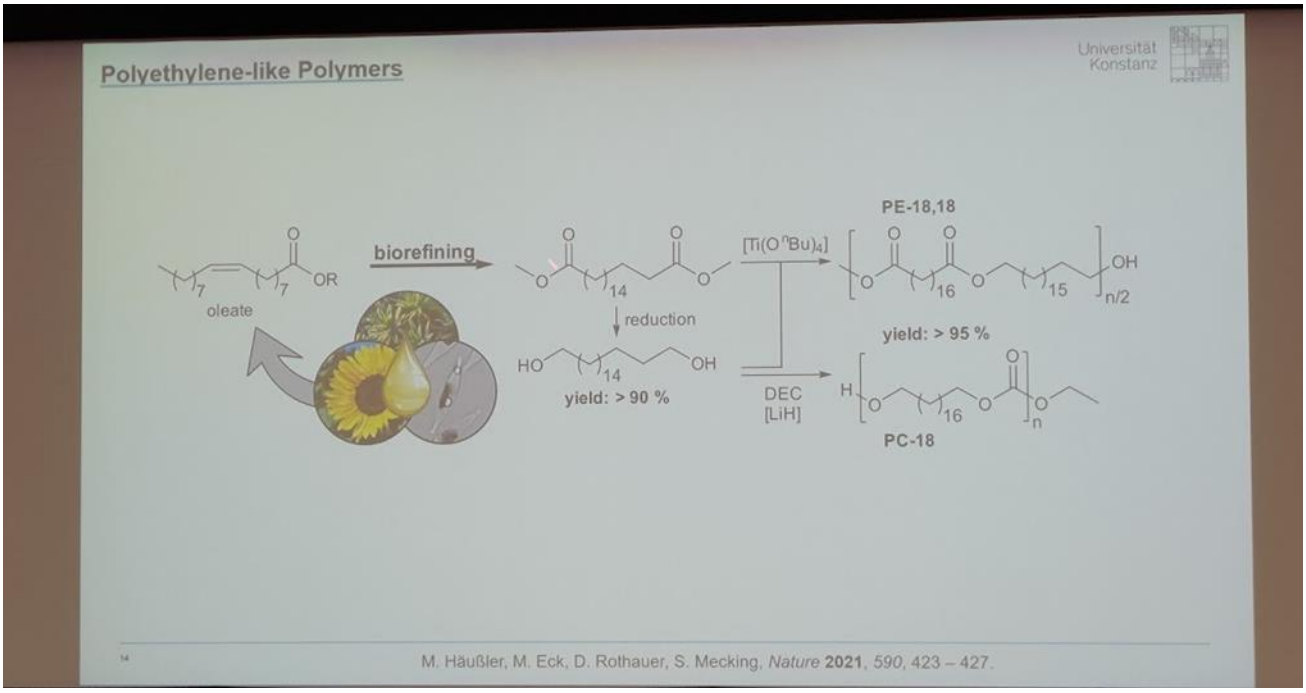


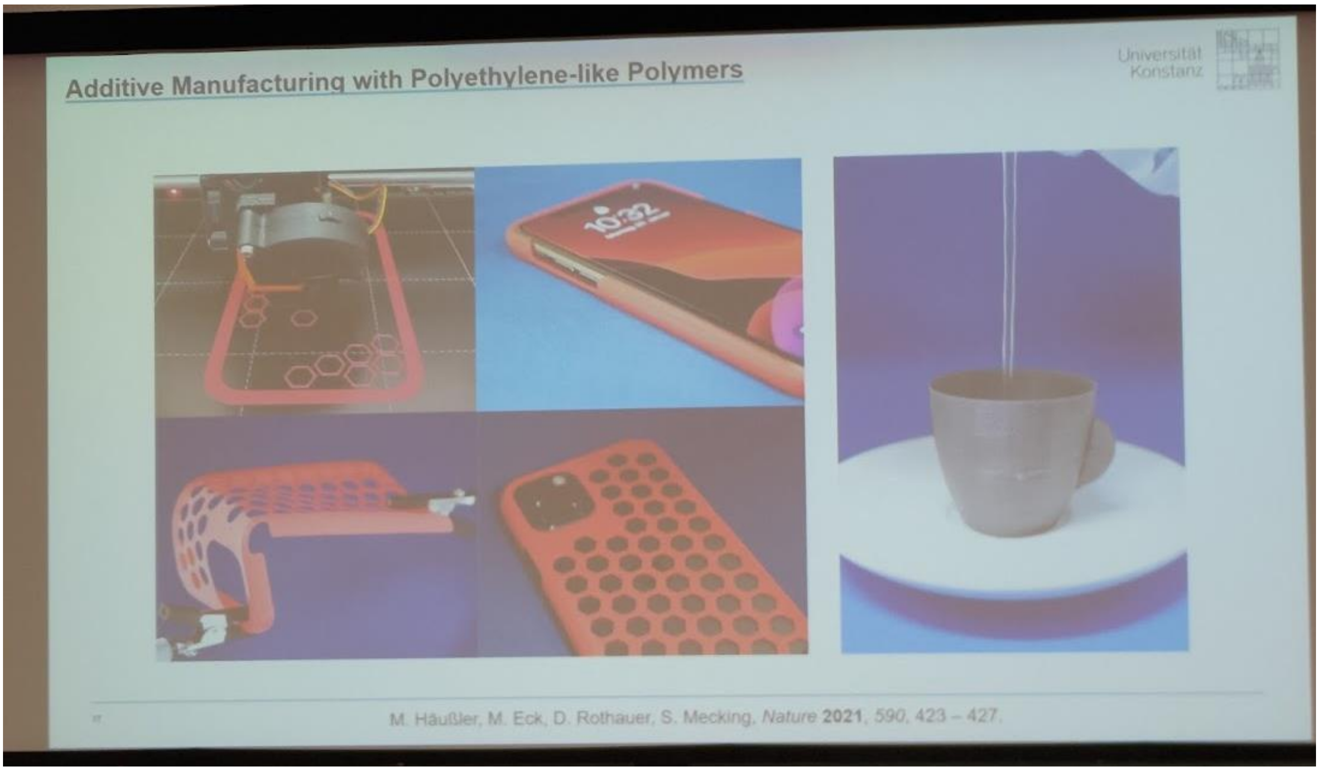
圖20、Stefan Mecking 教授於會議展示的聚乙烯類型材料的化學回收循環策略，從廢棄聚乙烯材料、天然植物油、石油及其他可再生料源的乙烯作為製造聚乙烯類型材料。來源: 10.1021/acs.chemrev.3c00587



Polyethylene-like Polymers

M. Häußler, M. Eck, D. Rothauer, S. Mecking, *Nature* **2021**, *590*, 423 – 427.

圖21、Stefan Mecking 教授研究團隊使用天然植物油開發可化學回收之聚乙烯類材料

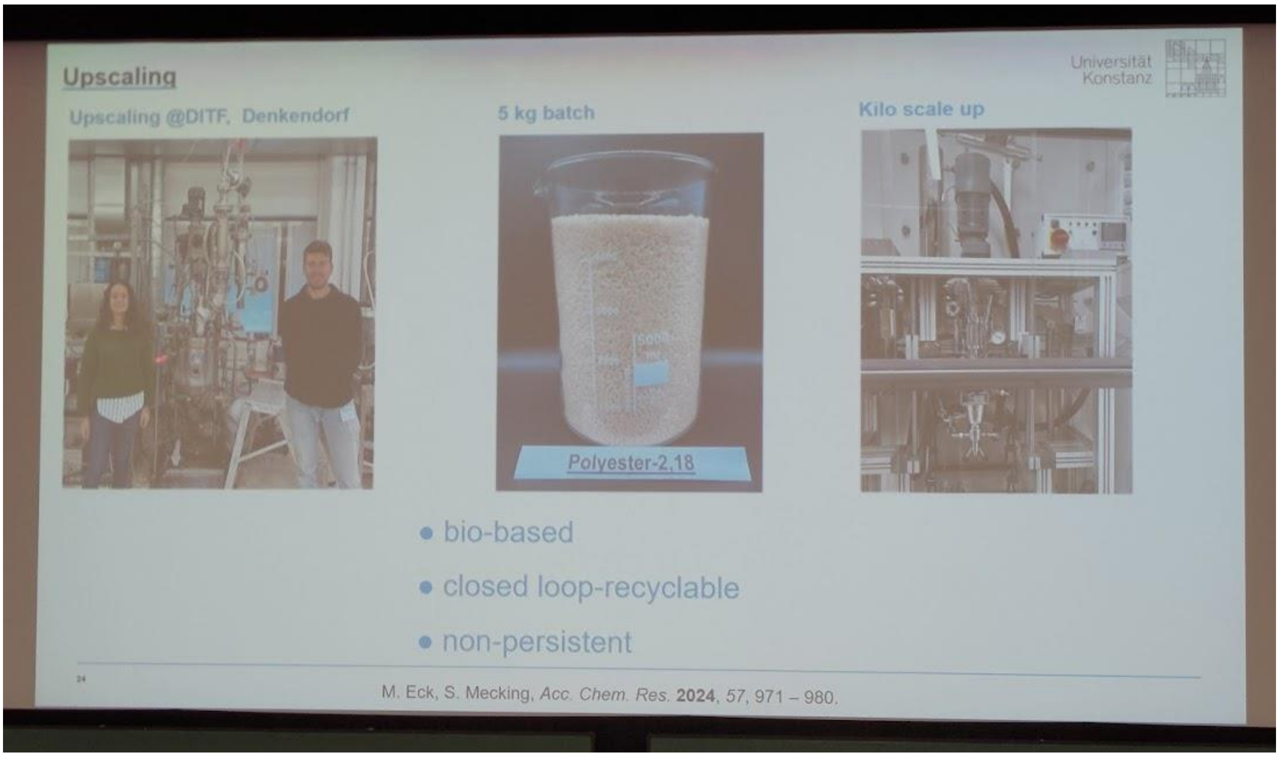


Additive Manufacturing with Polyethylene-like Polymers

Universität
Konstanz

M. Häußler, M. Eck, D. Rothauer, S. Mecking, *Nature* **2021**, *590*, 423 – 427.

圖22、Stefan Mecking 教授研究團隊使用天然植物油開發可化學回收之聚乙烯類材料作為3D 列印材料印出手機保護殼等應用



Upscaling

Universität
Konstanz

Upscaling @DITF, Denkendorf

5 kg batch

Kilo scale up

Polyester-2,18

- bio-based
- closed loop-recyclable
- non-persistent

M. Eck, S. Mecking, *Acc. Chem. Res.* **2024**, *57*, 971 – 980.

圖23、Stefan Mecking 教授研究團隊開發可化學回收之聚乙烯類材料之量級提升。該研究團隊亦與德國國內多個化工大廠如 BASF、LANXESS、BYK 及阿拉伯 Sabic 大型公司產學合作共同開發。

4.3.3. 德國 Covestro 公司的熱塑材料之永續循環

Covestro (台灣稱科思創)公司是一家總部位於德國 Leverkusen 的化學材料製造商，該公司於 2015 年從德國 Bayer 公司的塑膠部門誕生，之前稱為 Bayer Material。Covestro 在歐洲、亞洲和美洲均有設廠及據點開發、生產和銷售聚合物材料，台灣分公司位於彰化。 根據該公司財報，2023年該公司年銷售額143.77億歐元（前一年：179.68億歐元），息稅前利潤（EBIT）達1.86億歐元（前一年：2.67億歐元）。

Covestro 最著名的材料之一為聚碳酸酯(Polycarbonate, PC)，全球有約五分之一的聚碳酸酯於為公司所生產。Covestro 近期推出的 RP 系列聚碳酸酯材料如 Makrolon® RP 等是首款與化學回收的消費後廢塑料相關的產品，約有至少25%成分為回收料件。Makrolon® RP 的原料由合作夥伴 Neste 和 Borealis 提供：Neste 提供高品質的回收原料，然後由 Borealis 將其轉化為苯酚和丙酮，最後運送到 Covestro 的工廠用於生產 Makrolon® RP (圖25)。

Sustainability and circularity of technical thermoplastic polymers in industrial life cycles

Eckhard Wenz
Business Entity Engineering Plastics
R&D – Development Blends

covestro.com

GDCh Makro 2024

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圖24、Covestro 工程混合塑膠部門研發長 Eckhard Wenz 博士於本次會議演講

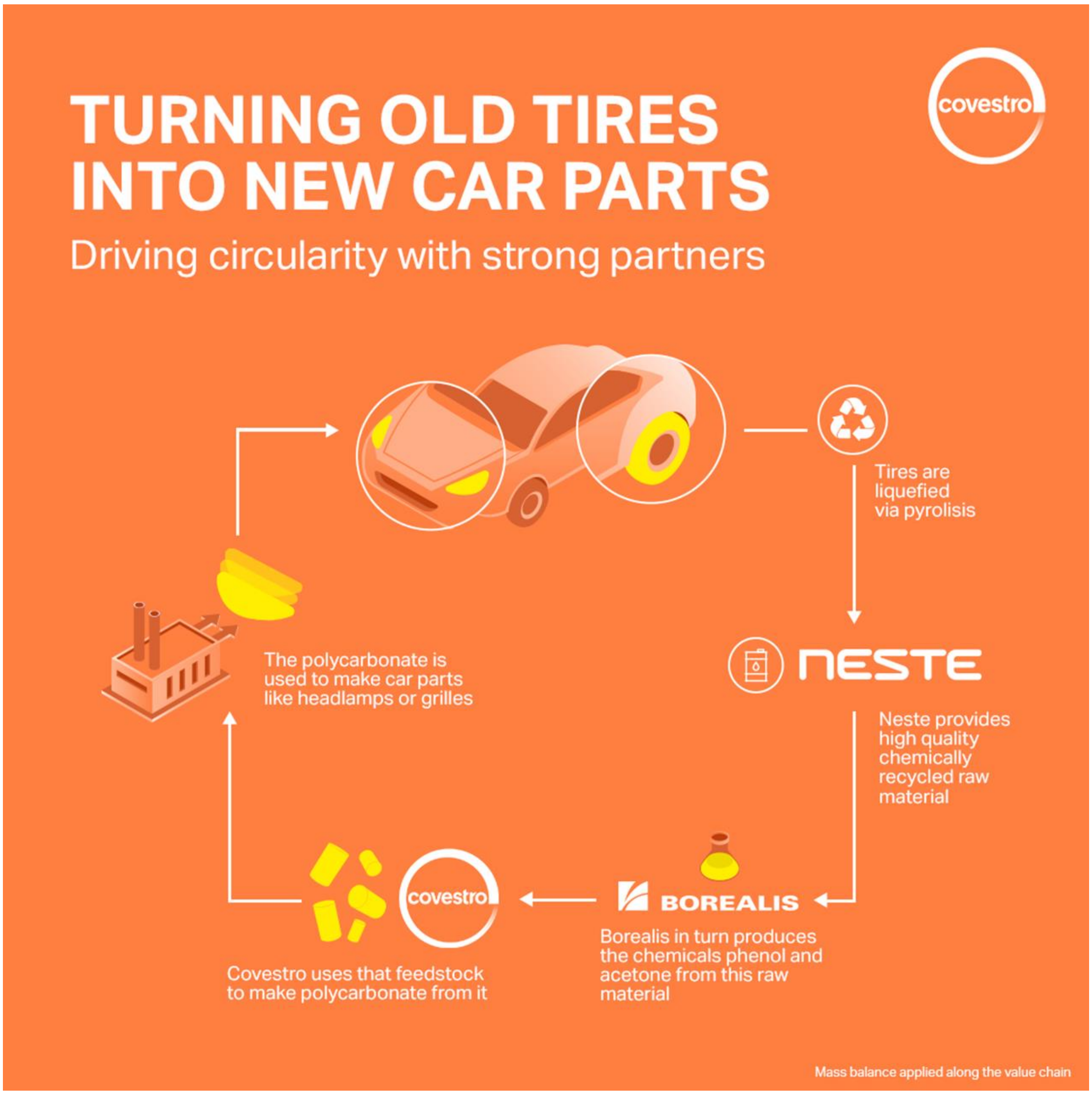
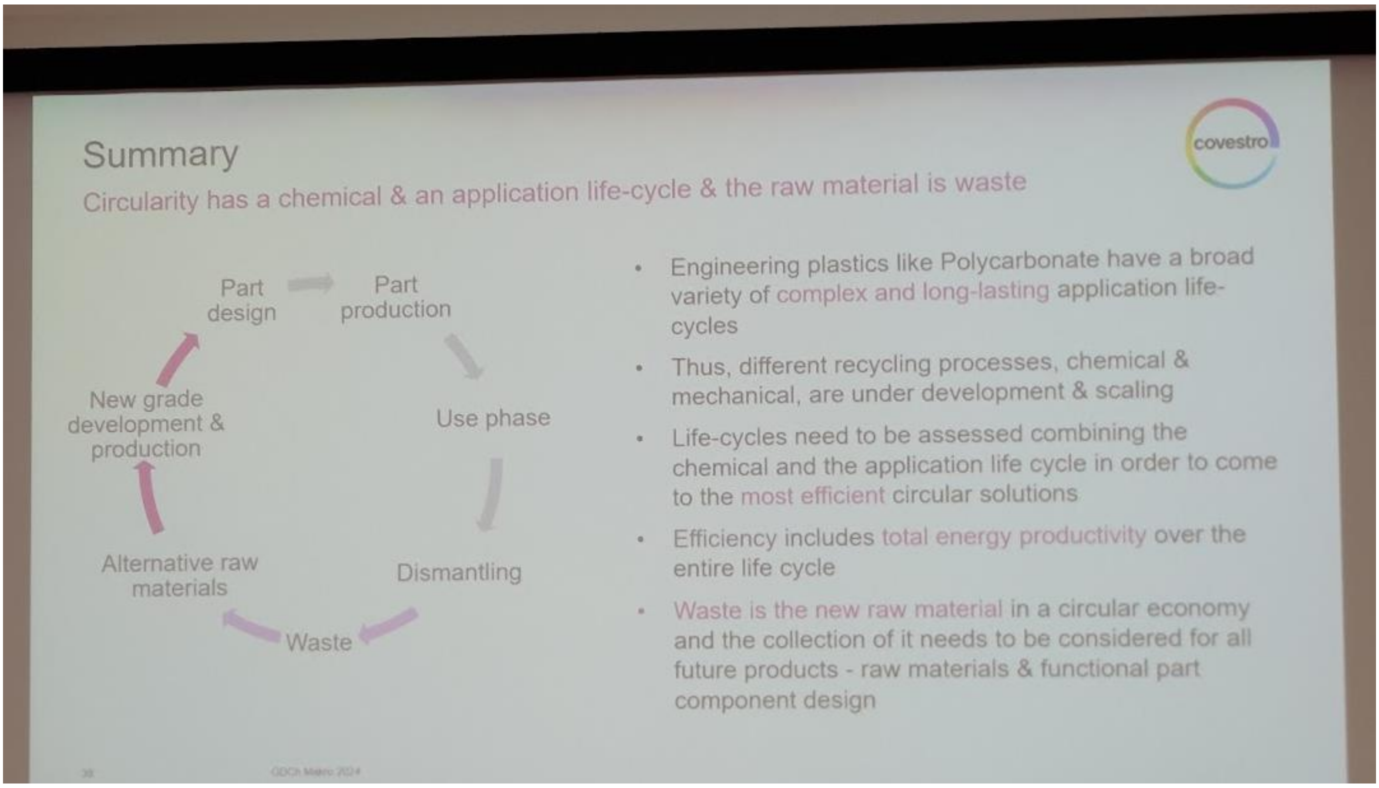


圖25、Covestro 與合作夥伴使用廢塑料源生產循環聚碳酸酯材料。來源：Covestro

Covestro 對於聚碳酸酯的化學回收製程一直投入開發，廢棄塑膠被轉化回其原料單體以便作為替代原料返回生產過程，目前正在工業規模化的過程，製程最佳化當中的階段。透過回收的塑膠取代了生產中的主要石化原料，Covestro 採用多種綜合回收方式有助於氣候中和和環境的保護，其中聚碳酸酯的物理性機械回收已成為科思創回收策略的重要組成部分，當廢塑料足夠乾淨且回收的聚碳酸酯已可滿足需求時，會使用較低成本的機械回收。Covestro 認為化學回收可與機械回收相輔相成，化學回收可以使不適合機械加工的較大量體的廢塑流可供回收轉化成原料單體，可以生產滿足較高品質要求的高分子材料。

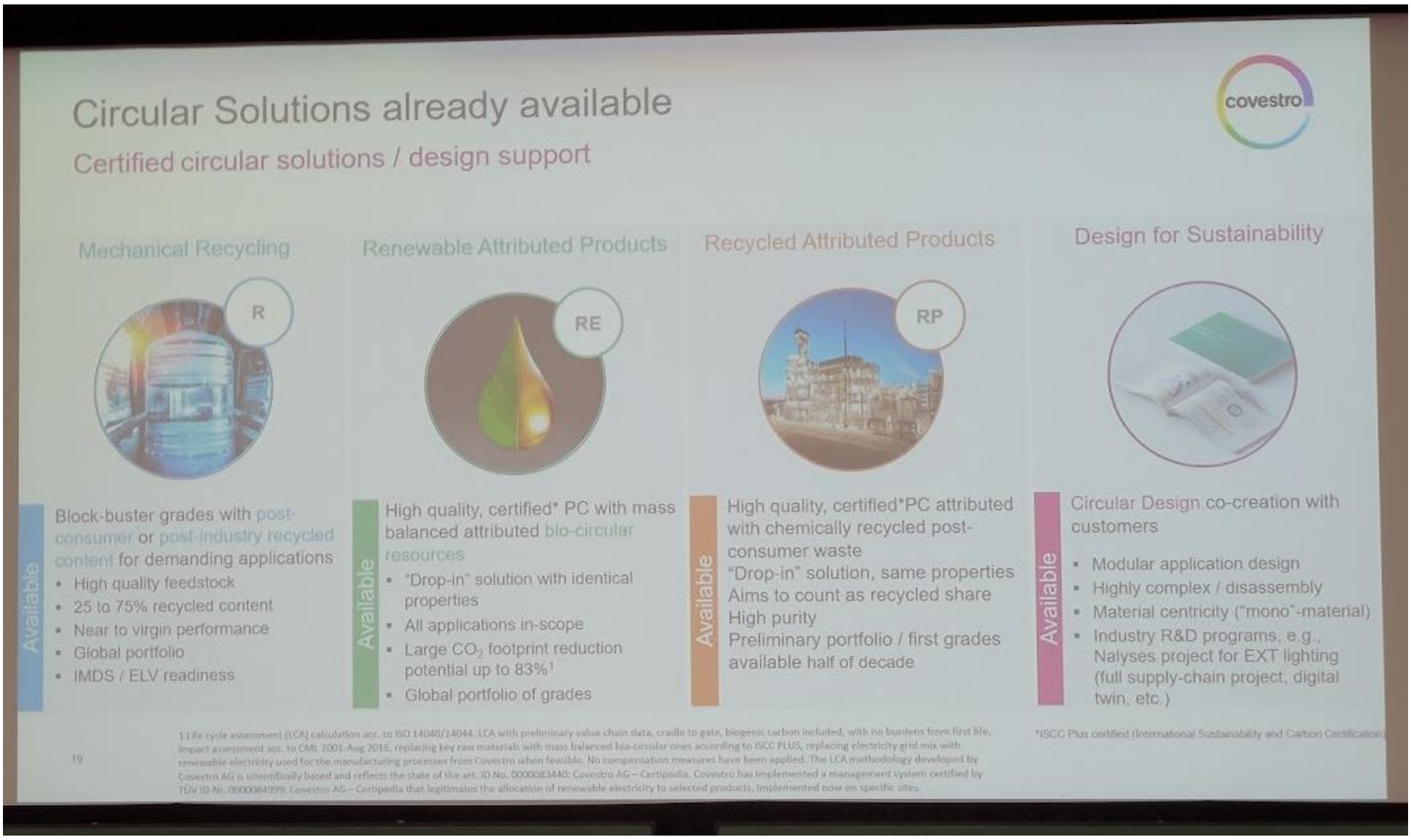


Summary

Circularity has a chemical & an application life-cycle & the raw material is waste

- Engineering plastics like Polycarbonate have a broad variety of complex and long-lasting application life-cycles
- Thus, different recycling processes, chemical & mechanical, are under development & scaling
- Life-cycles need to be assessed combining the chemical and the application life cycle in order to come to the most efficient circular solutions
- Efficiency includes total energy productivity over the entire life cycle
- Waste is the new raw material in a circular economy and the collection of it needs to be considered for all future products - raw materials & functional part component design

圖26、Eckhard Wenz 博士對於 Covestro 開發生產循環材料化學品的總結



Circular Solutions already available

Certified circular solutions / design support

Mechanical Recycling

Block-buster grades with post-consumer or post-industry recycled content for demanding applications

- High quality feedstock
- 25 to 75% recycled content
- Near to virgin performance
- Global portfolio
- IMDS / ELV readiness

Renewable Attributed Products

High quality, certified* PC with mass balanced attributed bio-circular resources

- "Drop-in" solution with identical properties
- All applications in-scope
- Large CO_2 footprint reduction potential up to 83%[1]
- Global portfolio of grades

Recycled Attributed Products

High quality, certified*PC attributed with chemically recycled post-consumer waste
"Drop-in" solution, same properties
Aims to count as recycled share
High purity
Preliminary portfolio / first grades available half of decade

Design for Sustainability

Circular Design co-creation with customers

- Modular application design
- Highly complex / disassembly
- Material centricity ("mono"-material)
- Industry R&D programs, e.g., Nalyses project for EXT lighting (full supply-chain project, digital twin, etc.)

[1] Life cycle assessment (LCA) calculation acc. to ISO 14040/14044. LCA with preliminary value chain data, cradle to gate, biogenic carbon included, with no burdens from first life, impact assessment acc. to CML 2001-Aug 2016, replacing key raw materials with mass balanced bio-circular ones according to ISCC PLUS, replacing electricity grid mix with renewable electricity used for the manufacturing processes from Covestro when feasible. No compensation measures have been applied. The LCA methodology developed by Covestro AG is scientifically based and reflects the state of the art. ID No. 0000083440: Covestro AG – Certipedia. Covestro has implemented a management system certified by TÜV ID-Nr. 0000084999: Covestro AG – Certipedia that legitimates the allocation of renewable electricity to selected products, implemented now on specific sites.

*ISCC Plus certified (International Sustainability and Carbon Certification

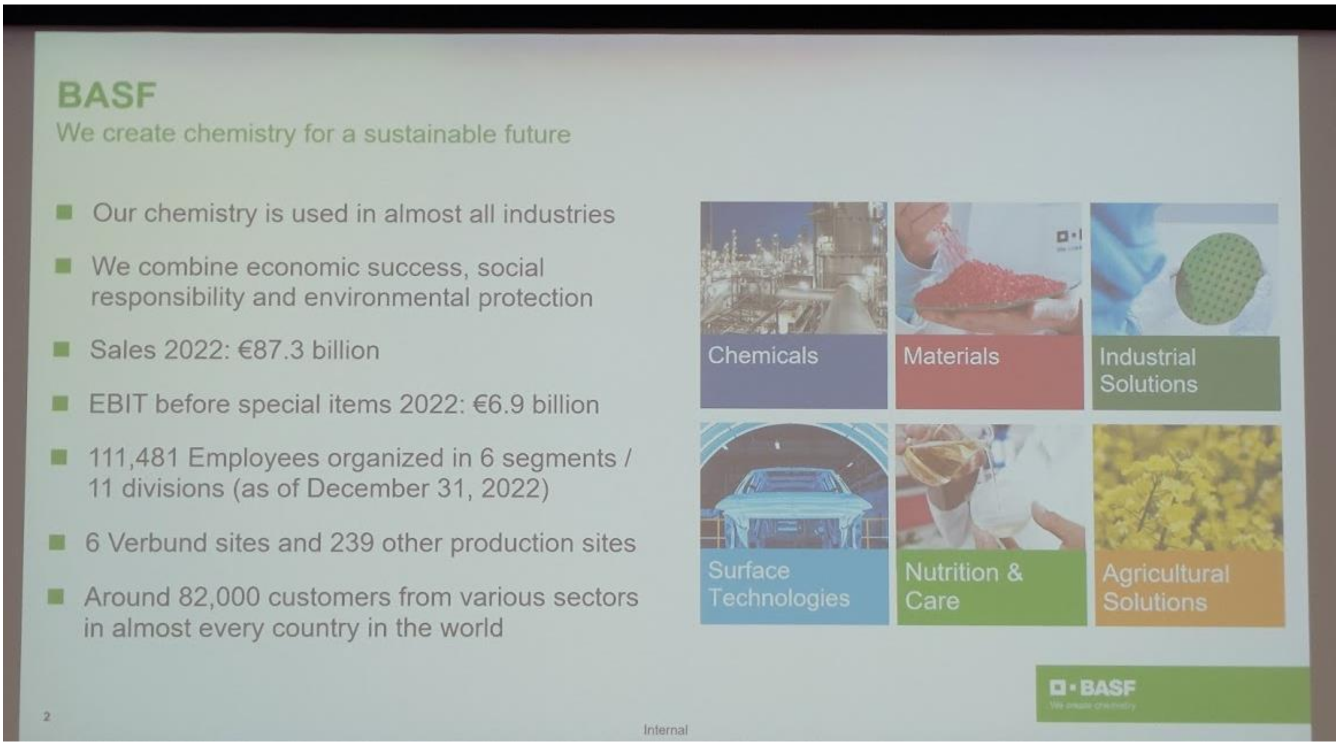
圖27、Covestro 循環策略，左一為機械回收(R 系列)，左二為生質再生資源(RE 系列)，右二為使用化學回收等的廢塑料源(RP 系列)，右一為材料設計會以可回收循環為主

4.3.5.BASF 的循環三角 Go Create

BASF
We create chemistry

We create chemistry
for a sustainable future

圖28、BASF 近期推出的循環三角 Go! Create 以製造、使用及回收做為一個完整循環



BASF
We create chemistry for a sustainable future

- Our chemistry is used in almost all industries
- We combine economic success, social responsibility and environmental protection
- Sales 2022: €87.3 billion
- EBIT before special items 2022: €6.9 billion
- 111,481 Employees organized in 6 segments / 11 divisions (as of December 31, 2022)
- 6 Verbund sites and 239 other production sites
- Around 82,000 customers from various sectors in almost every country in the world

2

Internal

圖29、會議提到 BASF 的概況

德國 BASF 循環高分子部門的明日之星 Bernhard von Vacano 博士在本次會議介紹了 BASF 再循環高分子的策略與因應，他認為建立塑膠材料的循環經濟、終結廢棄物

浪潮和達成淨零氣候中和方面的目標，需要相對應的大規模下的經濟循環運作，未來可預期將使用壽命結束的塑料做為產業源料源，且資源的可用性、品質及價格是決定價值鏈能否轉型的關鍵因素。

Bernhard von Vacano 博士將眾人熟知的高分子金字塔進行整理改造(圖30)，可透過該金字塔進行評估聚合材料的功能、預期使用期限及成本等等，該金字塔根據高分子結構特性(無定形與半結晶)來將已商業廣泛應用的聚合物(熱塑性塑料)分成不同組別，並按性能將其分層為大眾塑料、工程塑料和專業工程塑料。隨著性能的提升材料的價格也會上升，價格從大約1－2美元/公斤的大眾塑料到數十美元/公斤的高性能專業聚合物不等。以經濟學的角度來看性價比最划算的材料會被決定使用，因此聚合物的選擇取決於性能需求的充分性以及同時將成本最小化，這一點可以從生產量上也可以觀察的到，從大眾常用材料到專業高性能材料的生產量逐漸減少。

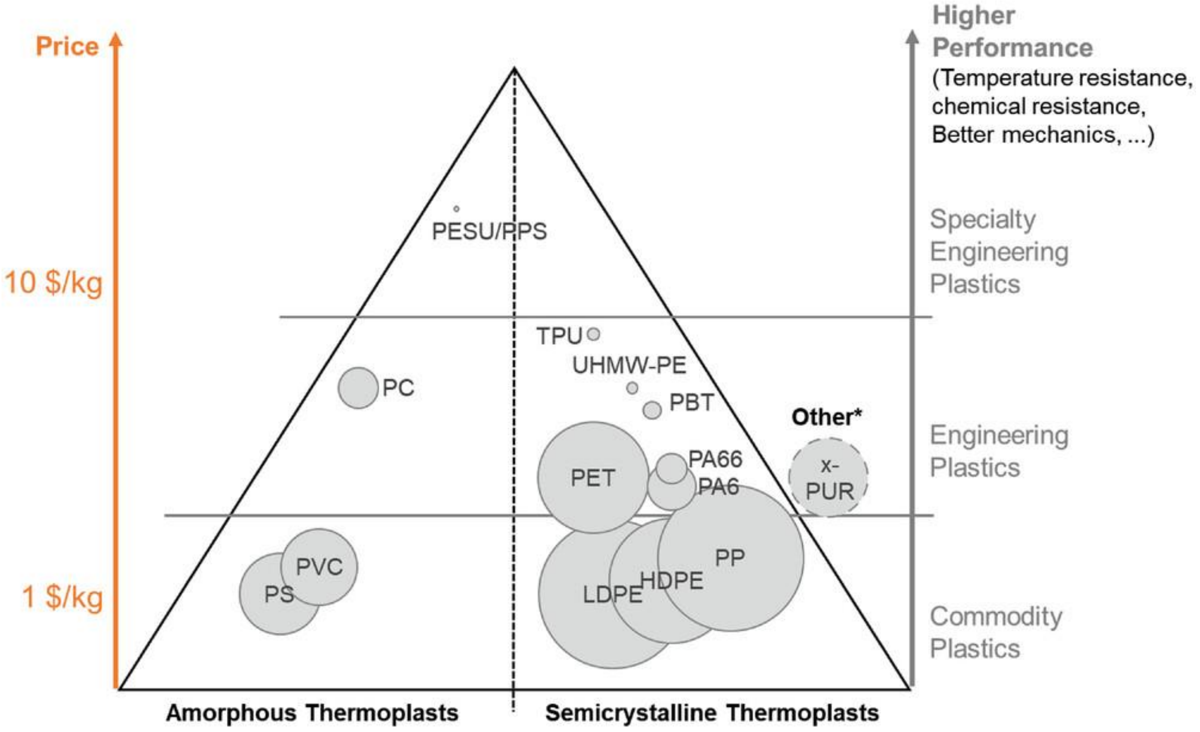
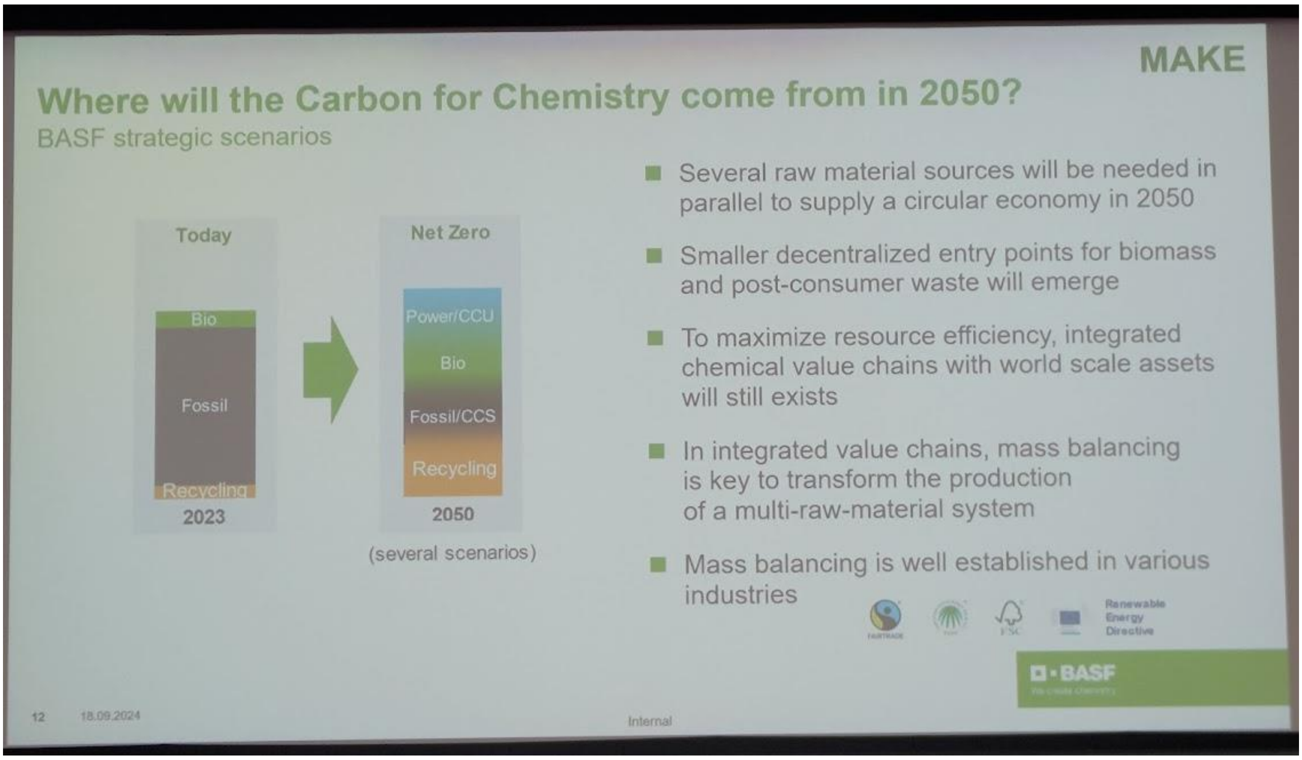


圖30、Bernhard von Vacano 博士於本次會議上提到的聚合物金字塔，根據高分子微觀結構將一些示例聚合物進行分組 (左側為無定形，右側為半結晶)。y 軸表示材料性能的提升(如機械性能、耐熱性)以及每公斤的材料價值(以美元計/2015年)。圖中各個圓氣泡的大小反映了2015年的相對生產量。圖內縮寫依序為 LDPE：低密度聚乙烯，HDPE：高密度聚乙烯，PP：聚丙烯，PS：聚苯乙烯，PVC：聚氯乙烯，PA6：聚酰胺-6，PA66：聚酰胺6,6，PET：聚對苯二甲酸乙二醇酯，x-PUR：交聯聚氨酯，PBT：聚對苯二甲酸丁二醇酯，PC：聚碳酸酯，UHMW-PE：超高分子量聚乙烯，TPU：熱塑性聚氨

酯，PESU：聚醚碸，PPS：聚苯硫醚。* x-PUR 不是熱塑性材料但為了比較而納入圖內。來源 : BASF 及 doi.org/10.1002/macp.202100488。

Bernhard von Vacano 博士表示在聚合物金字塔底部的材料通過不斷創新來調整性能，升級至下一個性能級別的應用，並以其有利的低成本優勢和既有的規模經濟進行競爭。這也為塑料回收材料設定了格式，若缺乏如回收內容的法規要求或補貼或對原本石油基高碳排等材料的罰款等措施的情況下，任何回收材料都會在各自的性能級別上與原材料競爭。回收的經濟與原材料的價值鏈不同：成本不再是原料的成本，而是收集、分類和預處理的成本。原材料的生產成本被相應的回收過程步驟的成本所取代。對於回收來說，原料需要以穩定的數量提供，並且在缺乏法規干預的情況下成本必須足夠低。回收料流的品質如聚合物材料的純度及污染物的存在等等直接決定了下列後續項目：1) 隨後分類和清洗步驟的成本；2) 回收過程的強度；以及 3) 可達到的品質、性能特性和市場的可能售價。為了實現成本和能源高效的回收，收集和分類是關鍵的前提條件。PET 寶特瓶回收系統是一個高效收集的範例，德國使用 PET 瓶的押金制度，幫助收集超過95%的 PET 瓶成就非常高的機械回收率，因為相對純淨的廢料流容易獲得。



MAKE

Where will the Carbon for Chemistry come from in 2050?

BASF strategic scenarios

- Several raw material sources will be needed in parallel to supply a circular economy in 2050
- Smaller decentralized entry points for biomass and post-consumer waste will emerge
- To maximize resource efficiency, integrated chemical value chains with world scale assets will still exists
- In integrated value chains, mass balancing is key to transform the production of a multi-raw-material system
- Mass balancing is well established in various industries

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圖31、BASF 藍圖策略中預測材料碳源會由2023年大部分出自石化，但到淨零2050年時會轉以生物質、回收材、石化+CCS、綠電+CCU 這四個碳源。

關於促進循環性的通用分子設計策略，Bernhard von Vacano 博士也在會議中大致分享方向，各類型聚合物的獨特結構特徵對各自聚合物的循環潛力非常重要。如上述Stefan Meking 教授團隊等的研究開發，酯基/酯鍵的功能性已經被應用導入可循環聚乙烯類高分子設計，更多的應用於聚酯胺(polyesteramides)和聚氨酯(PU)基本組件的情況下。由圖32所示，改善材料的循環潛力的分子設計策略包括：(1) 透過對分子層面的干預來降低系統層面的材料複雜性如分子量分佈控制，(2) 藉由重新單體化(分解成相對應的單體或基本組件)以促進回收效能，(3) 將熱固性材料轉變為熱塑性材料，同時仍然滿足相同的應用需求，以及 (4) 透過改質現有的天然生物聚合物來加以利用。

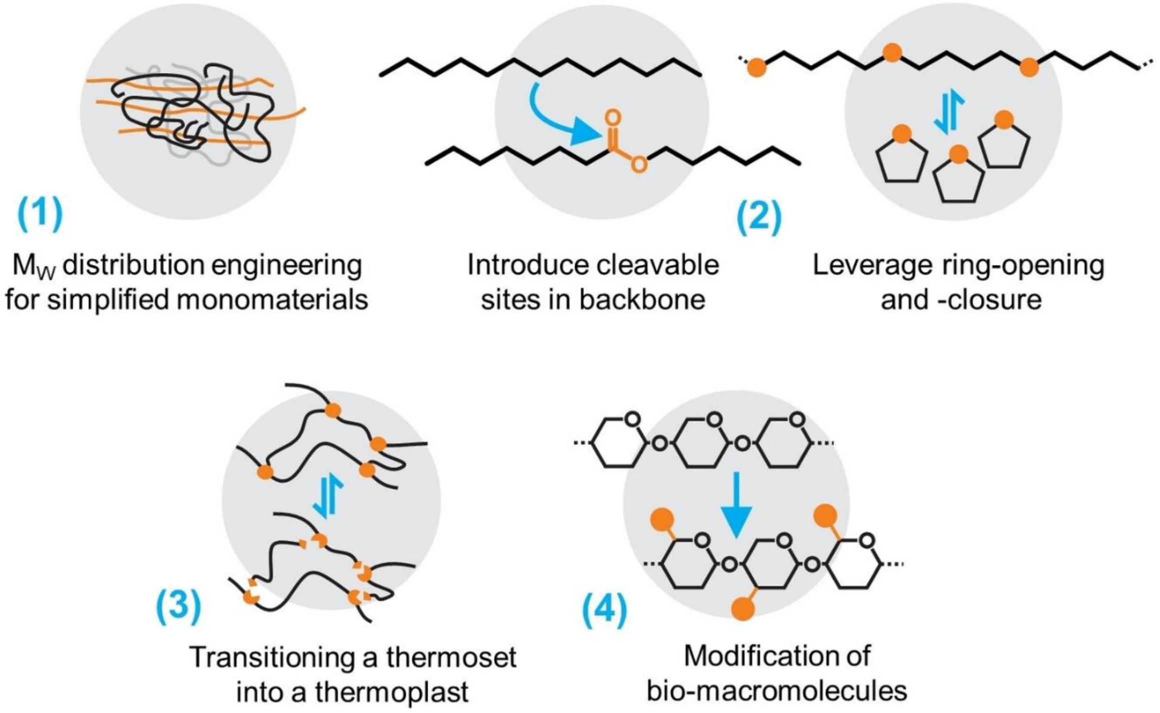


圖32、Bernhard von Vacano 博士於會議提到的「促進循環性的通用分子設計策略」。來源: doi.org/10.1002/anie.202210823

新興技術可使我們能夠將越來越多的塑料廢物回收成高價值應用例如能回到與第一次(Virgin)使用時相同的性能應用中；聚合物在重複加工和老化過程中的內在降解以及以廢棄物做為原料中不可避免的外在異物和污染都是最根本的挑戰，因這兩者都會直接影響性能和應用價值。對於被賦予特定性能的工程塑膠來說，任何性能損失都會直接被質疑其可用性，且高性能塑料通常價格較高以及從原料生產中產生的碳排放負擔也較高，雖然相較於常見大宗塑料產量較小但這些材料對更複雜的回收技術提供了潛在的發展機會及價值。廢棄塑料的可用性和純度是影響經濟性的關鍵因素，這兩者均可通過分類改善、回收性設計（design for recycling, DfR）和新的循環商業模式來直

接解決。發展促進循環回收技術如添加劑、回收需求時的斷鍵機制、改善機械回收中的熔融加工，以及化學回收的同時也要避免性能也被降低瓦解是至關重要的。新型循環取向聚合物在使用壽命結束時可以提供優勢，但在市場推出時會面臨與現行商品競爭的高障礙；回收產業鏈的數位轉型將會進一步支持塑料循環經濟的發展，要實現所有高分子塑膠材料的真正循環經濟，需要在價值鏈上進行合作，包括原料供應、材料生產、成品應用及使用，並最終盡可能以控制的方式返還塑材，政府當局的政策支持將是必要的，以使塑料廢物的填埋和焚燒變得不具吸引力以促進塑料回收，且具有必須回收的強制性政策也可以為回收市場需求產生增益效果。物理性機械和化學回收技術在許多方面是互補的，可共同協助我們實現塑料循環經濟的雄心目標，特別是在高價值應用的聚合物方面(圖33)。監管機構應中立地定義回收技術以涵蓋不同的可持續回收技術，對於這些技術可以通過生命周期評估(LCA)進行評估，並建立擴展生產者責任制度可以進一步促進回收足夠量和品質的廢棄塑料以達高效的回收效果。這些監管發展、技術進步的動態以及循環經濟與溫室氣體排放中和之間的內在聯繫，將會在未來持續塑造高分子塑膠產業的未來。

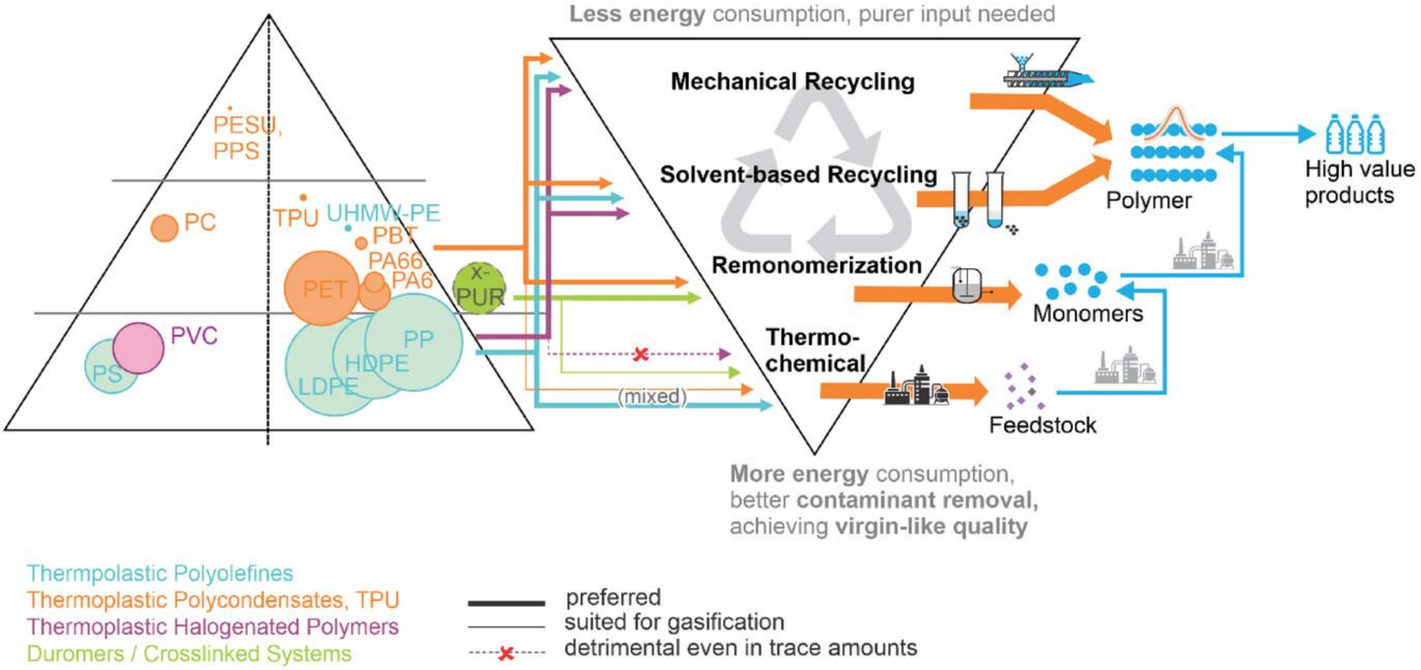
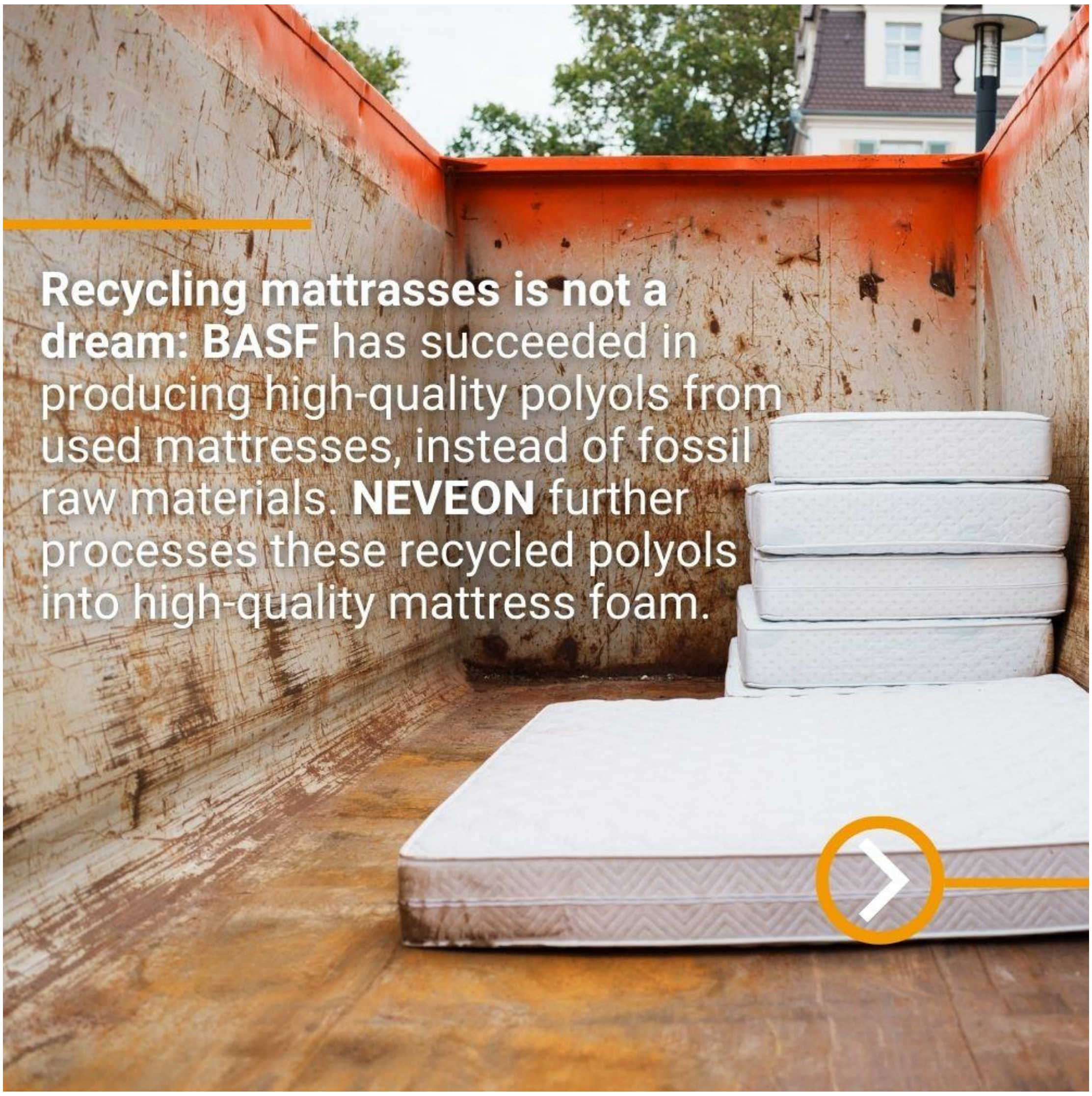
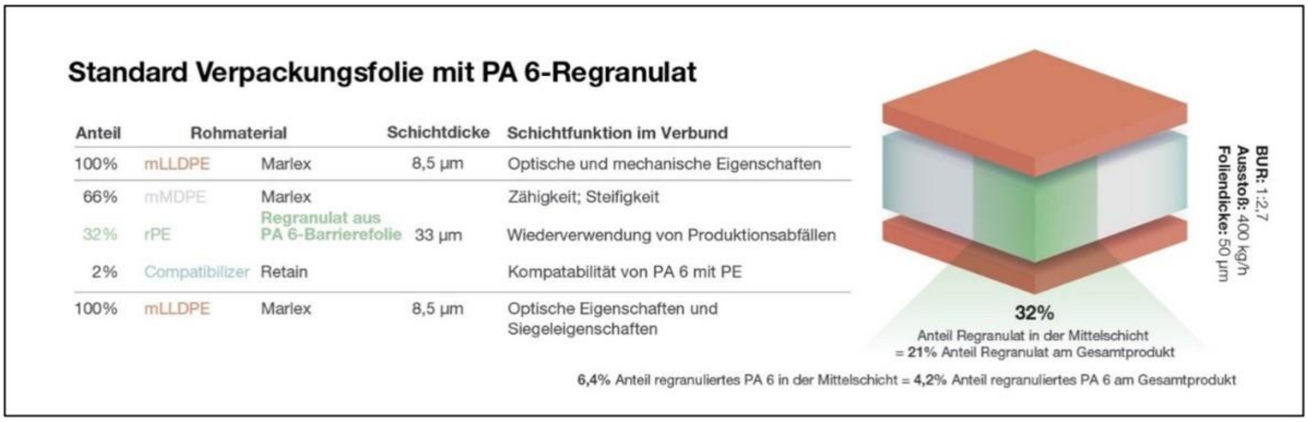


圖33、不同的廢棄塑料需使用不同的回用策略，閉環回收回高價值產品的回收技術方案的示意圖。只要能滿足高價值應用的必要性能，就優先選擇能耗最低和化學結構保值最高的方法。透過化學回收方法可以實現與原始產品相當的品質，如透過熱解或氣化進行再單體或熱化學轉化為原料。來源：doi.org/10.1002/macp.202100488



Recycling mattrasses is not a dream: BASF has succeeded in producing high-quality polyols from used mattresses, instead of fossil raw materials. **NEVEON** further processes these recycled polyols into high-quality mattress foam.

圖34、BASF 回收床墊材料。先前使用過的床墊經過 BASF 開發的回收程序以生產回收多元醇。 合作夥伴 Neveon 接著對此材料進行加工，製造出高品質的床墊使用之發泡材，其中 80%的成分為回收料。來源：BASF



Standard Verpackungsfolie mit PA 6-Regranulat

Anteil	Rohmaterial		Schichtdicke	Schichtfunktion im Verbund
100%	mLLDPE	Marlex	8,5 µm	Optische und mechanische Eigenschaften
66%	mMDPE	Marlex	33 µm	Zähigkeit; Steifigkeit
32%	rPE	Regranulat aus PA 6-Barrierefolie		Wiederverwendung von Produktionsabfällen
2%	Compatibilizer	Retain		Kompatabilität von PA 6 mit PE
100%	mLLDPE	Marlex	8,5 µm	Optische Eigenschaften und Siegeleigenschaften

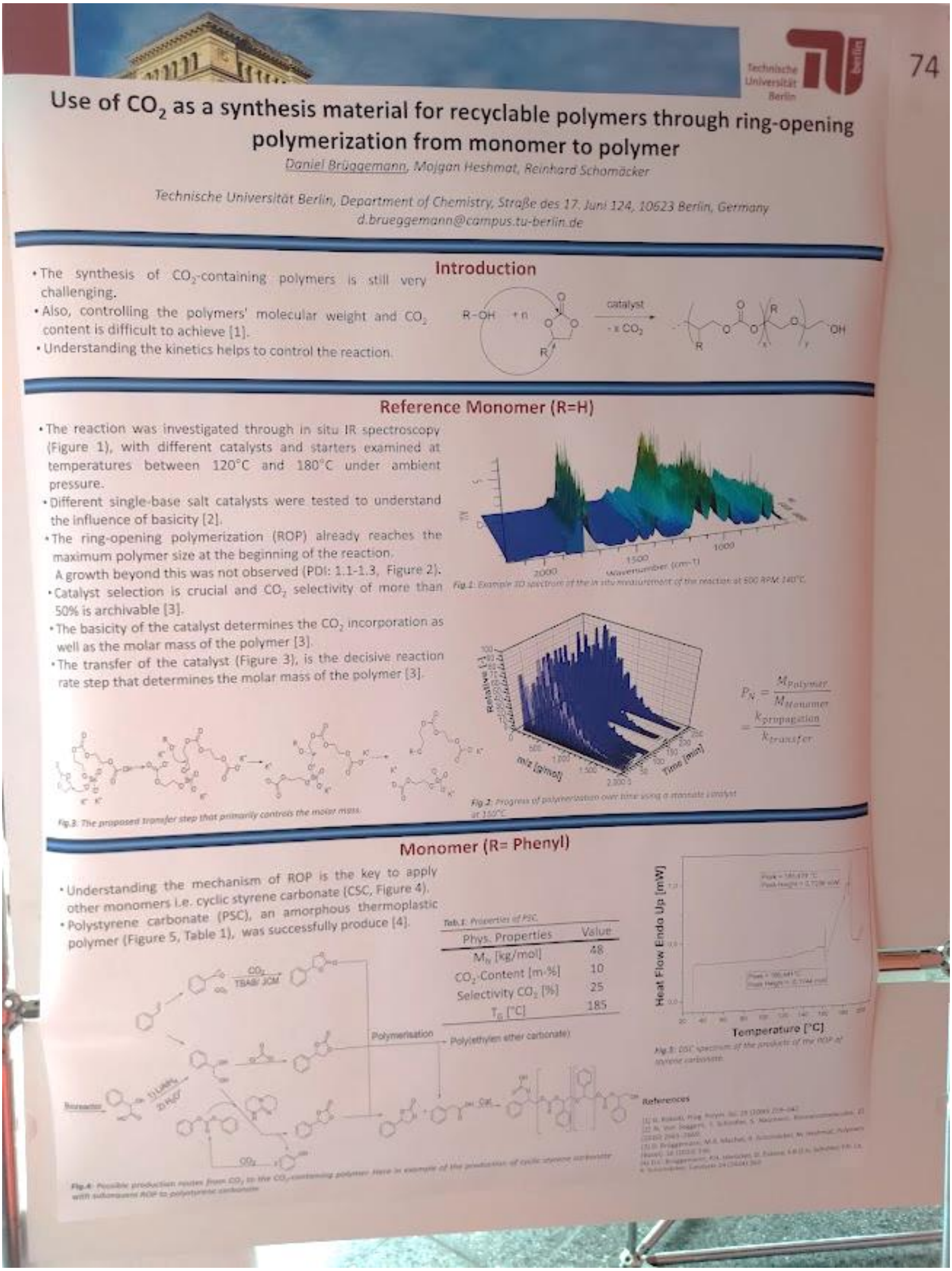
BUR: 1:2,7
Ausstoß: 400 kg/h
Foliendicke: 50 µm

32%
Anteil Regranulat in der Mittelschicht
= **21%** Anteil Regranulat am Gesamtprodukt

6,4% Anteil regranuliertes PA 6 in der Mittelschicht = **4,2%** Anteil regranuliertes PA 6 am Gesamtprodukt

圖35、BASF 與合作夥伴開發易於物理機械回收的 PE/PA (可用於食品等)包裝材剖面成分圖。來源：Windmöller & Hölscher

5. 會議有助於公司政策之技術發表論文摘選



Use of CO_2 as a synthesis material for recyclable polymers through ring-opening polymerization from monomer to polymer

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Introduction

- The synthesis of CO_2-containing polymers is still very challenging.
- Also, controlling the polymers' molecular weight and CO_2 content is difficult to achieve [1].
- Understanding the kinetics helps to control the reaction.

Reference Monomer (R=H)

- The reaction was investigated through in situ IR spectroscopy (Figure 1), with different catalysts and starters examined at temperatures between 120°C and 180°C under ambient pressure.
- Different single-base salt catalysts were tested to understand the influence of basicity [2].
- The ring-opening polymerization (ROP) already reaches the maximum polymer size at the beginning of the reaction. A growth beyond this was not observed (PDI: 1.1-1.3, Figure 2).
- Catalyst selection is crucial and CO_2 selectivity of more than 50% is archivable [3].
- The basicity of the catalyst determines the CO_2 incorporation as well as the molar mass of the polymer [3].
- The transfer of the catalyst (Figure 3), is the decisive reaction rate step that determines the molar mass of the polymer [3].

Fig.1: Example 3D spectrum of the in situ measurement of the reaction at 500 RPM 140°C.

Fig.2: Progress of polymerization over time using a monosalt catalyst at 150°C.

$$P_N = \frac{M_{Polymer}}{M_{Monomer}} = \frac{k_{propagation}}{k_{transfer}}$$

Fig.3: The proposed transfer step that primarily controls the molar mass.

Monomer (R= Phenyl)

- Understanding the mechanism of ROP is the key to apply other monomers i.e. cyclic styrene carbonate (CSC, Figure 4).
- Polystyrene carbonate (PSC), an amorphous thermoplastic polymer (Figure 5, Table 1), was successfully produce [4].

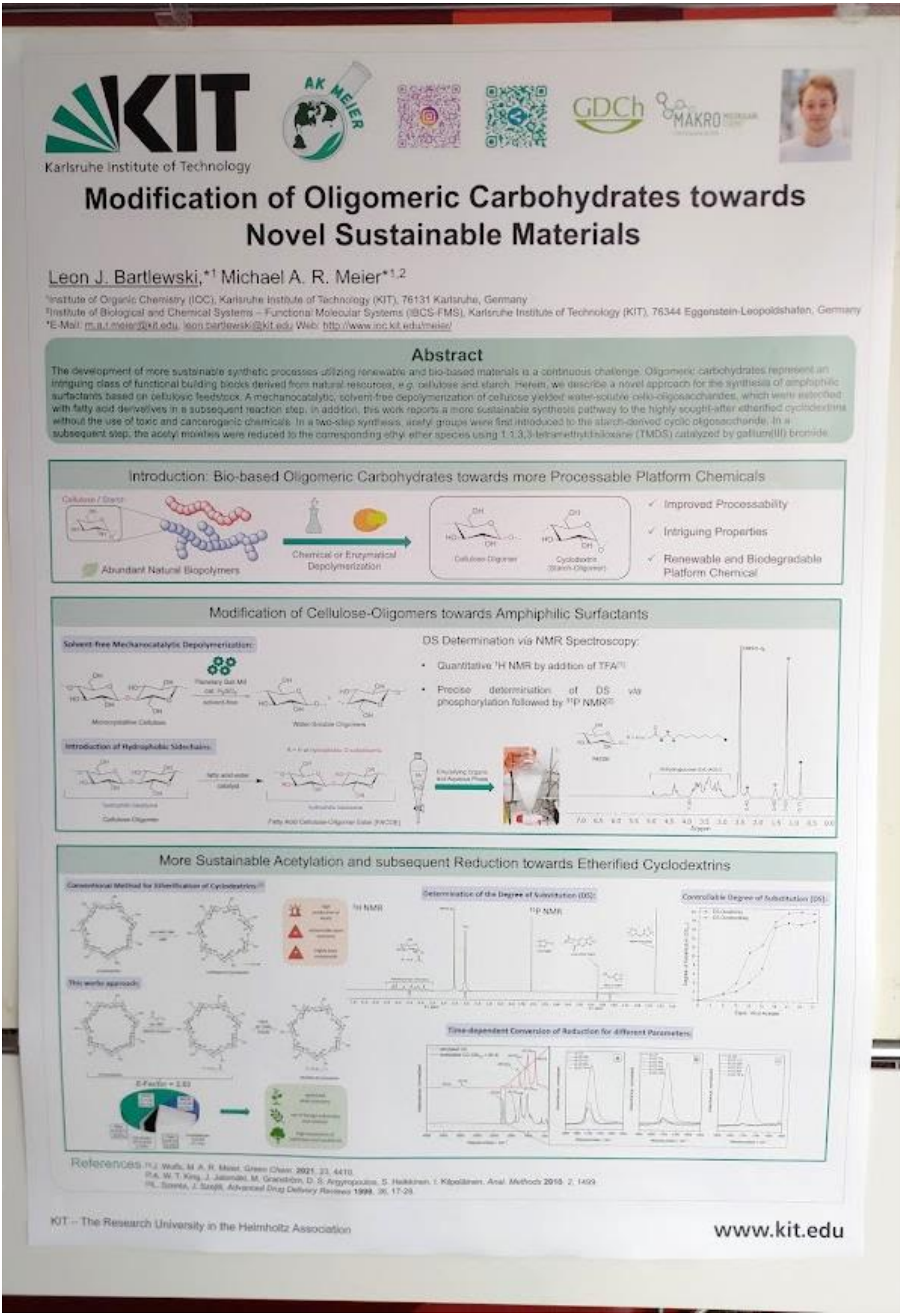
Tab.1: Properties of PSC

Phys. Properties	Value
M_N [kg/mol]	48
CO_2-Content [m-%]	10
Selectivity CO_2 [%]	25
T_G [°C]	185

Fig.4: Possible production routes from CO_2 to the CO_2-containing polymer. Here in example of the production of cyclic styrene carbonate with subsequent ROP to polystyrene carbonate

Fig.5: DSC spectrum of the products of the ROP of styrene carbonate.

References



Karlsruhe Institute of Technology

Modification of Oligomeric Carbohydrates towards Novel Sustainable Materials

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Abstract

The development of more sustainable synthetic processes utilizing renewable and bio-based materials is a continuous challenge. Oligomeric carbohydrates represent an intriguing class of functional building blocks derived from natural resources, *e.g.* cellulose and starch. Herein, we describe a novel approach for the synthesis of amphiphilic surfactants based on cellulosic feedstock. A mechanocatalytic, solvent-free depolymerization of cellulose yielded water-soluble cello-oligosaccharides, which were esterified with fatty acid derivatives in a subsequent reaction step. In addition, this work reports a more sustainable synthesis pathway to the highly sought-after etherified cyclodextrins without the use of toxic and cancerogenic chemicals. In a two-step synthesis, acetyl groups were first introduced to the starch-derived cyclic oligosaccharide. In a subsequent step, the acetyl moieties were reduced to the corresponding ethyl ether species using 1,1,3,3-tetramethyldisiloxane (TMDS) catalyzed by gallium(III) bromide.

Introduction: Bio-based Oligomeric Carbohydrates towards more Processable Platform Chemicals

- ✓ Improved Processability
- ✓ Intriguing Properties
- ✓ Renewable and Biodegradable Platform Chemical

Modification of Cellulose-Oligomers towards Amphiphilic Surfactants

Solvent-free Mechanocatalytic Depolymerization:

Introduction of Hydrophobic Sidechains:

DS Determination via NMR Spectroscopy:

- Quantitative ^{1}H NMR by addition of TFA[1]
- Precise determination of DS via phosphorylation followed by ^{31}P NMR[2]

More Sustainable Acetylation and subsequent Reduction towards Etherified Cyclodextrins

Conventional Method for Etherification of Cyclodextrins:[3]

This work's approach:

Determination of the Degree of Substitution (DS):

Controllable Degree of Substitution (DS):

Time-dependent Conversion of Reduction for different Parameters:

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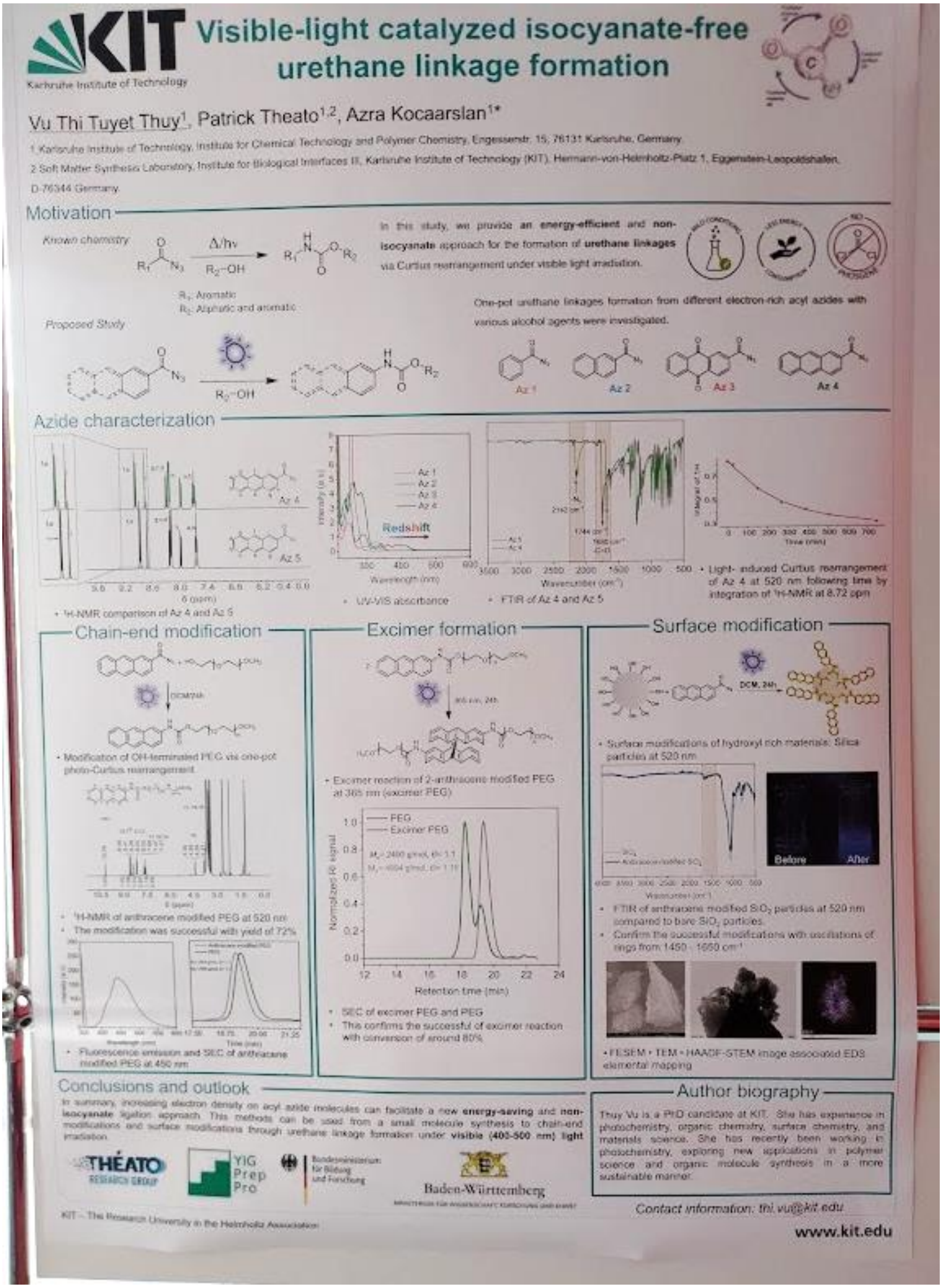

Visible-light catalyzed isocyanate-free urethane linkage formation

Vu Thi Tuyet Thuy[1], Patrick Theato[1,2], Azra Kocaarslan[1*]

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2 Soft Matter Synthesis Laboratory, Institute for Biological Interfaces III, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, D-76344 Germany

Motivation

Known chemistry

R_1: Aromatic
R_2: Aliphatic and aromatic

Proposed Study

In this study, we provide **an energy-efficient** and **non-isocyanate** approach for the formation of **urethane linkages** via Curtius rearrangement under visible light irradiation.

One-pot urethane linkages formation from different electron-rich acyl azides with various alcohol agents were investigated.

Azide characterization

- ^{1}H-NMR comparison of Az 4 and Az 5
- UV-VIS absorbance
- FTIR of Az 4 and Az 5
- Light- induced Curtius rearrangement of Az 4 at 520 nm following time by integration of ^{1}H-NMR at 8.72 ppm

Chain-end modification

- Modification of OH-terminated PEG via one-pot photo-Curtius rearrangement
- ^{1}H-NMR of anthracene modified PEG at 520 nm
- The modification was successful with yield of 72%
- Fluorescence emission and SEC of anthracene modified PEG at 450 nm

Excimer formation

- Excimer reaction of 2-anthracene modified PEG at 365 nm (excimer PEG)
- SEC of excimer PEG and PEG
- This confirms the successful of excimer reaction with conversion of around 80%

Surface modification

- Surface modifications of hydroxyl rich materials: Silica particles at 520 nm
- FTIR of anthracene modified SiO_2 particles at 520 nm compared to bare SiO_2 particles.
- Confirm the successful modifications with oscillations of rings from 1450 - 1650 cm^{-1}
- FESEM • TEM • HAADF-STEM image associated EDS elemental mapping

Conclusions and outlook

In summary, increasing electron density on acyl azide molecules can facilitate a new **energy-saving** and **non-isocyanate** ligation approach. This methods can be used from a small molecule synthesis to chain-end modifications and surface modifications through urethane linkage formation under **visible (400-500 nm) light** irradiation.

Author biography

Thuy Vu is a PhD candidate at KIT. She has experience in photochemistry, organic chemistry, surface chemistry, and materials science. She has recently been working in photochemistry, exploring new applications in polymer science and organic molecule synthesis in a more sustainable manner.

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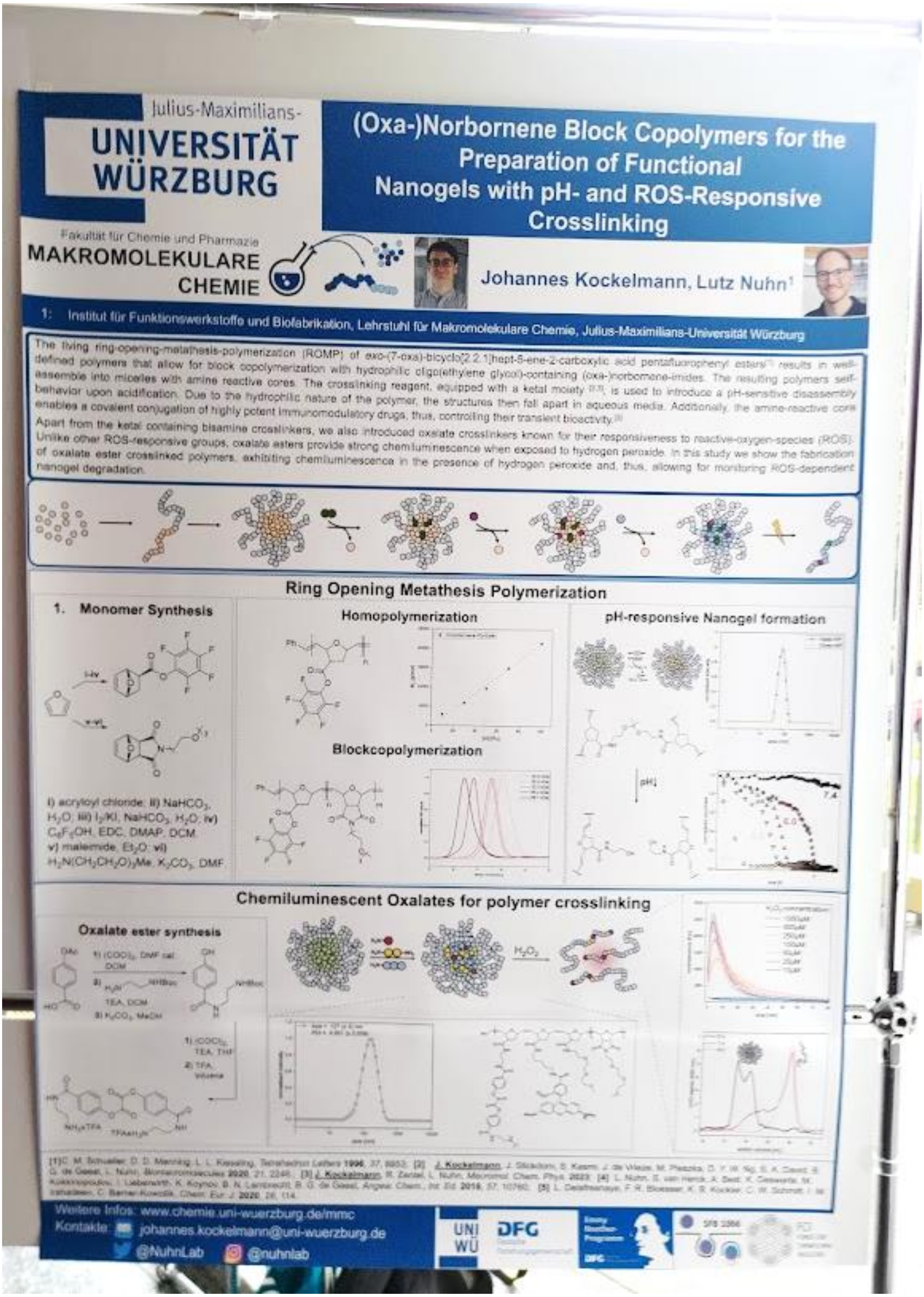

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CHEMIE

(Oxa-)Norbornene Block Copolymers for the Preparation of Functional Nanogels with pH- and ROS-Responsive Crosslinking

Johannes Kockelmann, Lutz Nuhn[1]

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The living ring-opening-metathesis-polymerization (ROMP) of exo-(7-oxa)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid pentafluorophenyl esters[1] results in well-defined polymers that allow for block copolymerization with hydrophilic oligo(ethylene glycol)-containing (oxa-)norbornene-imides. The resulting polymers self-assemble into micelles with amine reactive cores. The crosslinking reagent, equipped with a ketal moiety [2,3], is used to introduce a pH-sensitive disassembly behavior upon acidification. Due to the hydrophilic nature of the polymer, the structures then fall apart in aqueous media. Additionally, the amine-reactive core enables a covalent conjugation of highly potent immunomodulatory drugs, thus, controlling their transient bioactivity.[4]

Apart from the ketal containing bisamine crosslinkers, we also introduced oxalate crosslinkers known for their responsiveness to reactive-oxygen-species (ROS). Unlike other ROS-responsive groups, oxalate esters provide strong chemiluminescence when exposed to hydrogen peroxide. In this study we show the fabrication of oxalate ester crosslinked polymers, exhibiting chemiluminescence in the presence of hydrogen peroxide and, thus, allowing for monitoring ROS-dependent nanogel degradation.

Ring Opening Metathesis Polymerization

1. Monomer Synthesis

i) acryloyl chloride; ii) $NaHCO_3$, H_2O; iii) I_2/KI, $NaHCO_3$, H_2O; iv) C_6F_5OH, EDC, DMAP, DCM
v) maleimide, Et_2O; vi) $H_2N(CH_2CH_2O)_3Me$, K_2CO_3, DMF

Homopolymerization

Blockcopolymerization

pH-responsive Nanogel formation

Chemiluminescent Oxalates for polymer crosslinking

Oxalate ester synthesis

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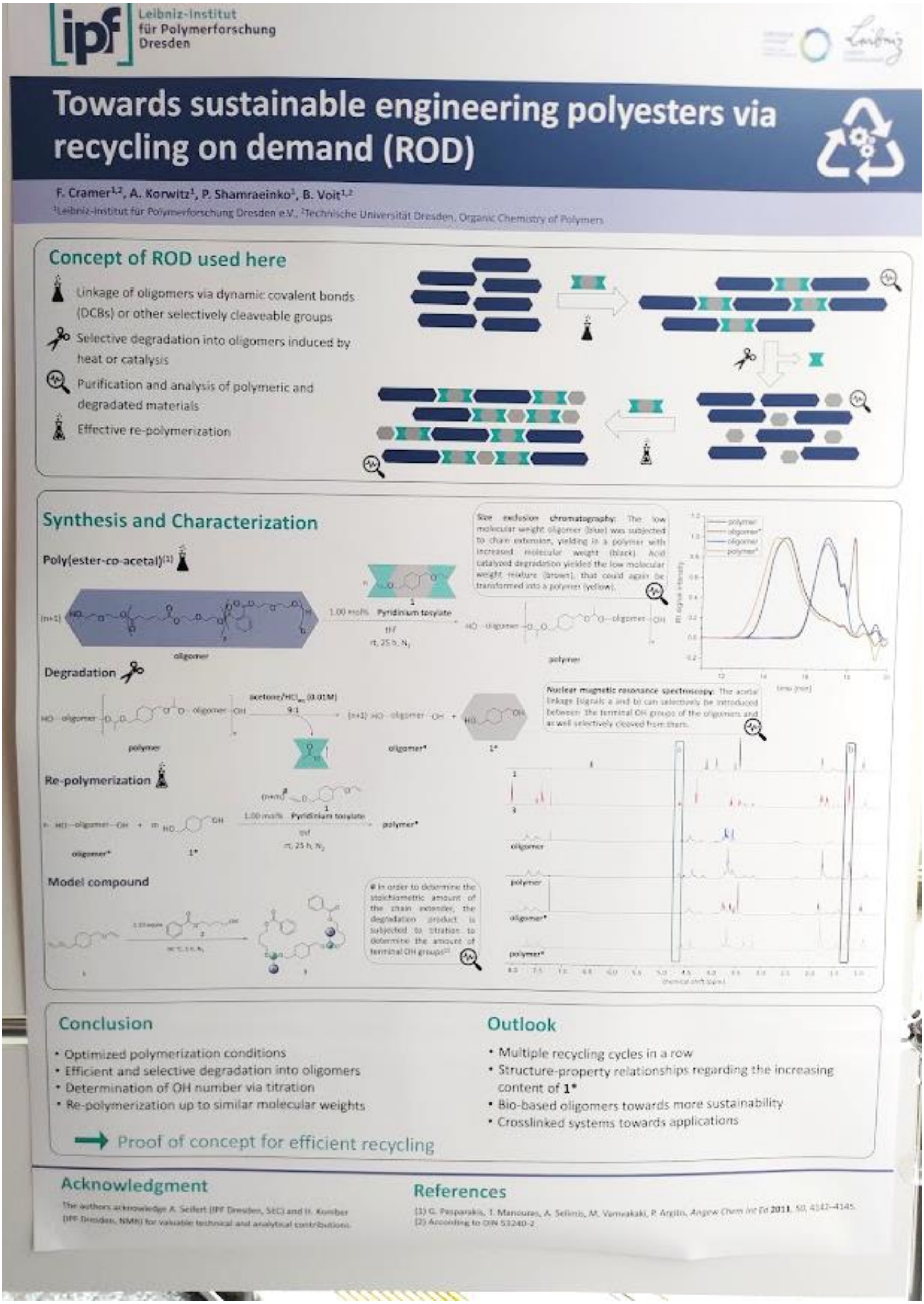

Towards sustainable engineering polyesters via recycling on demand (ROD)

F. Cramer[1,2], A. Korwitz[1], P. Shamraeinko[1], B. Voit[1,2]
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Concept of ROD used here

- Linkage of oligomers via dynamic covalent bonds (DCBs) or other selectively cleaveable groups
- Selective degradation into oligomers induced by heat or catalysis
- Purification and analysis of polymeric and degradated materials
- Effective re-polymerization

Synthesis and Characterization

Poly(ester-co-acetal)[1]

Degradation

Re-polymerization

Model compound

In order to determine the stoichiometric amount of the chain extender, the degradation product is subjected to titration to determine the amount of terminal OH groups[2]

Size exclusion chromatography: The low molecular weight oligomer (blue) was subjected to chain extension, yielding in a polymer with increased molecular weight (black). Acid catalyzed degradation yielded the low molecular weight mixture (brown), that could again be transformed into a polymer (yellow).

Nuclear magnetic resonance spectroscopy: The acetal linkage (signals a and b) can selectively be introduced between the terminal OH groups of the oligomers and as well selectively cleaved from them.

Conclusion

- Optimized polymerization conditions
- Efficient and selective degradation into oligomers
- Determination of OH number via titration
- Re-polymerization up to similar molecular weights

→ Proof of concept for efficient recycling

Outlook

- Multiple recycling cycles in a row
- Structure-property relationships regarding the increasing content of **1***
- Bio-based oligomers towards more sustainability
- Crosslinked systems towards applications

Acknowledgment

The authors acknowledge A. Seifert (IPF Dresden, SEC) and H. Komber (IPF Dresden, NMR) for valuable technical and analytical contributions.

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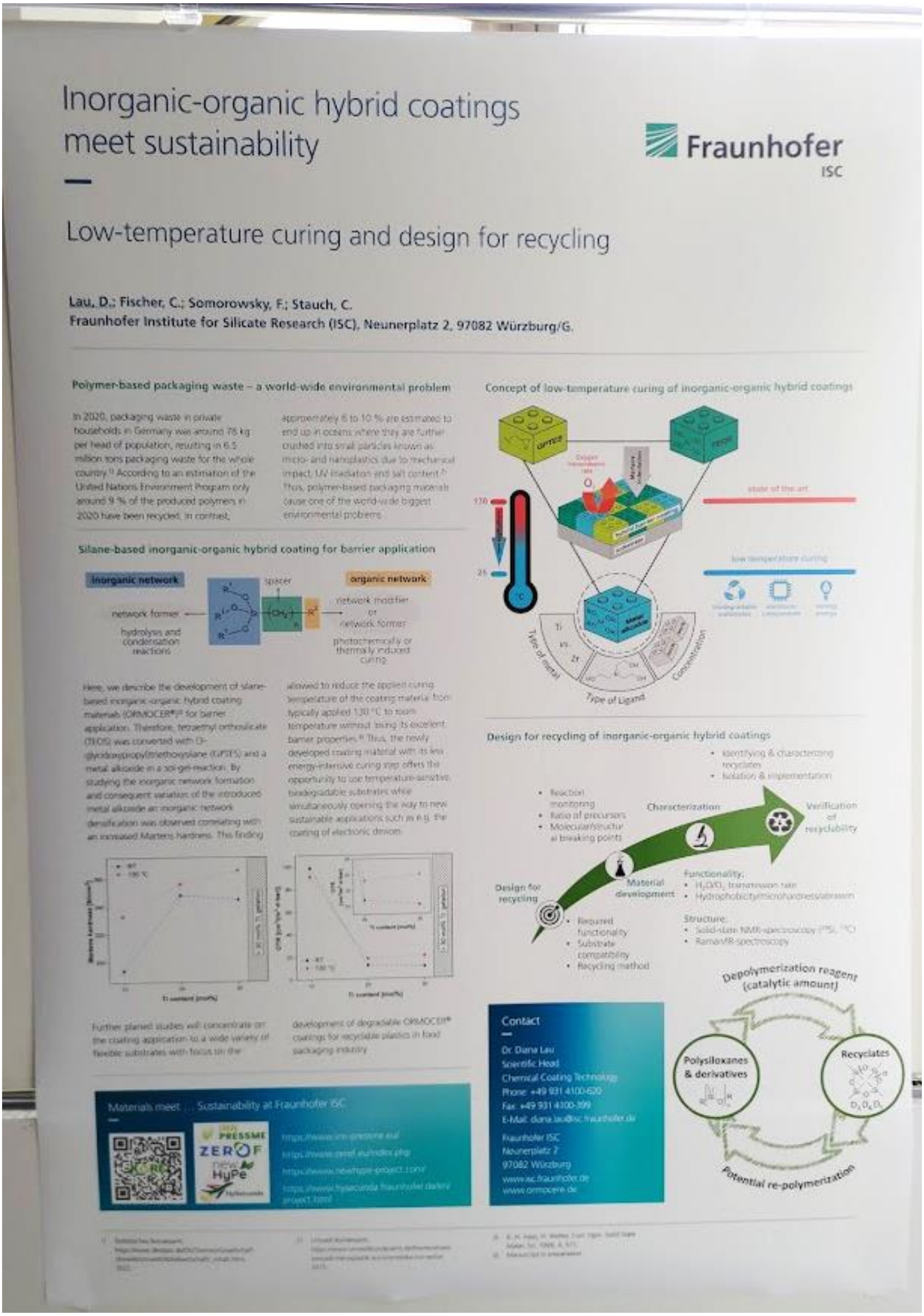

Inorganic-organic hybrid coatings meet sustainability

Fraunhofer ISC

Low-temperature curing and design for recycling

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Polymer-based packaging waste – a world-wide environmental problem

In 2020, packaging waste in private households in Germany was around 78 kg per head of population, resulting in 6.5 million tons packaging waste for the whole country.[1] According to an estimation of the United Nations Environment Program only around 9 % of the produced polymers in 2020 have been recycled. In contrast, approximately 6 to 10 % are estimated to end up in oceans where they are further crushed into small particles known as micro- and nanoplastics due to mechanical impact, UV irradiation and salt content.[2] Thus, polymer-based packaging materials cause one of the world-wide biggest environmental problems.

Silane-based inorganic-organic hybrid coating for barrier application

Here, we describe the development of silane-based inorganic-organic hybrid coating materials (ORMOCER®)[3] for barrier application. Therefore, tetraethyl orthosilicate (TEOS) was converted with (3-glycidoxypropyl)triethoxysilane (GPTES) and a metal alkoxide in a sol-gel-reaction. By studying the inorganic network formation and consequent variation of the introduced metal alkoxide an inorganic network densification was observed correlating with an increased Martens hardness. This finding allowed to reduce the applied curing temperature of the coating material from typically applied 130 °C to room temperature without losing its excellent barrier properties.[4] Thus, the newly developed coating material with its less energy-intensive curing step offers the opportunity to use temperature-sensitive biodegradable substrates while simultaneously opening the way to new sustainable applications such as e.g. the coating of electronic devices.

Further planed studies will concentrate on the coating application to a wide variety of flexible substrates with focus on the development of degradable ORMOCER® coatings for recyclable plastics in food packaging industry.

Concept of low-temperature curing of inorganic-organic hybrid coatings

Design for recycling of inorganic-organic hybrid coatings

- Identifying & characterizing recyclates
- Isolation & implementation

- Reaction monitoring
- Ratio of precursors
- Molecular/structural breaking points

Characterization

Verification of recyclability

Design for recycling

Material development

Functionality:
- H_2O/O_2 transmission rate
- Hydrophobicity/microhardness/abrasion

- Required functionality
- Substrate compatibility
- Recycling method

Structure:
- Solid-state NMR-spectroscopy (^{29}Si, ^{13}C)
- Raman/IR-spectroscopy

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—
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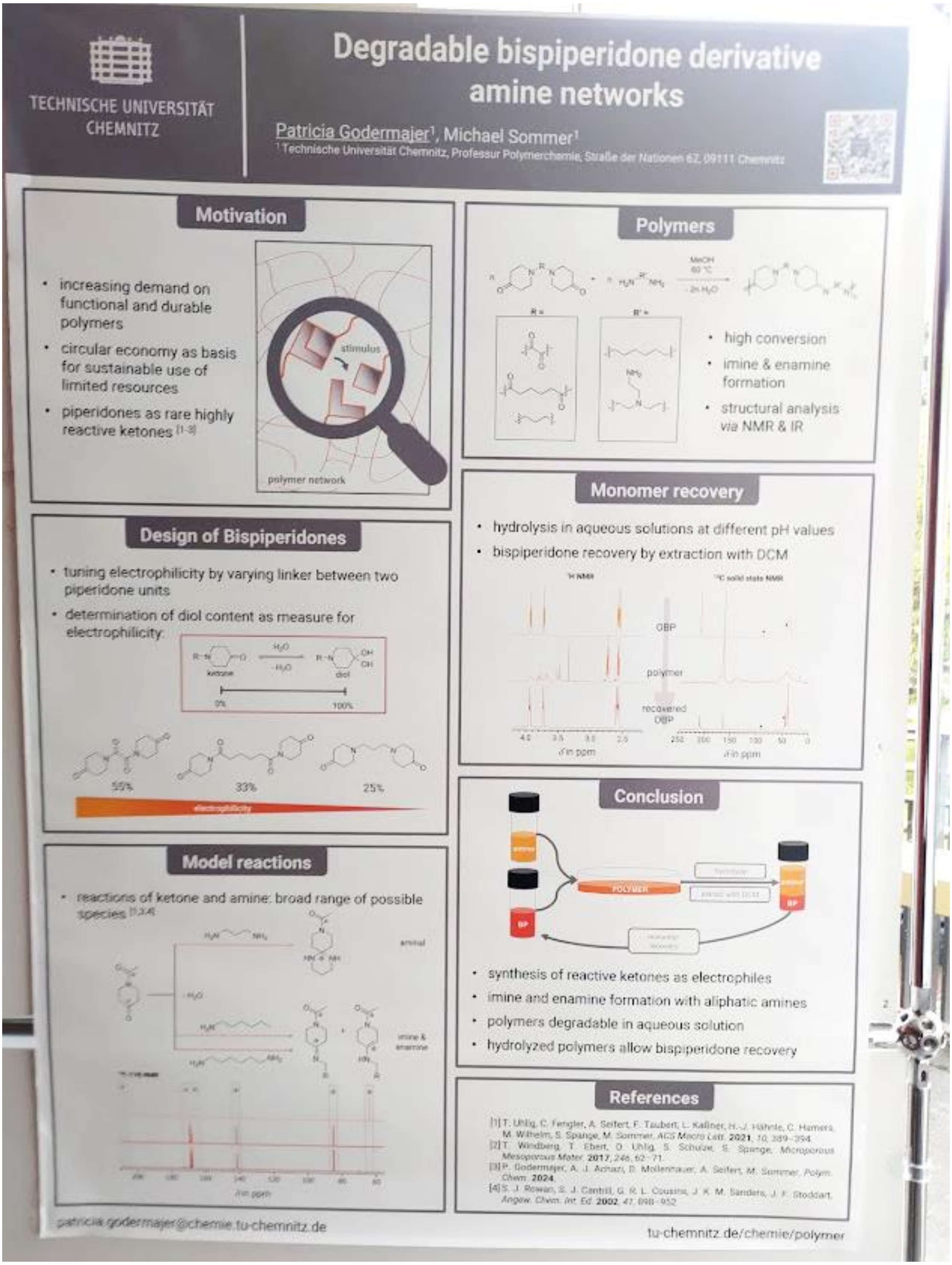

TECHNISCHE UNIVERSITÄT CHEMNITZ

Degradable bispiperidone derivative amine networks

Patricia Godermajer[1], Michael Sommer[1]
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Motivation

- increasing demand on functional and durable polymers
- circular economy as basis for sustainable use of limited resources
- piperidones as rare highly reactive ketones [1-3]

Design of Bispiperidones

- tuning electrophilicity by varying linker between two piperidone units
- determination of diol content as measure for electrophilicity:

Model reactions

- reactions of ketone and amine: broad range of possible species [1,3,4]

Polymers

- high conversion
- imine & enamine formation
- structural analysis via NMR & IR

Monomer recovery

- hydrolysis in aqueous solutions at different pH values
- bispiperidone recovery by extraction with DCM

Conclusion

- synthesis of reactive ketones as electrophiles
- imine and enamine formation with aliphatic amines
- polymers degradable in aqueous solution
- hydrolyzed polymers allow bispiperidone recovery

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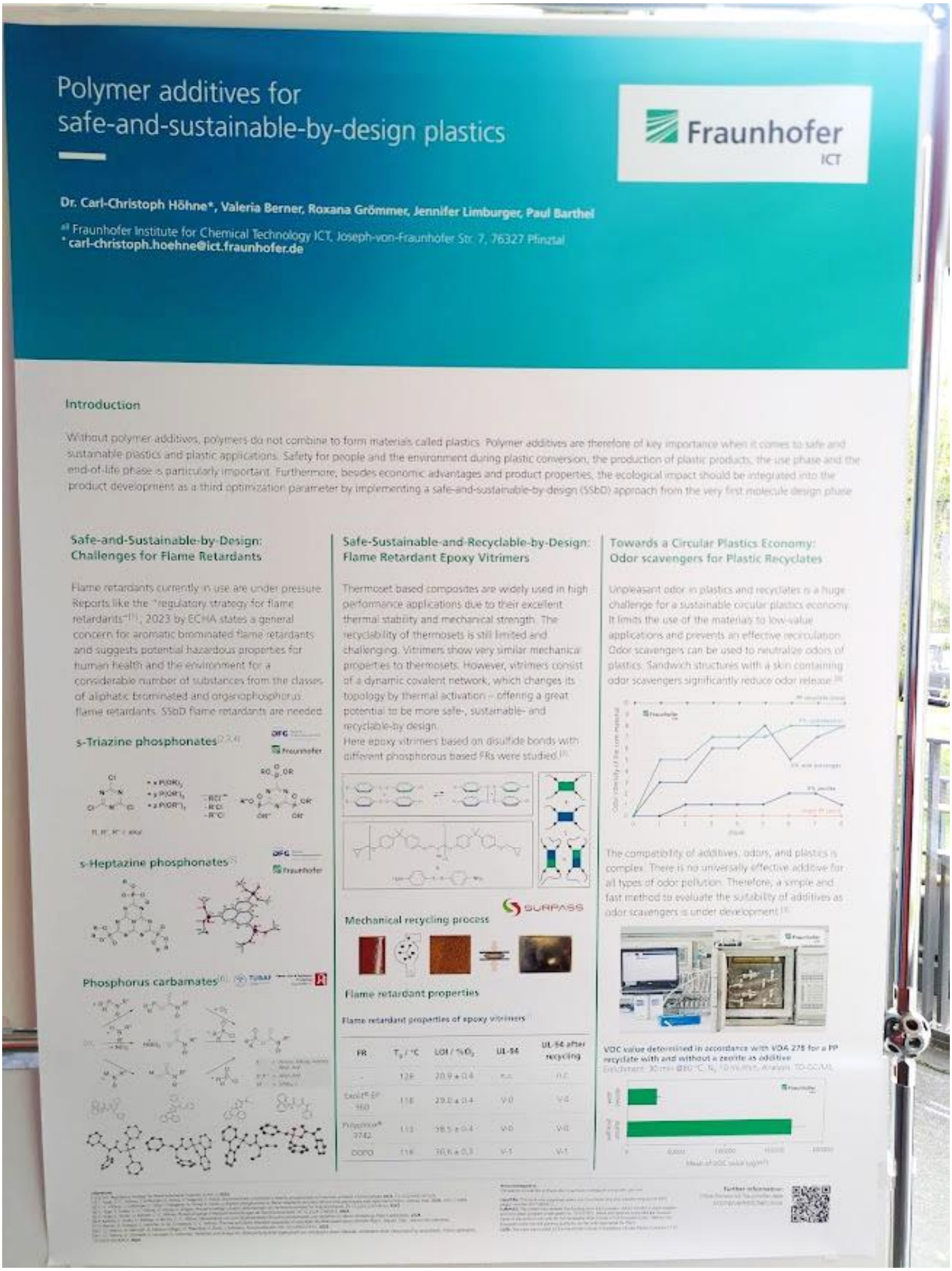

Polymer additives for safe-and-sustainable-by-design plastics

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Introduction

Without polymer additives, polymers do not combine to form materials called plastics. Polymer additives are therefore of key importance when it comes to safe and sustainable plastics and plastic applications. Safety for people and the environment during plastic conversion, the production of plastic products, the use phase and the end-of-life phase is particularly important. Furthermore, besides economic advantages and product properties, the ecological impact should be integrated into the product development as a third optimization parameter by implementing a safe-and-sustainable-by-design (SSbD) approach from the very first molecule design phase

Safe-and-Sustainable-by-Design: Challenges for Flame Retardants

Flame retardants currently in use are under pressure. Reports like the "regulatory strategy for flame retardants"[1], 2023 by ECHA states a general concern for aromatic brominated flame retardants and suggests potential hazardous properties for human health and the environment for a considerable number of substances from the classes of aliphatic brominated and organophosphorus flame retardants. SSbD flame retardants are needed.

s-Triazine phosphonates[2,3,4]

R, R', R'' = alkyl

s-Heptazine phosphonates[5]

Phosphorus carbamates[6]

Safe-Sustainable-and-Recyclable-by-Design: Flame Retardant Epoxy Vitrimers

Thermoset based composites are widely used in high performance applications due to their excellent thermal stability and mechanical strength. The recyclability of thermosets is still limited and challenging. Vitrimers show very similar mechanical properties to thermosets. However, vitrimers consist of a dynamic covalent network, which changes its topology by thermal activation – offering a great potential to be more safe-, sustainable- and recyclable-by design.
Here epoxy vitrimers based on disulfide bonds with different phosphorous based FRs were studied.[7]

Mechanical recycling process

Flame retardant properties

Flame retardant properties of epoxy vitrimers

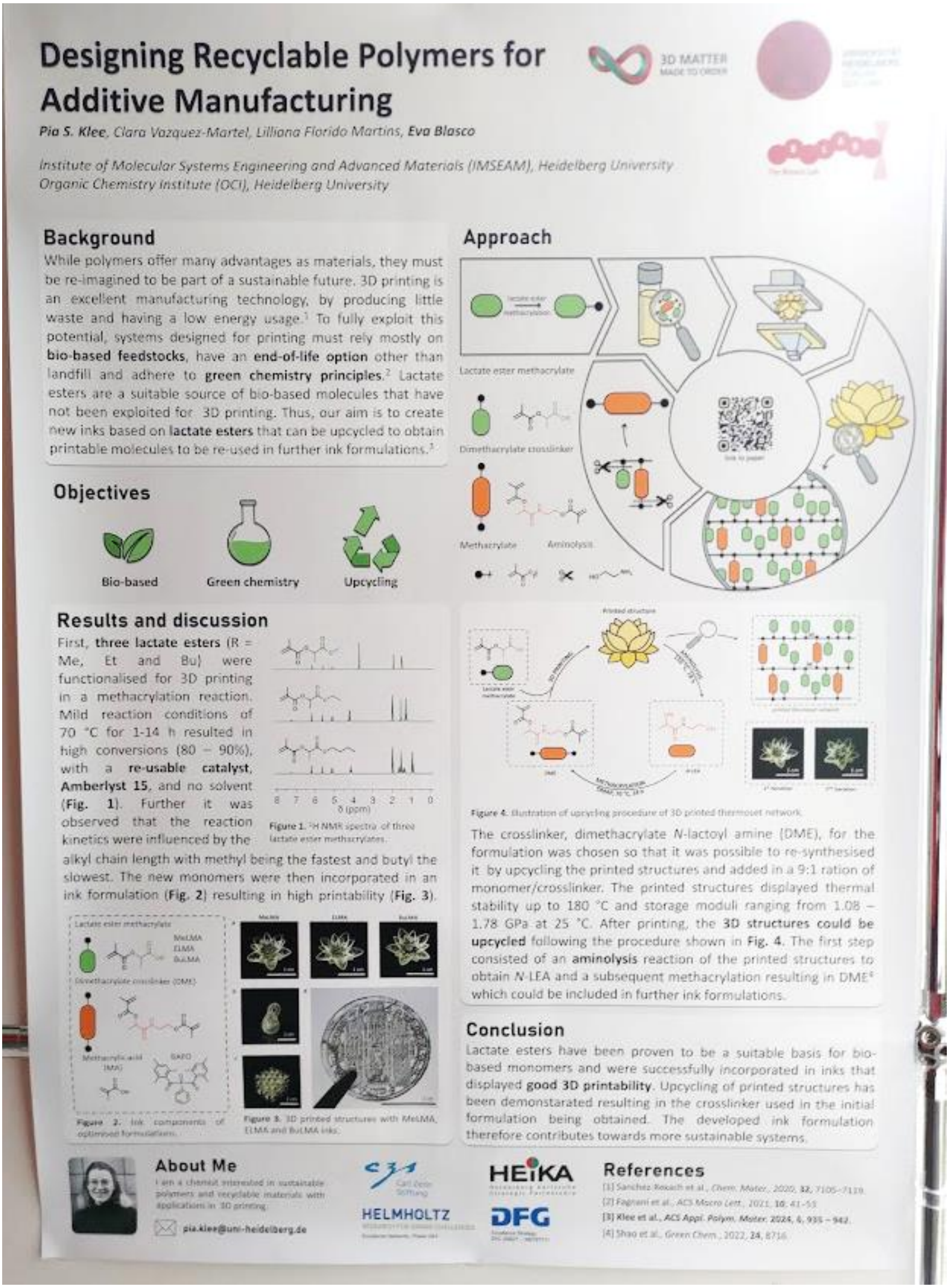
FR	T_g / °C	LOI / % O_2	UL-94	UL-94 after recycling
-	126	20.9 ± 0.4	n.c.	n.c.
Exolit® EP 360	118	29.0 ± 0.4	V-0	V-0
Polyphlox® 3742	113	38.5 ± 0.4	V-0	V-0
DOPO	118	30.6 ± 0.3	V-1	V-1

Towards a Circular Plastics Economy: Odor scavengers for Plastic Recyclates

Unpleasant odor in plastics and recyclates is a huge challenge for a sustainable circular plastics economy. It limits the use of the materials to low-value applications and prevents an effective recirculation. Odor scavengers can be used to neutralize odors of plastics. Sandwich structures with a skin containing odor scavengers significantly reduce odor release.[8]

The compatibility of additives, odors, and plastics is complex. There is no universally effective additive for all types of odor pollution. Therefore, a simple and fast method to evaluate the suitability of additives as odor scavengers is under development.[9]

VOC value determined in accordance with VDA 278 for a PP recyclate with and without a zeolite as additive



Designing Recyclable Polymers for Additive Manufacturing

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Background

While polymers offer many advantages as materials, they must be re-imagined to be part of a sustainable future. 3D printing is an excellent manufacturing technology, by producing little waste and having a low energy usage.[1] To fully exploit this potential, systems designed for printing must rely mostly on **bio-based feedstocks**, have an **end-of-life option** other than landfill and adhere to **green chemistry principles**.[2] Lactate esters are a suitable source of bio-based molecules that have not been exploited for 3D printing. Thus, our aim is to create new inks based on **lactate esters** that can be upcycled to obtain printable molecules to be re-used in further ink formulations.[3]

Objectives

Bio-based

Green chemistry

Upcycling

Results and discussion

First, **three lactate esters** (R = Me, Et and Bu) were functionalised for 3D printing in a methacrylation reaction. Mild reaction conditions of 70 °C for 1-14 h resulted in high conversions (80 – 90%), with a **re-usable catalyst, Amberlyst 15**, and no solvent (**Fig. 1**). Further it was observed that the reaction kinetics were influenced by the alkyl chain length with methyl being the fastest and butyl the slowest. The new monomers were then incorporated in an ink formulation (**Fig. 2**) resulting in high printability (**Fig. 3**).

Figure 1. ^{1}H NMR spectra of three lactate ester methacrylates.

Figure 2. Ink components of optimised formulations.

Figure 3. 3D printed structures with MeLMA, ELMA and BuLMA inks.

Approach

Figure 4. Illustration of upcycling procedure of 3D printed thermoset network.

The crosslinker, dimethacrylate *N*-lactoyl amine (DME), for the formulation was chosen so that it was possible to re-synthesised it by upcycling the printed structures and added in a 9:1 ration of monomer/crosslinker. The printed structures displayed thermal stability up to 180 °C and storage moduli ranging from 1.08 – 1.78 GPa at 25 °C. After printing, the **3D structures could be upcycled** following the procedure shown in **Fig. 4.** The first step consisted of an **aminolysis** reaction of the printed structures to obtain *N*-LEA and a subsequent methacrylation resulting in DME[4] which could be included in further ink formulations.

Conclusion

Lactate esters have been proven to be a suitable basis for bio-based monomers and were successfully incorporated in inks that displayed **good 3D printability**. Upcycling of printed structures has been demonstarated resulting in the crosslinker used in the initial formulation being obtained. The developed ink formulation therefore contributes towards more sustainable systems.

About Me

I am a chemist interested in sustainable polymers and recyclable materials with applications in 3D printing.

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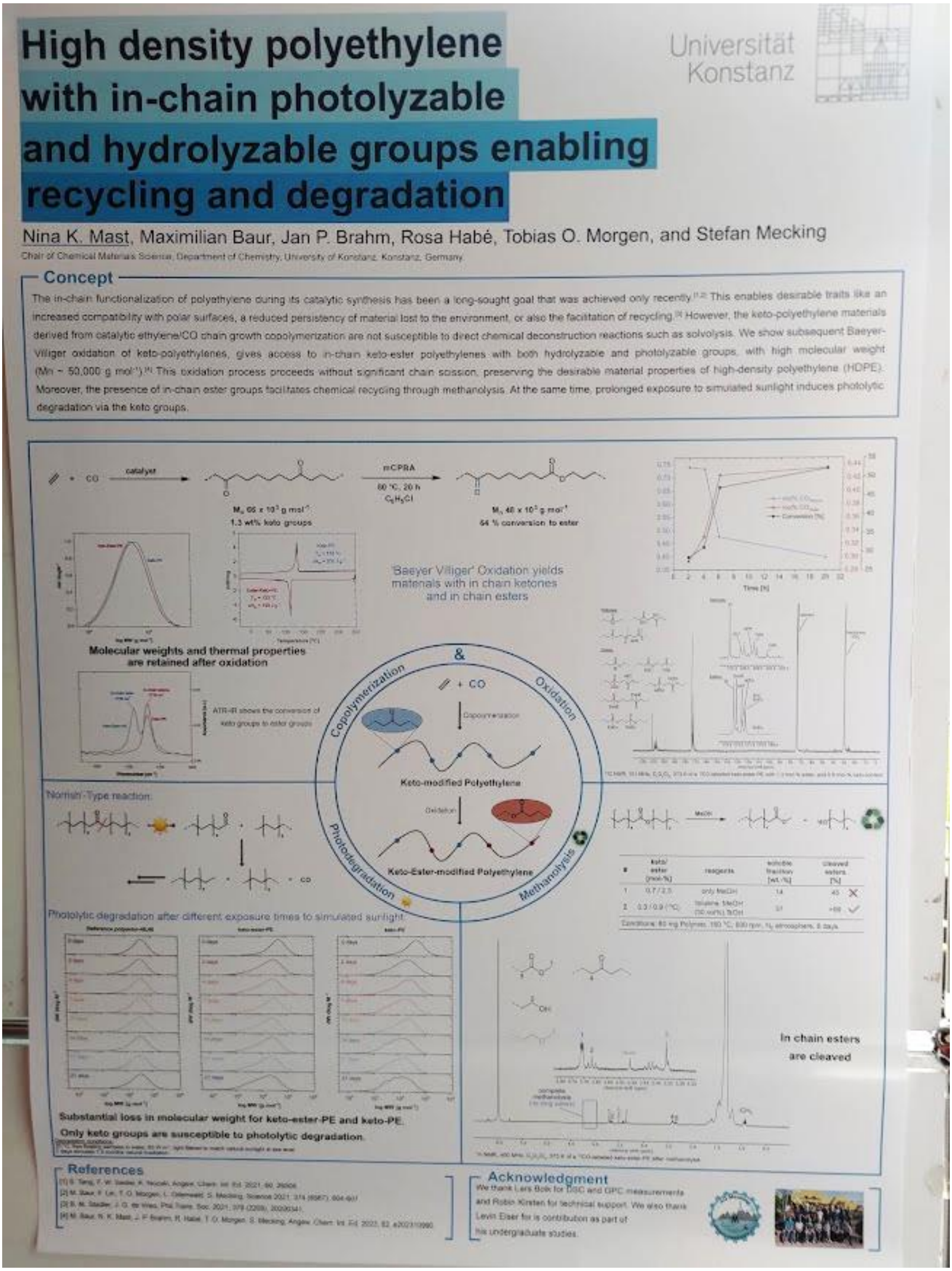

High density polyethylene with in-chain photolyzable and hydrolyzable groups enabling recycling and degradation

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Concept

The in-chain functionalization of polyethylene during its catalytic synthesis has been a long-sought goal that was achieved only recently.[1,2] This enables desirable traits like an increased compatibility with polar surfaces, a reduced persistency of material lost to the environment, or also the facilitation of recycling.[3] However, the keto-polyethylene materials derived from catalytic ethylene/CO chain growth copolymerization are not susceptible to direct chemical deconstruction reactions such as solvolysis. We show subsequent Baeyer-Villiger oxidation of keto-polyethylenes, gives access to in-chain keto-ester polyethylenes with both hydrolyzable and photolyzable groups, with high molecular weight (M_n ~ 50,000 g mol^{-1}).[4] This oxidation process proceeds without significant chain scission, preserving the desirable material properties of high-density polyethylene (HDPE). Moreover, the presence of in-chain ester groups facilitates chemical recycling through methanolysis. At the same time, prolonged exposure to simulated sunlight induces photolytic degradation via the keto groups.

M_n 65 x 10^3 g mol^{-1}
1.3 wt% keto groups

M_n 48 x 10^3 g mol^{-1}
64 % conversion to ester

'Baeyer Villiger' Oxidation yields materials with in chain ketones and in chain esters

Molecular weights and thermal properties are retained after oxidation

ATR-IR shows the conversion of keto groups to ester groups

Norrish-Type reaction:

Photolytic degradation after different exposure times to simulated sunlight:

Substantial loss in molecular weight for keto-ester-PE and keto-PE.

Only keto groups are susceptible to photolytic degradation.

#	keto/ ester [mol-%]	reagents	soluble fraction [wt.-%]	cleaved esters [%]
1	0.7 / 2.3	only MeOH	14	45 ✗
2	0.3 / 0.9 (13C)	toluene: MeOH (50 vol%) TsOH	[illegible]	>99 ✓

Conditions: 80 mg Polymer, 150 °C, 800 rpm, N_2 atmosphere, 5 days

In chain esters are cleaved

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From Waste to Wonder: Efficient C2-Type Molecular Unit for the Synthesis of Sulfur Decorated Polymers

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Motivation & Design

Linear Economy

Take
Make
Dispose

Great Pacific Garbage Patch is the most recognazible consiquence 'take-make-dispose' approach

If current trends continue, our oceans could contain more plastic than fish by 2050

Circular Economy (Circular Materials)

- ✓ Conserves resources and protects the environment
- ✓ Adopt renewable energy in plastic production
- ✓ Transition from fossil-derived plastics to biopolymers
- ✓ Reduces the carbon footprint of plastics

From Waste to Wonder...

Using calcium carbide, an industrial waste, not only addresses waste management but also adds potential value to its residue

Emerging Area: Re-using waste materials in the chemical industry for novel polymeric materials aligns with the circular economy objectives
Carbon-Containing Wastes: Conversion of wastes to C_2-type molecules is compatible with modern industry
Sulfur-Containing Polymers: Increasing focus due to excellent optical performance, degradation, chemical recyclability

Results & Discussion

Structures confirmed with ^{1}H NMR and ATR-IR

Crystalline behavior
High thermal **stability** ($T_{d,5\%}$ > 280 °C)

Maximum emission wavelength of 410 nm was detected with a bimodal emission at λ_{ex} = 355 nm

At higher λ_{ex}, a slight bathochromic shift is noticed, which is typical for organic materials showing **nonconventional photoluminescence** (in P1)

Conclusion

Promoting sustainability and circular economy

Industrial waste derived monomer and polymers

Outlook

Further exploration of degradability

Varied sulfur moieties polymers offer diverse properties and applications

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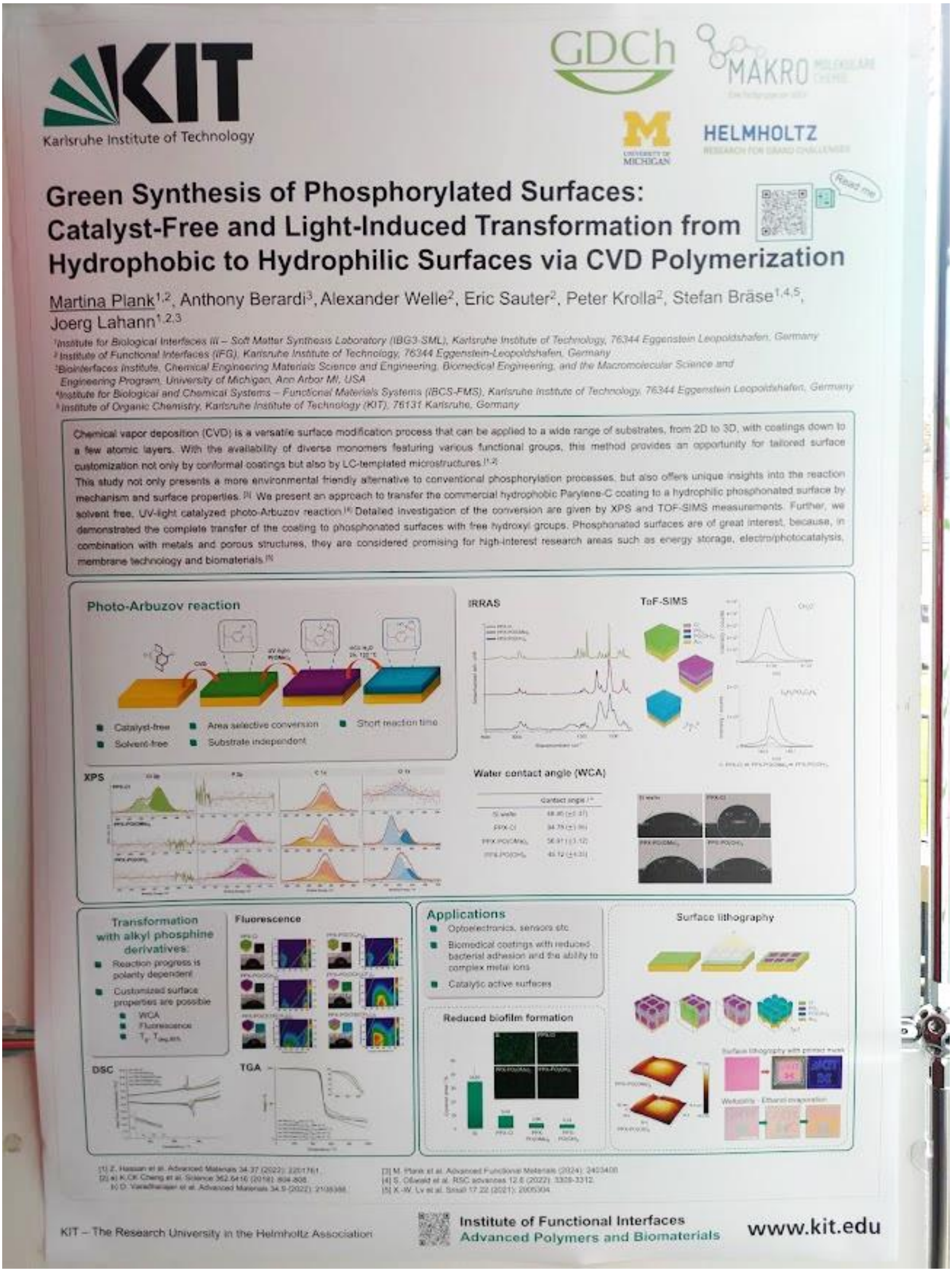

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Green Synthesis of Phosphorylated Surfaces: Catalyst-Free and Light-Induced Transformation from Hydrophobic to Hydrophilic Surfaces via CVD Polymerization

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Chemical vapor deposition (CVD) is a versatile surface modification process that can be applied to a wide range of substrates, from 2D to 3D, with coatings down to a few atomic layers. With the availability of diverse monomers featuring various functional groups, this method provides an opportunity for tailored surface customization not only by conformal coatings but also by LC-templated microstructures.[1-2]

This study not only presents a more environmental friendly alternative to conventional phosphorylation processes, but also offers unique insights into the reaction mechanism and surface properties.[3] We present an approach to transfer the commercial hydrophobic Parylene-C coating to a hydrophilic phosphonated surface by solvent free, UV-light catalyzed photo-Arbuzov reaction.[4] Detailed investigation of the conversion are given by XPS and TOF-SIMS measurements. Further, we demonstrated the complete transfer of the coating to phosphonated surfaces with free hydroxyl groups. Phosphonated surfaces are of great interest, because, in combination with metals and porous structures, they are considered promising for high-interest research areas such as energy storage, electro/photocatalysis, membrane technology and biomaterials.[5]

Photo-Arbuzov reaction

- Catalyst-free
- Solvent-free
- Area selective conversion
- Substrate independent
- Short reaction time

IRRAS

ToF-SIMS

XPS

Water contact angle (WCA)

Transformation with alkyl phosphine derivatives:

- Reaction progress is polarity dependent
- Customized surface properties are possible
  - WCA
  - Fluorescence
  - T_g, $T_{deg,95\%}$

Fluorescence

DSC

TGA

Applications

- Optoelectronics, sensors etc
- Biomedical coatings with reduced bacterial adhesion and the ability to complex metal ions
- Catalytic active surfaces

Reduced biofilm formation

Surface lithography

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