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Nícolas Soares Urruth

**Simultaneous Enzymatic Transesterification and Ring-Opening Reactions
for PBS Copolymer Production and the Chemical Recycling of PBS via
Glycolysis**

Florianópolis
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Glycolysis**

Dissertação de mestrado apresentada para o Programa de Pós-Graduação em Engenharia Química da Universidade Federal de Santa Catarina, para a obtenção do grau de Mestre em Engenharia Química.

Orientador: Profa. Cláudia Sayer.

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Nícolas Soares Urruth

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O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Certificamos que esta é a **versão original e final** do trabalho de conclusão que foi julgado adequado para obtenção do título de mestre em Engenharia Química



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Florianópolis, Dia 5 de março de 2026

À minha família que sempre me apoiou incondicionamente.

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RESUMO

Apesar de 420 milhões de toneladas de plásticos produzidas globalmente (2019), mais de 90% dos resíduos são descartados inadequadamente do ponto de vista circular (aterro sanitário, descarte irregular, etc.). Neste contexto, tecnologias para o desenvolvimento sustentável na produção de polímeros são essenciais. Esta dissertação analisou pontos-chave do ciclo de vida do poli(succinato de butileno) (PBS) para economia circular, integrando a síntese enzimática de copolímeros de PBS-polilactonas e a reciclagem química de PBS por meio da glicólise. A partir da revisão da literatura, foram identificadas lacunas inexploradas na polimerização simultânea por abertura de anel e condensação (SROCP) de PBS, assim como sua reciclagem por glicólise, e evidenciou que catalisadores, glicol, cinética, tipo de material e aditivos são aspectos cruciais para melhores conversões. A síntese de copolímeros por SROCP foi investigada em reator batelada (enzima N435 10% m/m, 90-150°C). Foram sintetizados os copolímeros Poli(butileno succinato-co-caprolactona)(PBS-co-CL), Poli(butileno succinato-co-globalide)(PBS-co-GL) e Poli(butileno succinato-co-caprolactona-co-globalide)(PBS-co-CL-co-GL), cujas massas molares e composição foram analisadas por Cromatografia de Permeação em Gel (GPC) e Ressonância Magnética Nuclear (RMN). Em relação à ϵ -caprolactona (lactona menor; $M_w = 3,3-10,5\text{kDa}$), o Globalide (isomer mixture of Oxacyclohexadecen-2-one) ($M_w = 4,4-5,9\text{kDa}$) apresentou melhores resultados na copolimerização medidos a partir de análises por RMN, com consistente proporção próxima de 50:50 (BS:GL) em sua composição, enquanto a copolimerização com ϵ -caprolactona integrou o copolímero em menor proporção (<12%). Adicionalmente, as condições ótimas da glicólise de PBS com NaHCO_3 foram investigadas por meio de planejamento fatorial 2^3 com réplicas no ponto central, seguido de planejamento composto central rotacional (CCR). As variáveis de entrada analisadas foram temperatura (109-190°C), razão de 1,4-butanodiol por unidade de repetição do PBS (1,29-6,70 mol/mol) e razão de catalisador por unidade de repetição do PBS (0,29-5,70% mol) e de saída foram a fração de monômero, fração de dímero e LMF (fração de baixa massa molar para coluna de GPC com detecção acima de 500 Da). Os efeitos foram significativos de acordo com os modelos estatísticos e ANOVA. Além disso, a presença do efeito quadrático na temperatura confirma a reversibilidade da reação de glicólise, que estabelece a condição ótima (Temperatura = 172,59°C, 1,4-butanodiol:unidade de repetição (PBS) = 6,71mol/mol, NaHCO_3 :unidade de repetição (PBS) = 4,69%mol ; 72,06% monômero). As reações de repolimerização catalisadas por $\text{Ti}(\text{OBu})_4$ e pela enzima N435 produziram polímeros com M_w de 10.835 Da e 3.854 Da, respectivamente. Portanto, esta pesquisa

valida o PBS como bioplástico circular, contribuindo com o desenvolvimento de sua reciclagem química por glicólise e avaliação da SROCP como estratégia para obtenção de copolímeros sustentáveis.

Palavras-chave: PBS, Polimerização Simultânea por Condensação e Abertura de Anel, Reciclagem Química, Economia circular, Planejamento de Experimentos.

ABSTRACT

Despite the global production of 420 million tons of plastics (2019), over 90% of waste is disposed of improperly (landfill, littering, mismanaged waste, etc.). In this context, technologies for sustainable polymer production are essential. This dissertation analyzed the key aspects of the poly(butylene succinate) (PBS) life-cycle for a circular economy, integrating the enzymatic synthesis of PBS-poly lactone copolymers and the chemical recycling of PBS through glycolysis. The literature review identified unexplored gaps in simultaneous ring-opening and condensation polymerization (SROCP) of PBS, as well as its glycolysis recycling, highlighting that catalysts, glycol, kinetics, material type, and additives are crucial points to better yield. Copolymer synthesis via SROCP was investigated in a batch reactor (10% m/m of N435 enzyme, 90-150°C). Poly(butylene succinate-co-caprolactone)(PBS-co-CL), Poly(butylene succinate-co-globalide)(PBS-co-GL) e Poly(butylene succinate-co-caprolactone-co-globalide)(PBS-co-CL-co-GL) copolymers were synthesized, with molar masses and composition analyzed by Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR). Compared to ϵ -Caprolactone (smaller lactone; $M_w = 3.3$ -10.5 kDa), Globalide ($M_w = 4.4$ -5.9 kDa) presented better copolymerization results in NMR analyses, with a consistent composition near 50:50, while copolymerization with ϵ -caprolactone incorporated a lower proportion (<12%). Additionally, optimal glycolysis conditions of PBS with NaHCO_3 were investigated using a 2^3 factorial design with central point replicates, followed by a rotatory central composite design (CCD). Input variables analyzed were temperature (109-190°C), 1,4-butanediol:PBS repeating unit ratio (1.29-6.70 mol/mol), and catalyst:PBS repeating unit ratio (0.29-5.70% mol), while the output variables were monomer fraction, dimer fraction, and LMF (low molar mass fraction for GPC column with detection above 500 Da). Effects were significant according to statistical models and ANOVA. Moreover, the presence of a quadratic temperature effect confirms the reversibility of the glycolysis reaction, establishing the optimal condition (Temperature = 172.59°C, 1,4-butanediol:repeating unit (PBS) = 6.71 mol/mol, NaHCO_3 :repeating unit (PBS) = 4.69% mol; 72.06% monomer). Repolymerization reactions catalyzed by $\text{Ti}(\text{OBu})_4$ and enzyme N435 produced polymers with M_w of 10,835 Da and 3,854 Da, respectively. Therefore, this research validates PBS as a circular bioplastic, contributing to the development of its chemical recycling by glycolysis reactions and evaluation of SROCP as a strategy for obtaining sustainable copolymers.

Keywords: PBS, Simultaneous Condensation and Ring-Opening Polymerization, Chemical

Recycling, Circular Economy, Experimental Design.

RESUMO EXPANDIDO

Introdução

Apesar do crescimento global no consumo de plásticos (420 milhões de toneladas em 2019), mais de 90% dos resíduos plásticos são destinados a aterros ou incinerados, com apenas 9% reciclados mecanicamente. Bioplásticos como o PBS representam menos de 1% do mercado, mas oferecem potencial circular devido à origem renovável (derivados do ácido succínico e do 1,4-butanediol, de origem renovável) e à presença de ligações éster na unidade de repetição que é suscetível à despolimerização seletiva.

Neste contexto, esta dissertação de mestrado analisou os pontos chave do ciclo de vida do poli(butileno succinato) (PBS), bioplástico alifático e biodegradável promissor para economia circular, com ênfase em dois desafios críticos: a síntese sustentável de copolímeros de PBS-polilactonas por meio da polimerização enzimática simultânea por condensação e abertura de anel (SROCP), assim como a reciclagem química avançada do PBS por glicólise. A motivação reside nas seguintes lacunas científicas: reduzido número de estudos sobre SROCP para copolímeros de PBS-polilactonas e ausência da investigação da glicólise de PBS.

Objetivos

Esta dissertação tem por objetivo central contribuir para a circularidade na produção de polímeros, com ênfase na síntese sustentável de poliésteres renováveis de interesse comercial, como o PBS, bem como sua reciclagem avançada. Os objetivos específicos do estudo seguem abaixo:

- **Objetivo 1:** Investigar a copolimerização enzimática por transesterificação e reações de abertura de anel entre os monômeros precursores do PBS e lactonas;
- **Objetivo 2:** Investigar a reação de glicólise como método para reciclagem química do PBS;
- **Objetivo 3:** Otimizar as condições operacionais da glicólise do PBS por meio de planejamento experimental e desenvolvimento de modelos de superfície de resposta;

- **Objetivo 4** Demonstrar fechamento do ciclo por meio da repolimerização dos produtos da glicólise;

Metodologia

Foi realizada a revisão da literatura sobre a síntese de copolímeros de PBS, assim como uma extensa revisão de tecnologias para reciclagem química de poliésteres com ênfase na solvólise. A primeira destacou os principais copolímeros de PBS reportados na literatura, identificando lacunas e a possibilidade de inclusão de lactonas em sua cadeia. A segunda parte da revisão contemplou a descrição detalhada das principais tecnologias para solvólise com suas respectivas aplicações a diferentes poliésteres, sua utilização na síntese de novos produtos, com ênfase nas avaliações de ciclo de vida e técnico-econômica. Além disso, uma avaliação crítica das regulações vigentes foi apresentada, desde as empresas atuantes, assim como uma proposta conceitual para o desenvolvimento circular na produção de polímeros. Essa pesquisa incorpora, como método crítico, a análise estatística dos dados da literatura por matriz de correlação e ANOVA, com mais de 400 resultados da literatura analisados.

A síntese de copolímeros de PBS-lactonas por meio da polimerização simultânea de abertura de anel e condensação (SROCP) foi conduzida em reator batelada de 100 mL sob vácuo de -650mmHg. As reações foram catalisadas pela versão comercial imobilizada Novozim 435 da lipase CALB (10% m/m) nas seguintes condições: 90°C durante 4h, 90°C durante 24h e 90°C durante 4h seguido por um aumento na temperatura a 150°C durante 20h. Os monômeros envolvidos nas reações foram o dietil succinato, 1,4-butanodiol, e as respectivas lactonas precursoras do PCL e PGL (ϵ -caprolactona e globalide). A estequiometria da reação se deu em razão molar 1:1 em relação ao grupo succinato de butileno e à lactona. Os materiais poliméricos foram caracterizados por GPC e RMN $^1\text{H}/^{13}\text{C}$ (500 MHz) para validar a formação de copolímeros e avaliar as distribuições de massa molar.

A reação de glicólise do PBS foi conduzida em reator batelada de 50 mL. As condições de reação foram definidas conforme o planejamento experimental sequencial fatorial completo 2^3 (3 variáveis: 8+3 pontos centrais) e o plano composto rotacional (CCR). As seguintes variáveis foram investigadas: teor de bicarbonato de sódio (NaHCO_3) como catalisador (razão molar NaHCO_3 : unidade de repetição do PBS; 0,29-5,70%mol), teor de 1,4-butanediol (razão molar BDO: unidade de repetição de PBS; 1,29-6,70 mol/mol) e temperatura (109,41-190,59°C).

Os dados experimentais foram usados para desenvolver modelos de superfície de resposta, empregando-se a fração de monômero, a fração de dímero e a LMF (fração de baixa massa molar para uma coluna de GPC com faixa de análise acima de 500 Da) como variáveis de saída, por meio da técnica de mínimos quadrados. As reações de repolimerização dos produtos da glicólise do PBS foram conduzidas com dois catalisadores: $\text{Ti}(\text{OBu})_4$ (0,1%mol, 190°C, 2h sob vazão de nitrogênio e 5h sob vácuo de -650mmHg) e a enzima N435 (10% m/m, 90°C, 4h sob vácuo de -650mmHg).

Resultados e discussão

A SROCP produziu copolímeros PBS-co-CL (0-31% CL), PBS-co-GL (44-49% GL) e PBS-co-CL-co-GL (0-12% CL, 0-43% GL), cuja composição foi confirmada por RMN de ^1H e ^{13}C . O Globalide apresentou maior incorporação nas cadeias poliméricas em comparação com a ϵ -caprolactona. As análises de GPC revelaram distribuições de massas molares intermediárias em relação aos homopolímeros de PBS e às respectivas polilactonas (PCL e PGL). As massas molares médias numérica e ponderal (M_n e M_w) apresentaram valores na faixa de 1,2-2,5 kDa e 8-15 kDa, respectivamente, com índice de polidispersão entre 1,8 e 2,3. Os rendimentos em polímero das reações (35-55%) foram limitados pela remoção de suproduto em razão da elevada resistência à transferência de massa nas condições do meio reacional.

As reações de glicólise do PBS apresentaram valores satisfatórios em termos de conversão. Em particular, as análises estatísticas (ANOVA e intervalos de confiança) aplicadas ao modelo de superfície de resposta indicaram que a temperatura, razão de butanodiol e razão de catalisador são efeitos significativos na reação de glicólise do PBS. Adicionalmente, o planejamento fatorial completo com réplicas no ponto central indicou a significância do efeito de curvatura na superfície de resposta. O detalhamento deste efeito foi realizado a partir da aplicação do plano composto rotacional. As análises estatísticas identificaram a temperatura como fonte do efeito quadrático nas superfícies de resposta, confirmando a reversibilidade das reações de transesterificação. A glicólise do PBS atingiu conversões de 72,06% em monômero e 24,09 em dímero na condição ótima (Temperatura = 172,59°C, BDO:unidade de repetição = 6,71 mol/mol, NaHCO_3 :unidade de repetição = 4,69%mol) de acordo com o modelo estatístico.

Por fim, as reações de repolimerização aplicadas aos produtos de glicólise apresentaram taxas satisfatórias de produção de PBS para os dois catalisadores testados. Em particular, as

reações catalisadas pelo $\text{Ti}(\text{OBu})_4$ e pela enzima N435 apresentaram M_w igual a 10.835 Da e 3.854 Da, respectivamente, enquanto o PBS virgem empregado inicialmente nos experimentos apresentou M_w igual a 17.788 Da. As menores massas molares observadas nos experimentos de repolimerização podem ser explicadas pelo efeito de inibição causado pela presença de bicarbonato de sódio no meio reacional, assim como pelas limitações na remoção de supproduto em experimentos na escala de bancada.

Considerações finais

Esta dissertação integrou a produção sustentável e a reciclagem química do PBS, permitindo destacar seu potencial como bioplástico circular. A polimerização enzimática simultânea de abertura de anel e condensação (SROCP) demonstrou viabilidade técnica para a produção de copolímeros de PBS-lactonas em reatores batelada, com a incorporação preferencial de macro-lactonas (como o globalide). Adicionalmente, a glicólise emerge como método promissor de reciclagem química avançada, enquanto os modelos de superfície de resposta permitiram identificar as condições ótimas de despolimerização e as condições em que reações reversíveis são identificadas. Além disso, as reações de repolimerização dos produtos da glicólise confirmaram o fechamento do ciclo, produzindo polímeros com M_w comparáveis ao PBS virgem em condições laboratoriais.

Os principais desafios que devem ser superados são as massas molares e conversões baixas em SROCP, bem como o desenvolvimento de métodos eficientes de purificação do monômero após a despolimerização do PBS. Trabalhos futuros devem focar na otimização das condições da SROCP para obter maiores conversões e massas molares. Adicionalmente, a caracterização das propriedades térmicas deve ser realizada, visando a aplicação comercial desses copolímeros. Para a glicólise, os estudos devem focar no escalonamento, no desenvolvimento de operações de separação/purificação de oligômeros e integração com ACV/TEA completas. Estes avanços posicionam o PBS como solução viável para promover a transição para materiais circulares, contribuindo para a sustentabilidade em polímeros.

Palavras-chave: PBS, Polimerização Simultânea por Condensação e Abertura de Anel, Reciclagem Química, Economia circular, Planejamento de Experimentos.

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Chapter 1

Introduction

1.1 Motivation

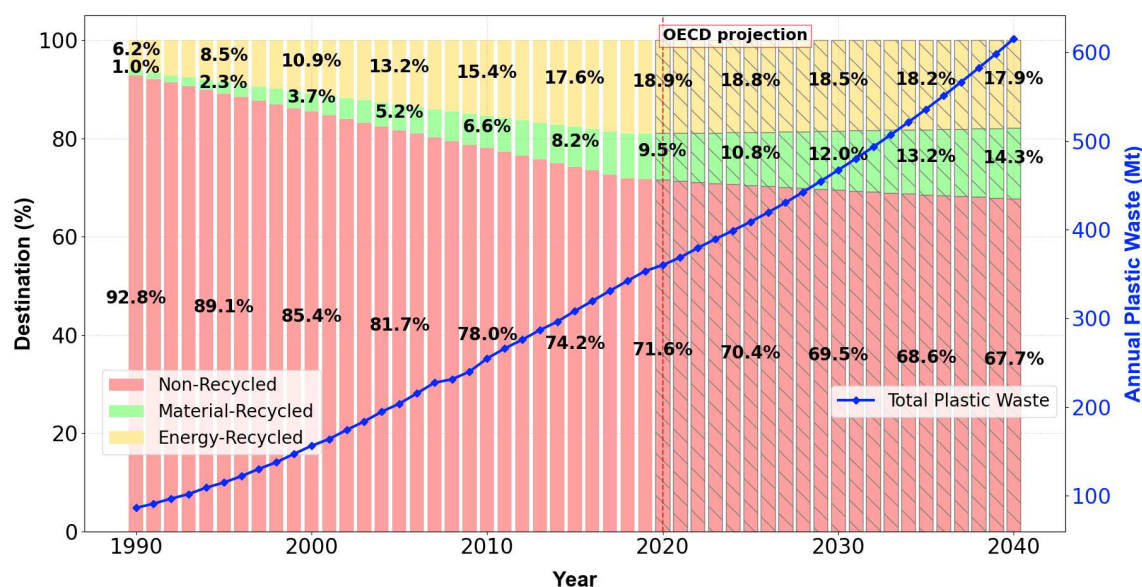
The first documented production of a plastic dates back to 1862, when Alexander Parkes invented Parkesine, an organic material derived from cellulose that was moldable upon heating. That was a remarkable invention for the 19th century. Many products synthesised from natural polymers, such as horns and other animal-derived tissues, began to face scarcity, requiring new, durable, and cheaper substitutes (Science Museum, 2019). The first fully synthetic plastic, Bakelite, was invented in 1909 by Leo Baekeland and is known today as phenol-formaldehyde (Greenwood, 2021). Subsequently, urea-formaldehyde resins and polyester resins were synthesised around the 1920s and 1930s, respectively (IUPAC, 2025).

From that time on, plastics became increasingly popular, catalysed by military demands during the two world wars, escalating to domestic products and to the colossal industry that we know today, with 460 million tons produced annually by 2019 and a cumulative plastic production of ca. 9 billion tons (OECD, 2024c).

Despite their widespread use in modern society, most plastics take a long time to decompose under natural conditions, such as in landfills, persisting for 20 to over 500 years. Yet, only 9% of all plastic waste was recycled in 2019, 22% was mismanaged, and 49% was landfilled. Even countries with the highest recyclability rates reached only ca. 14% (OECD, 2022b). Since 1990, in terms of non-recycled destination (landfilled, littering and mismanaged plastic waste (MPW)) was over 90% globally, a number which was still close to 70% in 2019 (Figure 1.1.1). Although some of the materials could have been decomposed, most will remain intact for many years, which represents an amount of plastic waste higher than 5 billion tons from 2020 on, as

the estimated 4,878 billion tons sample data of landfilled and MPW dates from 1990 to 2019 (OECD, 2024b). As a matter of fact, owing to their low degradation rates at ambient conditions, the seminal Parkesine and Bakelite may still be untouched in nature.

Figure 1.1.1: Global OECD end-of-life estimations, from 1990-2019, detailing annual plastic waste generation and non-recycled (mismanaged, landfilled, and littered), material-recycled, and energy-recycled waste percentages to total plastic waste (OECD, 2024c,a).



Source: The author (2024).

Different from all other classes of plastics presented above, polyesters bear ester groups on repeating units, as part of the polymer backbone (Payne; Jones, 2021). Among commercially relevant polyesters, poly(ethylene terephthalate) (PET) stands out with the highest production and marketing volumes, making it the primary subject in recycling studies due to its suitability for various methods. In addition to PET, the use and interest in biopolymers – e.g. poly(lactic acid) (PLA), poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT), polyhydroxyalkanoates (PHAs) – have been rising considerably. Driven by the goals of a sustainable and circular market, industry and society alike are showing support for this type of solution alongside the push for energy transition, aiming for a low-carbon circular production system (OECD, 2024a; Ishimwe, 2024).

The presence of enzymatically hydrolysable ester bonds in the backbone of polyesters makes them theoretically all susceptible to biodegradation (i.e. biologically recyclable) or depolymerisation (i.e. chemically recyclable). In practice, biodegradability is also highly dependent on crystallinity, molar mass, and environmental conditions. For instance, aromatic

polyesters such as PET are poorly biodegradable under environmental conditions, whereas aliphatic counterparts like PLA and PBS degrade more readily. Yet, considering the high electronegativity of the oxygen atom, polyester waste is a promising raw material for advanced recycling technologies (Ismail et al., 2024).

The scenario described above requires that plastics, despite being *sine-qua-non* in modern society, undergo a paradigm shift towards circularity. In this context, products designed for circularity and recycling technologies play a key role, although these processes still require several improvements. (Clark; Shaver, 2024; Aarsen et al., 2024) For a truly sustainable economy, both raw materials and products, as well as their end-of-life trajectory, must be designed for a circular production, with easy-to-recycle material, products designed for easy disposal, technology to integrate production and recycling processes and, if needed, easy-to-recycle enhanced biodegradation for possible logistic leakage (Nixon et al., 2024).

On the material level, bioplastic technology is an interesting approach to achieve a sustainable production, but considerable improvement on material properties, processing technologies and economic feasibility should be reached (Rafiqah et al., 2021). From this perspective, copolymerization of biobased monomers is a viable route to provide materials with modified properties for specific applications. In addition, it keeps its sustainable characteristics and enables functional performance with circularity. (Peñas et al., 2022)

Conversely, from the perspective of the material life cycle, end-life scenario for plastic disposal and its recycling technologies are usually divided into four categories, namely: primary (mechanical or closed-loop), secondary (mechanical or open-loop), tertiary (chemical or feedstock), and quaternary (energy recovery or waste valorisation). These categories reflect different approaches to managing plastic waste, each with distinct advantages, limitations, and environmental impacts (Lamberti; Román-Ramírez; Wood, 2020).

- **Primary recycling** relies on uncontaminated plastic waste, such as industrial waste and scraps, with known composition and properties. It allows a re-processing of material by inputting the scraps back to production. It requires high-quality, uncontaminated waste, which limits the capacity of this recycling process (Conroy; Zhang, 2024).
- **Secondary recycling** deals with plastic waste by mechanical recycling after collection of typically unknown waste composition, sorting, pre-treatment (e.g. washing, milling, drying), and reprocessing (e.g. melt extrusion, injection moulding, spinning). Low-contaminated waste is aimed to avoid downcycling; however, the open-loop system limits

the reuse options (Conroy; Zhang, 2024).

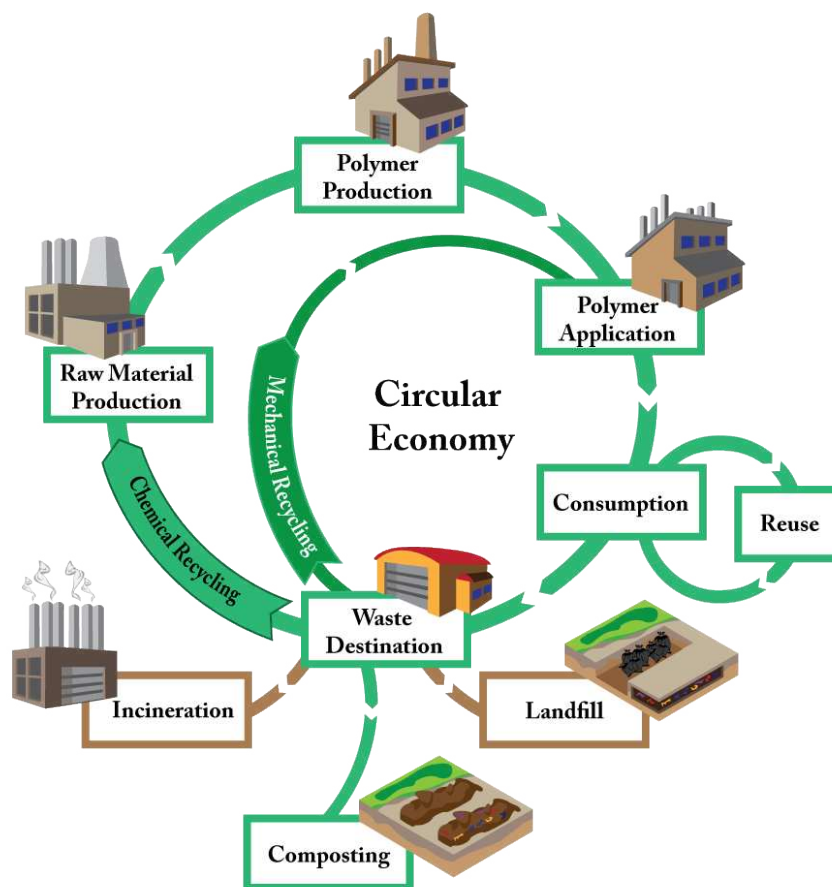
- **Tertiary recycling**, also termed chemical recycling, employs controlled depolymerization (e.g. solvolysis) or thermomechanical cleavage (e.g. pyrolysis, gasification) to break down polymers into lower-molar mass chemicals, sometimes even monomers. This strategy can handle contaminated or mixed plastic waste and broaden the possibilities of plastic recycling, as it may lead to plastics bearing virgin-like quality (Conroy; Zhang, 2024).
- **Quaternary recycling** relies on energy recovery, converting waste plastics into heat, electricity, and/or fuel. While this method reduces landfilling and generates energy, it has intensive greenhouse gas (GHG) emissions as an important environmental side effect. Even if the process is simple and can be applied to mixed plastic waste, the carbon atoms that are entrapped in the solid state are emitted as GHG, which poses an important footprint (Conroy; Zhang, 2024).

In an advanced recycling scenario, selective depolymerization technologies, i.e. solvolysis, play an important role in the industrial framework of a circular plastic production chain. IUPAC defined the top 10 emerging technologies for 2023, designating two of them for the depolymerization of polymers. One of them highlighted enzymatic depolymerization, while the other focused on general chemical depolymerization technologies, including thermochemical and solvolysis technologies (Gomollón-Bel, 2023). Figure 1.1.2 provides an overview of the most common circularity strategies for plastics.

It is important to emphasise that chemical recycling does not directly compete with mechanically recycled products, as the former targets distinct applications and produces virgin-like materials. In this sense, chemically recycled products will mostly compete with bio-based and fossil-based virgin polymers.

Chemical recycling should be strategically implemented where mechanical recycling fails to deliver virgin-like properties, particularly for contaminated, mixed, or heavily degraded streams. The role of chemical recycling should complement, rather than replace, lower-impact strategies such as reuse and mechanical recycling. Although chemical recycling represents a promising global industrial solution for waste management, it will need to achieve competitiveness with first-generation polymers. This can be facilitated through mechanisms such as recycling subsidies or the implementation of environmental responsibility levies on virgin poly-

Figure 1.1.2: Scheme of Waste Treatment According to Destination Impact.



Source: The author (2024).

mer waste, encouraging the adoption of more sustainable practices.

This dissertation aims to contribute to both ends of PBS life cycle technology. The first part focuses on the synthesis of PBS-based copolymers through simultaneous enzymatic transesterification and ring-opening polymerization, enabling structural modification and performance enhancement. The second part addresses the chemical recycling of PBS via glycolysis, evaluating the key operational parameters which affect depolymerization yield and the feasibility of a circular approach. Together, these studies provide complementary insights into the design of sustainable polymer systems and end-of-life solutions.

1.2 Objectives

This work aims to analyze both ends of the life cycle of PBS. The sustainable development of new materials through bio-based co-polymerization of PBS monomers with selected

lactones using enzymatic catalysts, and an advanced recycling strategy through glycolysis. Specific objectives include: :

- Investigate the copolymerization of PBS monomers and lactones.
- Develop and characterize PBS-lactone copolymers with defined compositions.
- Assess the compositional properties and molar mass distribution of the synthesized materials.
- Establish and validate a design of experiments (DoE) framework to optimize PBS glycolysis.
- Evaluate the effects of reaction parameters on glycolysis performance via DoE.
- Identify optimal conditions for enhanced glycolysis efficiency and process characteristics.
- Quantify the overall effectiveness of the glycolysis recycling process.
- Derive statistical insights from DoE results to model process behavior.
- Demonstrate feasibility of laboratory-scale polymer recovery via repolymerization.

1.3 Dissertation structure

This work is structured to address both the synthesis of Butylene Succinate-Lactone copolymers and the recycling of poly(butylene succinate) (PBS), aiming to establish a comprehensive understanding of their circular life cycle. In particular, the work is divided into five chapters, which summarize the logical flow of the research.

- **Chapter 1** introduces the problem and contextualization data, research motivation, objectives, and general context of the study. This chapter is aimed to give a perspective on the environmental challenges related to plastic waste on current linear production and disposal. It highlights the growing interest in bio-based and biodegradable polymers, particularly PBS, as well as the possibilities for chemical recycling processes. The work adopts a dual approach addressing both ends of the PBS life cycle: the copolymerization of PBS monomers with lactone monomers and the depolymerization of PBS by glycolysis to enable an extended life cycle.

- **Chapter 2** presents a detailed literature review divided into two perspectives. The first section addresses the synthesis of PBS copolymers in general, with different technology approaches and monomer uses, discussing, in particular, the use of lactone monomers and enzymatic catalysis. The second part focuses on recycling technologies for polyesters, analyzing the mechanisms and environmental implications, followed by the data-driven process variables analysis for solvolysis methods such as glycolysis. Together, these sections establish the theoretical basis for the experimental investigations that follow in the last chapters.
- **Chapter 3** investigates the Simultaneous Ring-Opening and Condensation Polymerization (SROCP) of PBS monomers and lactones. This study investigates the mechanistic interactions between condensation and ring-opening reactions under enzymatic catalysis, aiming to develop new copolymers with modified structures and properties.
- **Chapter 4** explores the chemical recycling of PBS through glycolysis, applying statistical and experimental analyses to identify the influence of process variables involved on the depolymerization mechanism. This chapter aims to provide insights into a closed life cycle for a foresighted bioplastic industry.
- **Chapter 5** concludes the discussion, integrating both findings of chapters 3 and 4 for synthesis and depolymerization technologies, providing general conclusions and future work perspectives. It highlights the interdependence between polymer design and recyclability, reinforcing the concept of sustainable polymer engineering within the circular economy framework.

Chapter 2

State of the Art of Butylene Succinate Copolymers and Polyester Recycling

2.1 Introduction

PBS has emerged as a promising biodegradable polyester derived from renewable monomers such as succinic acid and 1,4-butanediol. Particularly, PBS exhibits mechanical and processing properties comparable to conventional polyolefins while maintaining high biodegradability and biocompatibility, which make it suitable for applications ranging from packaging to biomedical devices. (Peñas et al., 2022).

Despite these advantages, PBS, like most bioplastics, still faces challenges in achieving large-scale competitiveness and full integration within circular economy frameworks. To address these limitations, two complementary research pathways have attracted significant attention: 1) the synthesis of copolymers to improve physicochemical and mechanical properties of polymeric materials, and 2) the development of efficient recycling processes to extend the life cycle actively on the market. Together, these approaches can establish a more sustainable life cycle for PBS-based materials, from synthesis to recovery. (Platnieks et al., 2021; Fredi; Dorigato, 2021)

The first part of this chapter focuses on the current status of PBS copolymer synthesis, highlighting the molecular mechanisms and the possibility of modified material properties. Several comonomers, including aliphatic, aromatic, and lactone-based monomers, have been explored to produce copolymers with enhanced flexibility, crystallinity, and degradation rates. Among these, lactone-derived units stand out due to their chemical compatibility and fast re-

action through ring-opening polymerization. Moreover, the recent exploration of enzymatic catalysis presents a greener route for PBS copolymerization, enabling polymer formation under mild and selective conditions.

The second part of the chapter transitions to the chemical recycling of polyesters, particularly through solvolysis reactions such as glycolysis, hydrolysis, and alcoholysis. In particular, solvolysis is an emerging process that can turn plastic waste back into its monomers, facilitating the separation between polymer, impurities and additives to bring a virgin-like polymer production out of waste.

Although not directed altogether to PBS, this review section provides important perspectives for the recycling technology as a whole, enabling the use of the analyzed data to redirect it to the case of study of PBS, since polyesters depolymerize approximately alike, as they share the same cleavage mechanism.

These interconnected approaches form the conceptual and technical foundation for the experimental investigations that follow in Chapters 3 and 4, which explore in detail the mechanisms of simultaneous polymerization and chemical depolymerization of PBS.

2.2 Current Status of PBS Copolymers Synthesis

Modern day industry presents high interest into environmentally designed products, and bioplastics have been of particular interest due to its both low carbon emission and technological possibilities. From this perspective, particular applications and properties enhancements of established bioplastics present a demand for technological advancements, such as polymer blends and copolymerizations. (Peñas et al., 2022)

Thus, this section will provide context on polymerization mechanisms and bio-based monomers on market. It discusses on recent copolymerizations based on PBS, focused on polycondensation and ring-opening polymerization, for better understanding of subsequent experimental procedures.

2.2.1 Polyester

Polyester is a category of polymers characterized by the presence of ester groups as repeating units in the polymer chains (ASTM, 2025). Among commercial polyesters, PET stands out with the highest production and marketing volumes, making it the primary subject in

recycling studies due to its suitability for various methods (Statista, 2025; OECD, 2022a).

In addition to PET, the use and interest in biopolymers (e.g. poly lactic acid(PLA), poly(butylene succinate) (PBS), poly butylene adipate-co-terephthalate (PBAT), and polyhydroxyalkanoates (PHA)) have been rising considerably (Ishimwe, 2024). Driven by the goals of a sustainable and circular market, industry and society alike are supporting this type of solution alongside the push for energy transition, aiming for a low-carbon and circular production system. In particular, the intrinsic structure of polyesters also provides a particular capacity for chemical recycling through depolymerization reactions, enabling a virgin grade full circularity on a product life cycle scale (Ismail et al., 2024).

The main monomers for a polyester synthesis are lactones, diacids and anhydride derivatives, diesters, diols and polyols. The reaction occurs mainly under a esterification of a diacid and a dialcohol, a transesterification of an diester and a dialcohol or a ring-opening polymerization of a lactone (Jiang; Loos, 2016; ASTM, 2025).

2.2.2 Bioplastic Monomers

Bioplastics are defined as polymers from biological and renewable origin, those that are biodegradable or compostable, besides the special group that merges or possesses both characteristics (European Bioplastics, 2024). Therefore, many monomers for bioplastic synthesis originated from renewable sources.

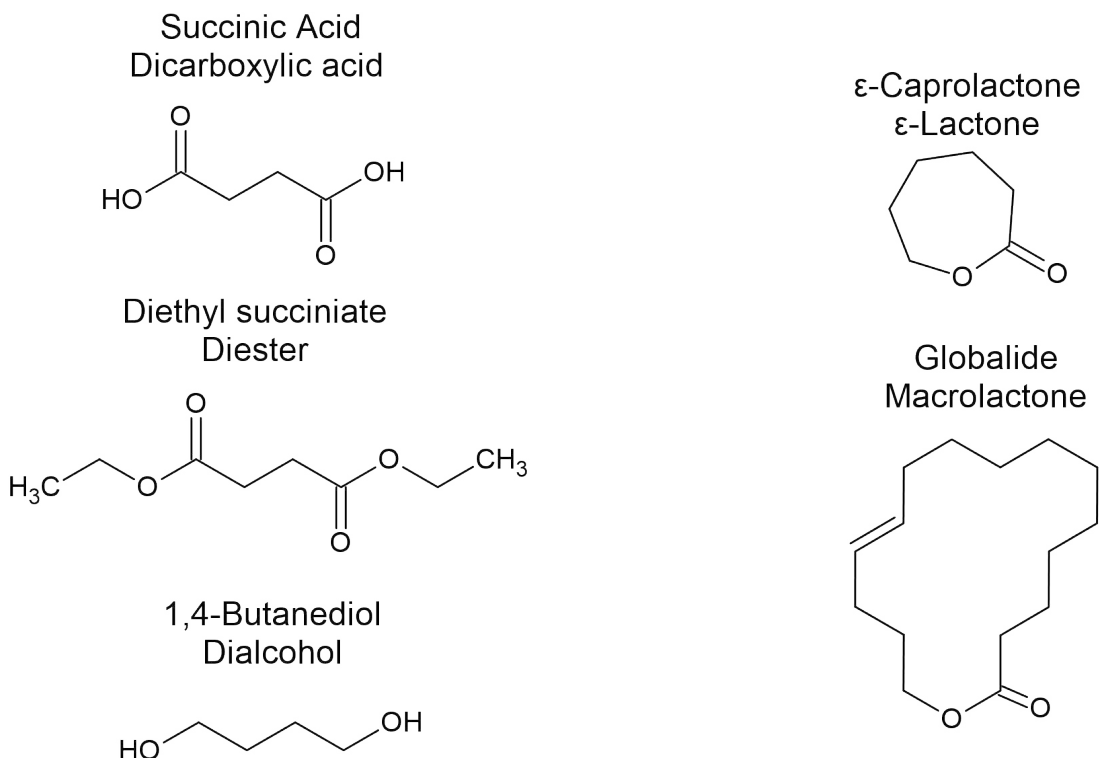
Most biobased monomers are produced by fermentation of carbohydrates or glycerol using engineered bacteria or yeast, where the microorganisms show a specific selectivity towards a monomer related to each microbial strain (Patel et al., 2018).

Although not all traditional fossil-based monomer has a commercial biobased pathway, studies show a high interest in its production with the use of various feedstock. In particular, monomers can be produced through fermentation processes of glucose, xylose and fructose from most agricultural products, as well as cellulose and hemi-cellulose on 2° generation production mostly by agricultural waste treatment and also by the use algae on 3° generation production. On that perspective, the biobased aliphatic acids, such as succinic acid, stand out as important building blocks for bioproducts (Jiang; Loos, 2016).

Many monomers are used in the polyester synthesis, giving a wide range of molecules that can be used with the properties highlighted. However, this work will be focused on the following monomer: succinic acid and its esters, 1,4-butanediol as a dialcohol and the macro-

lactones. Figure 2.2.1 shows examples of monomers used on a polymerization reaction.

Figure 2.2.1: Examples of molecules used as monomers for polymerization.



Source: the author (2026).

2.2.2.1 Succinic acid

Succinic acid (SA), a C₄-dicarboxylic acid, is recognized as an important building block molecule in modern industry. Currently, it can be produced by oxidation of fossil-derived maleic acid (anhydride), as the main industrial pathway. However, the fermentation route also deserves to be highlighted. In this case, succinates can be produced by fermentation from carbohydrates, obtained as a intermediate in the tricarboxylic acid (TCA) cycle during biosynthesis. Its dual carboxylic acid groups and central role in metabolism make it a versatile precursor for producing chemicals, polymers, food industry products and biofuels (Bechthold et al., 2008; Liu et al., 2022).

2.2.2.2 1,4-Butanediol

1,4-Butanediol (BDO) is a versatile chemical compound widely used in various industrial applications. It is a C₄-diol with two hydroxyl groups (-OH) positioned at the terminal

ends of a four-carbon chain. BDO is produced through multiple chemical pathways, including the hydrogenation of maleic anhydride or through a biobased approach carried out by reduction of sugar-derived succinic acid. It serves as a key precursor for synthesizing polymers, solvents, and other high-value chemicals, making it a critical component in the production of many materials, including polybutylene succinate (PBS) (Jiang; Loos, 2016).

2.2.2.3 Lactones

Lactones are defined by IUPAC as “cyclic esters of hydroxy carboxylic acids, containing a 1-oxacycloalkan-2-one structure, or analogues having unsaturation or heteroatoms replacing one or more carbon atoms of the ring.”(IUPAC, 2019). These compounds are widely found in nature (plants, bacteria, fungi, marine sponges, and other organisms) (Tănase; Pintilie; Tănase, 2021), and can be synthesized by biobased compounds (such as a 4-step ϵ -caprolactone synthesis from levulinic acid) (Jiang; Loos, 2016).

The smallest lactones, classified as α -, β -, γ -, δ -, and ω -lactones, consist of 3-, 4-, 5-, 6-, and 7-membered rings, respectively. Among these, γ - and δ -lactones are the most abundant, with over 3,000 known γ -lactone molecules. This abundance is attributed to the higher stability of their ring structures, which results from favorable stereochemical and electronic properties. Medium-sized lactones contain 8- to 11-membered rings, while macrolactones are characterized by rings with 12 or more members (Tănase; Pintilie; Tănase, 2021; Sartori; Diaz; Diaz-Muñoz, 2021).

Particularly, β -butyrolactone, δ -valerolactone, γ -butyrolactone, ϵ -caprolactone, pentadecanolides, and globalide are important lactones which can be used to produce polyesters, with considerable undergoing studies and applications for both homo and copolymerization processes (Dong et al., 2025; Bińczak; Dziuba; Chrobok, 2021).

2.2.3 Poly(butylene succinate)

PBS is a polyester which can be produced from renewable monomers, synthesized via fermentation routes (Bechthold et al., 2008). In particular, PBS has similar properties to commercial polyolefins; however, PBS stands out due to its biocompatibility and high biodegradability. PBS is currently considered one of the most important bioplastics, with interesting characteristics (Aliotta et al., 2022).

The most important applications include packaging, disposable items, agricultural films,

nonwoven fabrics, compostable bags and materials for biomedical devices, such as surgical sutures, scaffolds, drug delivery systems, and biodegradable implants (Barletta et al., 2022; Rafiqah et al., 2021; Kumagai et al., 2024).

PBS is generally produced on a two steps polycondensation reaction. The first step proceeds with a oligomerization of the monomers, in a pre-polymerization reactor, where a direct esterification reaction (of succinic acid) or transesterification reaction (of a succinic diester, such as diethyl succinate, for example) with 1,4 butanediol occurs with the continuous removal of a volatile by-product (water or an alcohol) on continuous nitrogen flow. The second step is conducted under higher temperature and vacuum pressure for continued transesterification of diesters formed in the first step and the removal of 1,4-butanediol, when in excess, providing a higher molar mass (Gigli et al., 2016; Barletta et al., 2022).

The process is usually carried out on stoichiometric amounts of succinic acid (or its ester) and BDO, but an BDO excess of 15% at maximum can be desired. The first step is carried out under 160–190 °C until complete conversion of succinic acid or its diester under a N₂ atmosphere with water or alcohol removal. The second step usually occurs subsequently at 220 – 240 °C under a vacuum until the established desired reaction time (Gigli et al., 2016; Barletta et al., 2022).

Many catalysts are used for the PBS synthesis; however, titanium tetrabutoxide (TBT) has been reported as the most common and effective. Other catalysts such as Zr(OBu)₄, Sn(Oct)₂, Sb(OBu)₃, Hf(OBu)₄, and Bi(ODec)₃, Sc(NTf₂)₃, Sc(CF₃SO)₃, titanium(IV) isopropoxide phosphate acid and composites of titanium and tin are also applied (Barletta et al., 2022; Nath et al., 2025).

Another catalyst class that has gained increased interest in recent studies are enzymes. In particular, the use of enzymes provides a greener synthesis pathway towards the use of a catalyst that allows the polymer production under mild conditions of temperature. Additionally, the enzymes are bio derivatives with non-toxic character, and, therefore, their use represents a more sustainable approach for biopolyester synthesis. However, few studies involve the use of lipases in the succinic acid esterification pathway, hence being limited to the transesterification process of a succinic ester with 1,4 butanediol (Lai et al., 2023; Gigli et al., 2016).

Candida antarctica Lipase B (CALB), on its immobilized form, is frequently utilized in the industry, mainly on fine chemicals. In particular, the better thermal stability, more stable performance and facility of separation and reuse, due to its granular form, have increased the

interest in the use of lipases in polymerization reactions (Jiang; Loos, 2016; Lai et al., 2023).

The most preponderant commercial product is the Novozym 435 (N435). It is composed of 10% CALB on a Lewatit VP OC 1600 bead, with bead sizes ranging from 0.3 to 1.0 mm. In this form, some studies have shown the CALB can tolerate temperatures up to 150°C (Jiang; Loos, 2016).

2.2.4 Polylactones

Polylactones are of particular interest due to their biodegradability and biocompatibility properties, with consistent applications on biomedical and pharmaceutical products, such as scaffolds and soft tissues. (Dong et al., 2025)

The use of enzymes to catalyze this reaction is also of great interest, since it allows the polymerization to reach high molar masses under mild conditions. (Polloni et al., 2018)

Some of the most prominent lactone-derived polymers are Poly(ϵ -Caprolactone) (PCL), Poly(pentadecalactone), Polyhydroxybutyrate (PHB) (Bińczak; Dziuba; Chrobok, 2021) and some recently studied polymers such as Poly(γ -valerolactone)(PVL) and Polyglobalide(PGL).

PCL, synthesized from ϵ -caprolactone, is presented as a polyester with good biocompatibility and degradation, with a high T_c (36.4 °C) and low T_m (60°C) and T_g (-60°C), used mainly on biomedical applications (Li; He; Inoue, 2001). Some of its main disadvantages include the low melting point, mechanical properties, such as low Young's modulus and its low solubility in a variety of solvents (Saeed, 2010; Li; He; Inoue, 2001).

PGL is synthesized from 12-pentadecene-15-olide, also known as globalide, which is an unsaturated macrolactone (Van der mulen et al., 2025). It shows similar applications as PCL, with a similar T_c (38 °C) and a lower T_m (42°C) (Tinajero-Díaz; Martínez De Ilarduya; Muñoz-Guerra, 2020; Guindani et al., 2022). Also, its instauration provides an interesting technological opportunity for specific applications, due to its possibility to provide a substitution reaction with a functionalization molecule (Polloni et al., 2020; Savin et al., 2018).

2.2.5 Polymerization Routes

Polymerization, as defined by the IUPAC's purple book, is a "process of converting a monomer or a mixture of monomers into a polymer". Monomer is defined as a molecule which can undergo polymerization and, thereby, insert constitutional units to the essential structure of a macromolecule, while the polymer is represented by a chain size distribution with distinct

number of repeating units. The polymer structure essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molar mass (Jones et al., 2009).

The polymer synthesis can be performed under various pathways, which involve specific reaction mechanisms, such as:

- **Chain polymerization:** In this pathway, the growth of a polymer chain proceeds exclusively by the reaction or reactions between a monomer or monomers and a reactive site or reactive sites on the polymer chain, with regeneration of the reactive site or reactive sites at the end of each growth step (Jones et al., 2009).
- **Polyaddition:** Polymerization in which the growth of polymer chains proceeds by addition reactions between molecules of all degrees of polymerization (Jones et al., 2009).
- **Step polymerization:** Polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all degrees of polymerization (Jones et al., 2009).
- **Ring-opening polymerization:** Polymerization in which a cyclic monomer yields an acyclic monomeric unit through ring-opening. This process occurs via chain propagation reactions. An active species (e.g., alkoxide or cation) attacks the cyclic monomer, opening the ring and forming a new reactive acyclic end. This end then adds successive monomers, propagating the linear polymeric chain. (Jones et al., 2009).

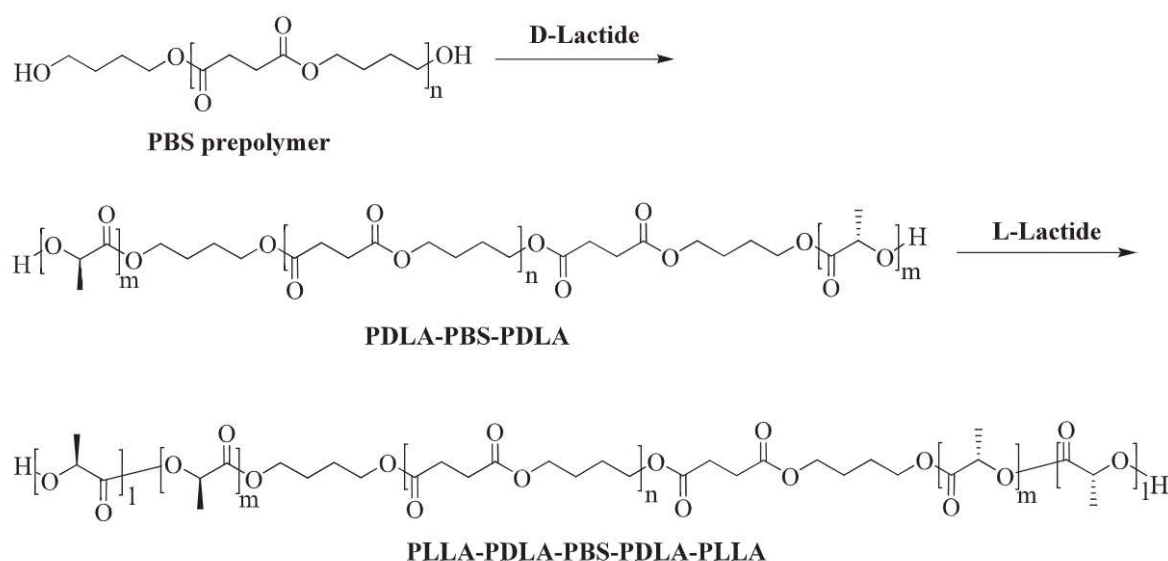
Polycondensation and Ring-opening polymerization are of particular interest from the polyester perspective. Most of the polyester monomers are cyclic hetero-atomic compounds or a combination of diacids or diesters and dialcohols. Therefore, its synthesis will occur mainly through the ring cleavage and sequential polymerization through esterification and transesterification reactions with the formation of a by-product (Jones et al., 2009).

Thus, a simultaneous ring-opening and condensation polymerization (SROCP) could have potential for the development of new products from polymerization reactions. Núñez, et al. have studied this reaction pattern through the copolymerization of 1,4-butanediol, dimethyl succinate and ϵ -caprolactone, presenting significant results.(Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021)

2.2.6 Butylene Succinate Copolymerization

Due to some undesired properties of a polymer, the copolymerization technique has been used to improve biodegradation rates, mechanical and thermal properties. The main produced copolymer of PBS to date has been the poly(butylene succinate-adipate) (PBSA), which shows higher biodegradability and flexibility (Aliotta et al., 2022; Bińczak; Dziuba; Chrobok, 2021).

Figure 2.2.2: Synthesis of penta-block copolymers via tri-block copolymers.



Source: (Lee et al., 2016).

Other designed polymers, the PLA-PBS multiblocks have been developed under various compositions, e.g. PLLA-b-PBS-b-PLLA triblock, (Ba et al., 2003), PDLA-b-PBS-b-PDLA Tri-block (D'Ambrosio et al., 2017), and PDLA-b-PLLA-b-PBS-b-PLLA-b-PDLA pentablock (Lee et al., 2016) copolymers. The PLA-PBS triblock and pentablock synthesis pathway is described in Figure 2.2.2.

Furthermore, many acids and diols were tested and applied in copolymerization reactions. Table 2.2.1 presents the main results about PBS copolymers published in the literature.

Table 2.2.1: PBS copolymerization summary.

Polymer	Comonomers ^a	Contribution	Properties	Reference
PBSA	Adipic acid	Reduces stiffness and soil biodegradability	T_g (°C):	(Simão; Bellani; Branciforti, 2017)
			T_c (°C) :	
			34	
			T_m (°C) : 91 T_d (°C): 424	
PBSCL	ε-Caprolactone	It exhibits an isodimorphic and pseudo-eutectic behavior, allowing a single copolyester to form only PCL crystals, only PBS crystals, or both, thereby displaying distinct thermal properties.	T_g (°C): -58 to -36	(Safari et al., 2018, 2021; Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021; Ciulik et al., 2017)
			T_c (°C) : -23 to 61	
			T_m (°C) : 11 to 104	
			T_d (°C): 471 to 476	
PBSFB	2,5-furandicarboxylic acid	It exhibits an amorphous, aromatic composition with good thermal stability, along with an increased T _g and satisfactory biodegradability.	T_g (°C): -20 to -40	(Morales-Huerta; Martínez de Ilarduya; Muñoz-Guerra, 2017)
			T_m (°C) : 100	
			T_d (°C): 391 to 400	
PLA-mb-PBS	L- or D-Lactide	Both homopolymers and copolymers with a higher PLA content exhibit negative spherulites, however, the copolymers with a lower PLA content had a dendritic morphology. Shows higher tensile strength and manipulable thermal properties.	T_g (°C): -21 to -7.9	(D'Ambrosio et al., 2017; Lee et al., 2016; Ba et al., 2003)
			T_c (°C) :	
			44 to 162	
			T_m (°C) : 92 to 201	

^a) Monomer copolymerized with the original PBS monomers 1,4-butanediol and succinic acid/ester for the butylene succinate block.

(continued from previous page)

Table 2.2.1: PBS copolymerization summary

Polymer	Comonomers ^a	Contribution	Properties	Reference
P(BSmTESn)	Triethylene succinate	With increasing triethylene block content, wettability increased, while T _m and the degree of crystallinity decreased, suggesting enhanced hydrolytic degradation.	T_g (°C): -35 to -32 T_c (°C) : 53 to 75 T_m (°C) : 78 to 111 ^{max}T_d (°C): 471 to 476	(Fabbri et al., 2018)
PPC-mb-PBS	Propylene oxide CO ₂	Changes the thermal characteristics, presenting a higher T _g and can effectively address the poor mechanical properties of PPC at low temperature, extending the potential and practical application.	T_g (°C): -40 to -38 T_m (°C) : 93 to 108 Crystallinity (%) : 15 to 47	(Qin et al., 2018)
PBSDLS	Dilinoleic diol	Suggested semicrystalline structure, crystallizing into monoclinic α -form crystals.	T_g (°C): -52 to -42 T_c (°C) : 14 to 68 T_m (°C) : 82 to 107	(Sokołowska et al., 2022)
P(BSBDTDP)	Dithiodipropionate	The addition of comonomer did not alter both hydrophobicity and thermal stability, but reduced crystallinity, elastic modulus, and increased the toughness, providing also an enhanced biodegradation.	T_g (°C): -35 to -32 T_c (°C) : 53 to 75 T_m (°C) : 78 to 111 ^{max}T_d (°C): 471 to 476	(Guidotti et al., 2020)

^a) Monomer copolymerized with the original PBS monomers 1,4-butanediol and succinic acid/ester for the butylene succinate block.

(continued from previous page)

Table 2.2.1: PBS copolymerization summary

Polymer	Comonomers ^a	Contribution	Properties	Reference
PBS-b-PBSe	Sebacic acid	Shows separated crystal lattices, with lower crystallinity and melting point. Moreover, the copolymer presented enhanced mechanical properties	T_g (°C): -35 to -32 T_c (°C) : 53 to 75 T_m (°C) : 78 to 111 ^{max}T_d (°C): 471 to 476	(Shang; Jiang; Qiu, 2021)
PBS-BF	Fumaric acid	Shows a higher T _m and T _c and elastic modulus, however decreased the strength and elongation at break.	T_g (°C): -29 to -24 T_c (°C) : 70 to 75 T_m (°C) : 115 to 118	(Sheikholeslami et al., 2016)
P(BS-co-SA)	Salicylic acid	Better degradability with similar properties in general. Shows a particular agricultural application with improved plant growth compared to pure PBS.	T_g (°C): -26 to -28 T_c (°C) : 77 to 83 T_m (°C) : 115 to 116 ^{50%}T_d (°C): 357 to 377	(Wang et al., 2019)
PBSPDGS	Diethylene glycol	The crystallization rate decreased, the work of chain folding increased, and the band spacing decreased with decreasing block length.	T_g (°C): -30 to -24 T_c (°C) : 55 to 95 T_m (°C) : 82 to 111	(Soccio et al., 2009)

^a) Monomer copolymerized with the original PBS monomers 1,4-butanediol and succinic acid/ester for the butylene succinate block.

(continued from previous page)

Table 2.2.1: PBS copolymerization summary

Polymer	Comonomers ^a	Contribution	Properties	Reference
PBSAsp	L-aspartic acid	Presented higher molar mass and good break strain.	T_g (°C): -28 to -39 T_c (°C) : 53 to 75 T_m (°C) : 108 to 111 maxT_d (°C): 299 to 323	(Oishi; Iida; Taguchi, 2010)
PBS-PBT	Terephthalic acid	Initial modulus and breaking stress of the copolymer decreased, but toughness and breaking strain of the copolymers increased.	T_g (°C): -31 T_m (°C) : 70 to 107	(Park; Cho, 2001)

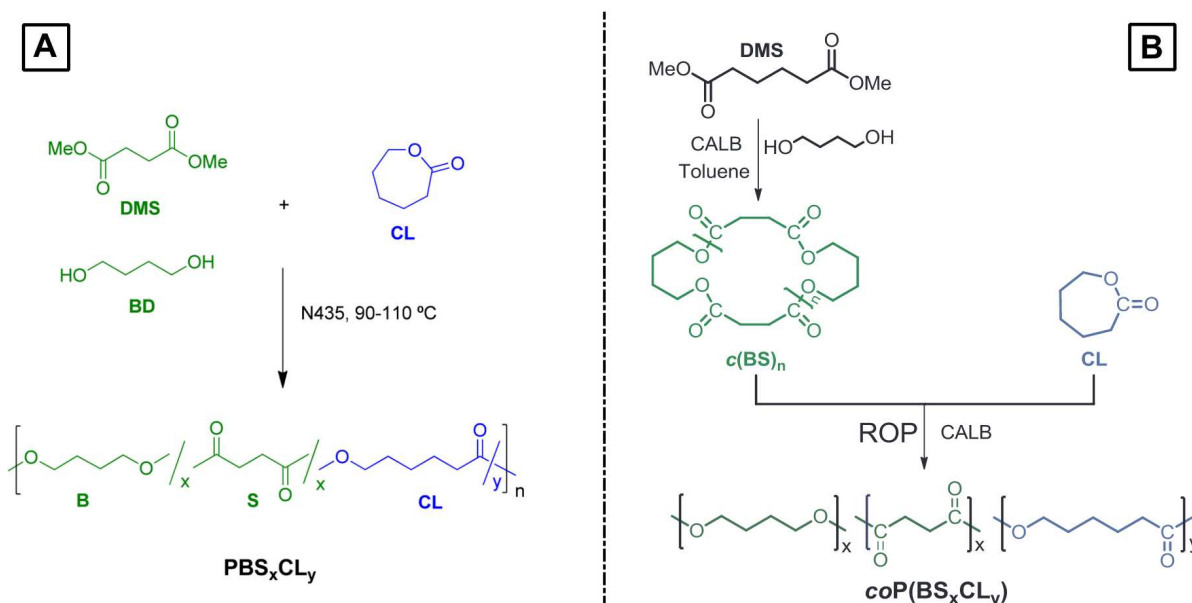
^a) Monomer copolymerized with the original PBS monomers 1,4-butanediol and succinic acid/ester for the butylene succinate block.

Source: The author (2024).

On another perspective, poly(butylene succinate-co- ϵ -caprolactone)(PBSCL) has been synthesized on simultaneous ring-opening and condensation polymerization (SROCP) and a ring-opening copolymerization. The first is conducted either in bulk or solution in a two-step SROCP (transesterification/esterification and polycondensation) with succinic acid or ester, 1,4 butanediol and ϵ -caprolactone, and the ring-opening copolymerization is conducted on another two-step polymerization, with the cyclization step of the cyclo(butylene succinate) unit under high solvent amount for a ring-closing reaction, and a ring-opening copolymerization with both cyclo(butylene succinate) and ϵ -caprolactone. Figure 2.2.3 presents both reaction mechanisms (Ciulik et al., 2017; Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021; Safari et al., 2019).

Of particular interest, the enzymatic SROCP of P(BS-CL) occurred not only under homopolymer (PBS) and homopolymer (PCL) conditions, but also at copolymer compositions of 30/70, 50/50, and 70/30 (PBS/PCL molar ratios). The enzyme activity of *Candida antarctica* lipase B was measured as 10,000 PLU/g after vacuum dried for 24 hours at 50 °C, and its quantity was defined to be 10% of total monomer mass in the experimental runs. The reactions were conducted at 90 °C for 4-6h (transesterification) and 7-24h (polycondensation) (Núñez;

Figure 2.2.3: PBSCL synthesized on (A) simultaneous ring-opening and condensation polymerization and B) ring-opening copolymerization. DMS: Dimethyl succinate; BD: 1,4-Butanediol; CL: Caprolactone.



Source: A) (Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021), B) (Ciulik et al., 2017).

Muñoz-Guerra; Martínez De Ilarduya, 2021). The copolymer structures showed weight average molar masses (M_w), by GPC evaluation, of 26,000 g/mol ($P(BS_{30}-CL_{70})$) to 36,000 g/mol ($P(BS_{70}-CL_{30})$), whereas the homopolymers showed, in the same work, 21,800 g/mol for PBS and 37,500 g/mol for PCL.

Recent studies have shown that the random copolymerization $P(BS\text{-}ran\text{-}CL)$ allows the production of copolymers with isodimorphic properties. In particular, the minor repeating unit compositions, randomly distributed, are included in at least one of the two crystalline phases in its crystal lattice. This behavior can be of remarkable interest, due to the capacity for thermal properties adjustment, which cannot be done on homopolymer synthesis, providing an excellent alternative for product design to specific applications (Ciulik et al., 2017; Safari et al., 2018, 2019).

A ring-opening copolymerization has also been studied for the reaction between the cyclic(butylene succinate) and 2,5-furandicarboxylic acids, producing Poly(butylene succinate-co-2,5-furandicarboxylate) (PBSFB) (Morales-Huerta; Martínez de Ilarduya; Muñoz-Guerra, 2017).

2.3 Chemical recycling as a tool for enabling a second life for polyesters

The second part of the review analyzes the recycling processes for polyesters as a whole to provide, with literature data, the possible avenues in which a polyester recycling technology could be reached, and to guide future researches on the area. Although it touches on general perspective of most recycling technologies, this section is focused on solvolysis processes.

It is an important step to the subsequent study to enlighten the chemical recycling possibilities for PBS, since it is scarce on information on current literature, with just a few studies on a few processes. Additionally, it is aimed to help the reader to have a better understanding of the chemical recycling market and the possibilities for a sustainable circular economy.

This section will present the processes and challenges of mechanical and thermochemical recycling, present and analyze the mechanisms, processes and studies on solvolysis technologies for the major polyesters. It shows recent life cycle assessments (LCA) and techno-economic analysis (TEA) for solvolysis processes as well as recent world policies aimed for stimulation of recycling process and the current global chemical recycling market. Additionally, it discourses on a particular perspective for a effective circular production ecosystem.

2.3.1 Mechanical Recycling

Mechanical recycling is often considered the best option for plastic recycling due to its relative simplicity, cost-effectiveness, and lower environmental impact compared to other methods (Bartolucci et al., 2023; Schyns; Shaver, 2021). This technology involves collecting waste plastic products, sorting by type, grade, and often an additional segregation by color. These plastic products must be fragmented into flakes before washing to remove coarse impurities, e.g. from packaged goods, residues of labels. The flakes should be separated and dried before the extrusion process, which results in pellets with homogeneous features (Ragaert; Delva; Van Geem, 2017). Drying is particularly important for polyesters as these are prone to extensive hydrolysis at extrusion conditions (Campos et al., 2025).

In the context of polyesters and polyamides, two important classes obtained by polycondensation reaction, a polishing and control technique is applied to standardize the polymer properties during the mechanical recycling step. Solid State Polymerization (SSP) allows increasing the molar mass of polymers (mainly in flake form) at temperatures between the glass transition (T_g) and melting (T_m) temperatures with a chain extension additive, removing reac-

tion by-products through vacuum or using inert gas. This is an interesting technique with advantages as low temperatures (reducing thermal degradation reactions of polymer chains) and simple equipment (low cost); however, step-growth polymerization reactions present low rates, requiring long times to reach the desired molar masses, besides the necessity to remove the by-products to avoid reverse reactions, which could be applied as a mechanical recycling step, but is not restricted to it (Vouyiouka; Karakatsani; Papaspyrides, 2005). Also, this approach is flexible enough to allow the increase of molar mass of biopolymers such as PLA (Vouyiouka et al., 2013) and Poly(butylene sebacate-co-terephthalate) (PBSeT) (Lim; Park, 2023).

Although mechanical recycling has been a powerful tool to improve the circularity concept, this approach has limitations due to the thermal degradation of polymers during a high number of reprocessing cycles and downcycling by the presence of contaminants, as other polymers and compounds. In the context of biopolymers, Agüero et al. have shown that mechanical ductility and melt flow index (MFI) of PLA were sensitive due the hydrolysis of ester groups from the fourth reprocessing cycle on, which led to smaller chains by chain scission, resulting in increased mobility. The degree of crystallinity was also increased by the reprocessing cycles, since smaller polymer chains were suitable to organize themselves as an ordered structure (Agüero et al., 2019). For some biopolymers, including PLA, PBS, and PBAT, Nomadolo et al. managed to perform mechanical recycling for up to seven re-processing cycles. Except for PBAT, which seemed to be the least impacted by reprocessing cycles, PBS and PLA presented a decrease in tensile strength, strain at break, and impact strength. MFI, otherwise, was increased in every cycle for all bioplastics, and this property is fundamental to control polymer applicability in various processing techniques. Increased crystallinity was also observed for higher number of cycles (Nomadolo et al., 2024).

During the reprocessing of PET by injection molding and extrusion from mechanical recycling procedures, the use of temperature between 200 and 300 °C allows the release of a wide number of hazardous substances as toxic metals, volatile compounds and phthalates, with a consequent risk of exposure (Hahladakis et al., 2018). In terms of volatile compounds for PET, the comparison between virgin polymer with recycled one showed a larger number of new compounds through GC–MS analysis, including aldehydes, aromatic hydrocarbons and acetophenone, which have been produced by degradation reactions of PET (Dutra et al., 2011). There are deep cleaning processes, combined with SSP or extrusion processing, that could remove part of these contaminants, but other compounds as 2,4-di-tert-butylphenol and 2,6-di-

tert-butyl-4-methylphenol are able to remain in recycled PET by a deficiency of control during the collection of this plastic or even by recontamination (Dutra et al., 2011).

In the context of the intentionally added substances (IAS), the most important classes of additives applied in polymer industry include plasticizers, antioxidants, heat stabilizers and slip agents, each class is associated with the improvement of the polymer properties, to result in the increase of flexibility, decrease of oxidative and thermal degradation and improve of surface properties, respectively (Hahladakis et al., 2018). Otherwise, the heterogeneity on the composition of plastics become a particular challenge for the quality and safety of mechanically recycled polymer due to these included additives from the polymer processing industry and non-intentionally added substances (NIAS), which is result of the interactions among different compounds in the product from degradation reactions and impurities from raw materials (Hahladakis et al., 2018; Nerin et al., 2013). Degradation processes are frequently related to NIAS, which could be the result of reaction of the polymer chain and the additives in the mixture. (Nerin et al., 2013) In the case of packaging plastics, the use of additives, antioxidants and stabilizers, besides of the impurities of the raw materials themselves which are not in technical datasheets, could led to the appearance of new migrant compounds, which is a very concern especially when these substances are related to recycled plastics and the application is for food packaging, becoming a source of contamination (Nerin et al., 2013).

Additionally, some plastics, as from application in children toys, food-contact materials and household products, may retain brominated flame retardants (BFR), comprising persistent organic pollutants (POPs), phosphorus flame retardants, and phthalates (Hahladakis et al., 2018). A best available technique/environmental practice guidance related to the recycling, separation, and management of plastics with POP and BFR compounds was ratified by 180 countries as consequence of the Stockholm Convention, which can mitigate the problems arising from mechanical recycling (Hahladakis et al., 2018).

Typical mechanical recycling is limited to thermoplastics, i.e. non-covalently crosslinked polymers. Research activities have been intense in the last decade on a new class of polymers, intermediate to thermoplastics and thermosets, crosslinked via reversible covalent bonds (e.g. covalent adaptable networks, vitrimers) (Montarnal et al., 2011). Despite being particularly suitable for polyesters thanks to the transesterification chemistry (Debnath; Kaushal; Ojha, 2020), this concept is still in its infancy and, although promising, is not expected to solve the plastic burden in a short term. Moreover, the main disadvantage of the mechanical recycling is associ-

ated to the fact that since recycled polyester leads to lower grade product (downcycling) through the degradation of polymer chains, when this procedure is not suitable to be applied anymore, it results in a waste flow, which could potentially be turned into a value-added product once again by chemical recycling to recover its monomers (Lamberti; Román-Ramírez; Wood, 2020).

The polyester fabric perspective is also of particular importance to be considered under the mechanical recycling scenario. Similarly to thermoplastic films and parts, there are closed- and open-loop processes for recycling textile fibers, considering the purpose and the degree of degradation of the material. Two pathways are usually followed on a strict mechanical process, where the fibers are teared and fragmented into smaller pieces separating garments such as metal and zippers, assembling into another poorer in quality fiber, mainly due to lower fiber length (up to 40% shorter), for this reason it is usually on an open-loop cycle. The thermomechanical recycling involves the re-melting of synthetic fibers with the subsequent re-spinning. Nevertheless, due to polymer degradation, this approach usually leads to lower-quality products after each recycling cycle (Choudhury; Tsianou; Alexandridis, 2024; Lanz et al., 2024; Ziemińska-Stolarska et al., 2024).

This kind of recycling is limited by the need for high purity, compositional knowledge, and non-mixed/blended streams to lead to efficient processes and acceptable qualities. For that reason, it really limits the use of post-consumer waste (PCW) of fabric for the usually unknown polymer mixture, additives and contaminants composition. Consequently, less than 1% of the 10–12% of post-consumer textile waste collected is recycled in a closed loop (Choudhury; Tsianou; Alexandridis, 2024; Lanz et al., 2024; Tang, 2023).

For those reasons, most of the textile waste generated are usually landfilled or incinerated, which is a considerable opportunity for the chemical recycling industry, since heteropolymers can be both efficiently and selectively recycled into virgin-grade quality with good separation capabilities for contaminants, dyes, and polymer mixtures.

2.3.2 Chemical recycling

Chemical recycling is a group of processes characterized for the capacity of the fragmentation of a macromolecule into smaller molecules, aimed at the repolymerization with virgin related quality or upcycling processes. Its main objectives are the possibility of a repurpose of post consumer waste plastics into the material (closed loop) or new compounds (open loop). (Debowski et al., 2019) Technologies under this proposition are generally composed of

thermochemical and selective depolymerization (solvolysis) technologies.

Some proper terms, related to the context of chemical recycling that were already defined by the IUPAC Compendium of Chemical Terminology (IUPAC, 2019), were included below:

- **Depolymerization:** "The process of converting a polymer into a monomer or a mixture of monomers."
- **Unzipping:** "Depolymerization occurring by a sequence of reactions, progressing along a macromolecule and yielding products, usually monomer molecules at each reaction step, from which macromolecules similar to the original can be regenerated."
- **Solvolysis:** "Generally, reaction with a solvent, or with a lyonium ion or lyate ion involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for substitution elimination and fragmentation reactions in which a solvent species is the nucleophile ('alcoholysis' if the solvent is an alcohol, etc.)."

The use of some technological assistants have received much attention recently. The microwave irradiation is an alternative energy source that provides a series of advantages due to fast heating and reduction on reaction time. Kinetic investigations also verified an apparent reduction on the activation energy for the microwave irradiated processes compared to conventional heating.

Cosolvents use is also highly investigated due to its capability of enhancing the reaction through high dissolution and turning into a homogeneous reaction.

2.3.2.1 Thermochemical Recycling

Thermochemical reactions for plastic waste recycling are categorized mainly under four main processing routes, namely: pyrolysis, gasification, hydrogenation, and incineration (Deng et al., 2021).

Its main advantage as a recycling process is the capacity to use any type or composition of plastics with reduced pre-treatment steps. Such processes are, in general, based on the cleavage of both C-X (where X is a heteroatom) and C-C bonds to progressively convert polymers into a mixture of smaller molecules (Sasse; Emig, 1998; Qureshi et al., 2020).

The pyrolysis process involves the decomposition of macromolecules at high temperatures (350 °C to 600 °C) in an oxygen-free (inert) environment, breaking them down into smaller fractions. Pyrolysis yields a mixture of gaseous, liquid, and solid products (Deng et al., 2021).

The main obstacle to the effective implementation of pyrolysis as a successful thermochemical recovery based on pyrolysis is its high energy consumption and the complexity of product formation, making it difficult to fully understand and predict the full product distribution (Kruse; Wong; Broadbelt, 2003). Commercially, with high-quality plastic feedstock, the process can be optimized to yield up to 85% of liquid oil at ca. 500 °C (Soni et al., 2021).

Gasification is a two-stage process that begins with an inert pre-degrading step at high temperature, followed by an O₂ blown reaction at higher temperatures, reaching up to 1600 °C and a pressure of up to 150 bar. This process forms mainly H₂ and CO (syngas), which can be used for numerous industrial processes and products (Deng et al., 2021; Sasse; Emig, 1998).

Polymer hydrogenation is derived from coal refining processes and the processing of heavy crude oil residues. This process involves a first step with a pre-degradation reaction at around 500 °C, followed by the hydrocracking step in a bubble-column reactor, with an inlet of molecular hydrogen at high pressure (Sasse; Emig, 1998). The hydrocracking process has some limitations due to products formation, where polymers with heteroatoms can result in HCl and NH₃ formation.

The incineration process is used mainly for energy recovery and plastic material disposal. It is the last resort method for a plastic waste repurpose due to its high GHG emissions. Although it is not the ideal solution for circular production, incineration processes can be a potential solution for hard-to-degrade polymers, where even pyrolysis does not offer a sustainable alternative for waste degradation (Deng et al., 2021).

2.3.2.2 Selective Depolymerization

Selective depolymerization (or solvolysis) is an emerging process that aims to enhance circularity by enabling the efficient recovery of smaller molecules through the controlled decomposition of polymers. This process is based on polymer (e.g., post-consumer waste, PCW) cleavage, targeting the breakdown into new compounds, such as their corresponding monomers. Unlike thermochemical depolymerization, this process allows for greater selectivity in targeting specific groups.

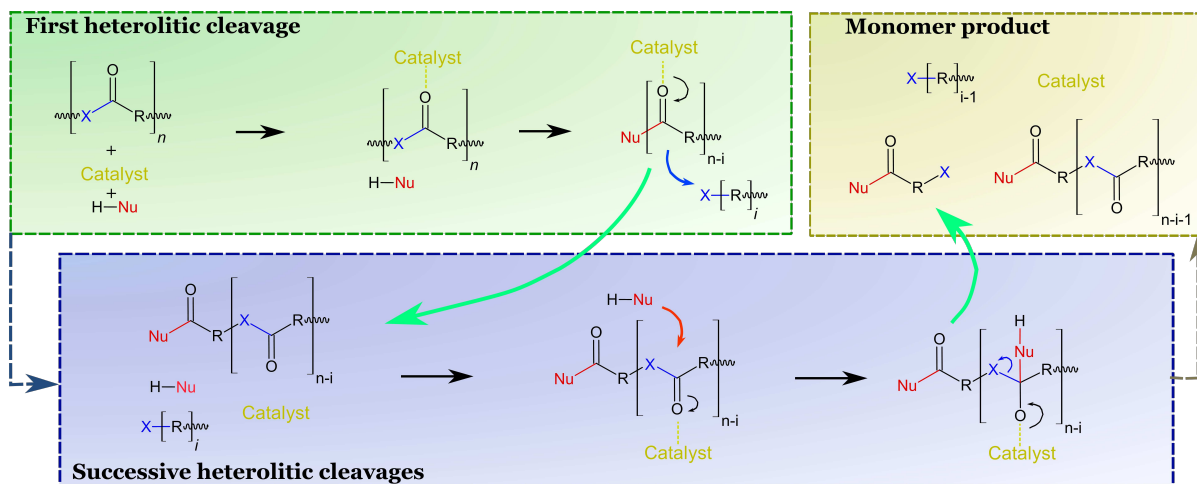
The key factor enabling such a controlled degradation is the presence of some heteroatoms, such as those in the backbones of polyesters, polycarbonates, polyvinyls, polyurethanes, and polyamides. These heteropolymers are composed of repeating units that contain at least one C-X bond, where X represents an atom more electronegative than carbon (such as oxygen and

nitrogen). These bonds (e.g., C-O and C-N) can undergo preferential chemical cleavage. Therefore, depolymerization and building block recovery support the development of a more circular production system (Clark; Shaver, 2024).

In this case, depolymerization occurs due to the polarity of C-X bonds and their susceptibility to heterolytic cleavage reactions. This polarity makes the bond more reactive, facilitating its breakdown under specific conditions. Moreover, the nature of the heteroatom X influences the reactivity of the bond and the nature of the depolymerization products.

2.3.2.2.1 Generic Mechanism Although the fundamental determination of the C-X bond reveals considerable interdependence between the degradation processes and the electrolytic heteroatom X, these processes can be generally described by a basic depolymerization mechanism (Figure 2.3.1) (Clark; Shaver, 2024).

Figure 2.3.1: Generic mechanism for a nucleophilic and catalytic depolymerization reaction. Where R is a representative for the polymer repeating unit, Nu is the nucleophilic molecule used on the depolymerization reaction and the X stands for a heteroatom on the polymer backbone, e.g. a oxygen for a polyester (Clark; Shaver, 2024).



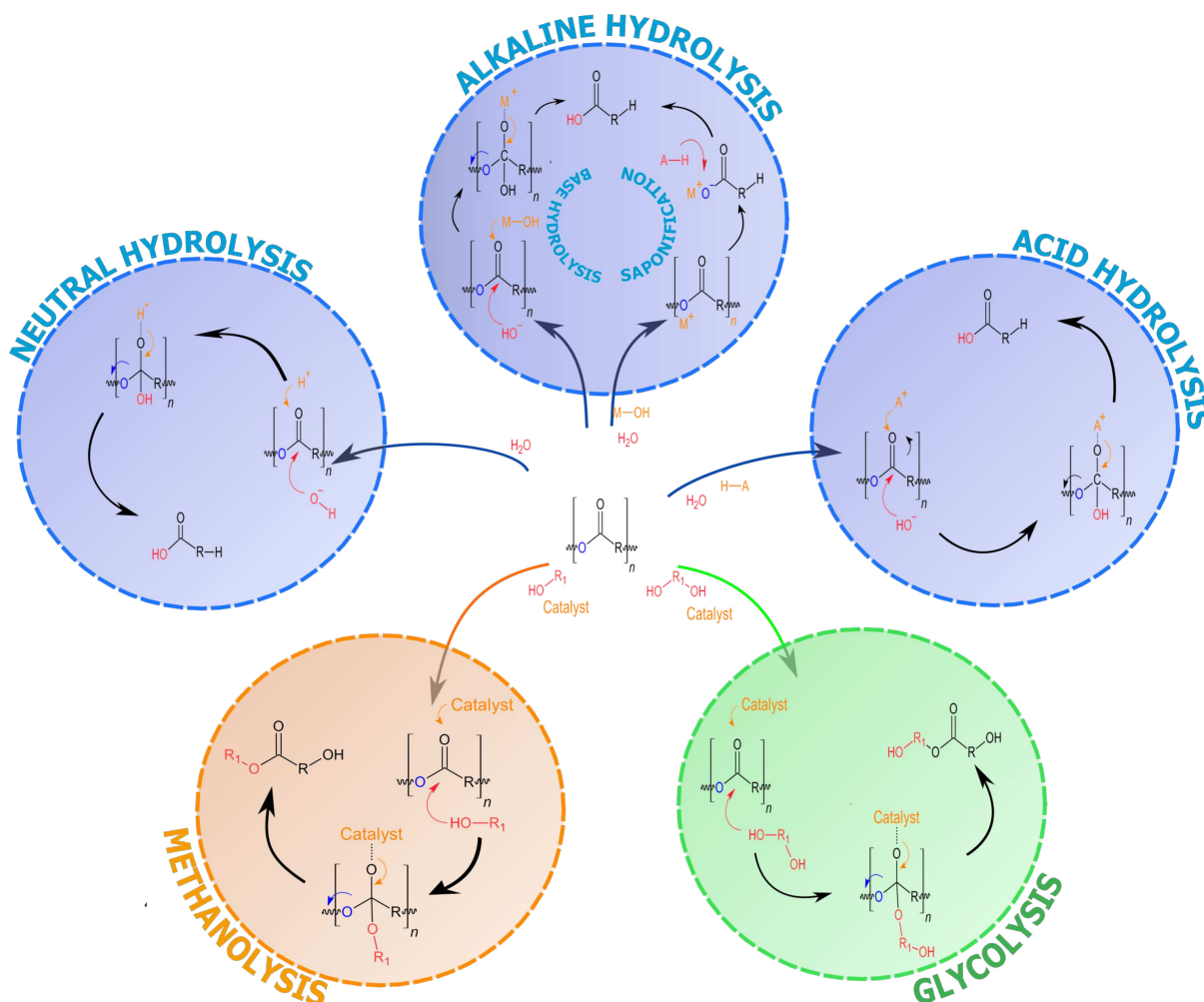
Source: The author (2024).

- 1. Activation of the C-X bond:** The first step involves activating the C-X bond, which can be achieved through various methods, such as the use of acid or base catalysts, free radicals, or transition metal complexes, associated with a solvent that defines the chemical pathway.
- 2. Heterolytic cleavage of the C-X bond:** The bond activation leads to its heterolytic cleavage, resulting in the formation of a carbocation or a carbanion, depending on the reaction conditions, which may lead to nucleophilic substitution.

3. **Chain propagation:** In some cases, the reactive species formed in the previous step can initiate a chain reaction, leading to the cleavage of other C-X bonds along the polymer chain.
4. **Termination:** The reaction concludes when the reactive species are consumed or when the reaction conditions change.

Overall, polyesters are the most explored polymers in selective depolymerization, primarily due to the high production volume of PET; however, this depolymerization can also be explored for polyamides, polyurethanes, and polyvinyls (Ait-Touchente et al., 2024). Tethered to the scope of this review, the following mechanisms (Figure 2.3.2) will be discussed from a polyester perspective:

Figure 2.3.2: General solvolysis mechanisms for each of the main categories. R is a representative of the polymer chain on repeating unit, and R_1 represents the type of alcohol, alcoholysis, and dialcohol, for glycolysis (Abed-soltan, 2023; Sinha; Patel; Patel, 2010; Clark; Shaver, 2024; Muszyński et al., 2023).



Source: The author (2024).

2.3.2.3 Hydrolysis

Within the context of this review, hydrolysis stands for the depolymerization process that occurs using water as a solvent or dispersant. It is commonly divided into four categories: neutral, alkaline, acidic, and enzymatic, based on the nature of the catalyst used (Abedsoltan, 2023). In general, hydrolysis occurs on the polymer surface through the substitution of C-X bonds with hydroxyl groups released by water, analogously to the highlighted general mechanism.

The products of a hydrolysis reaction are usually the initial monomers for the original polymerization – e.g. for PET, the products of hydrolysis are terephthalic acid (TPA) and ethylene glycol (EG). Neutral hydrolysis takes place with a large excess of water at a pH close to neutrality and at high temperature and pressure. The main advantages are the absence of organic solvents and catalysts like acids and bases. On the other hand, this process has problems with the operational cost of the high temperatures and pressures (Abedsoltan, 2023).

Alkaline hydrolysis takes place at higher pH and with the use of a base catalyst, usually a metal oxide catalyst. There are generally two pathways for an alkaline hydrolysis:

1. Metal ionizes carbon, weakening the double bond, allowing for the heterolytic attack of the hydroxyl group, which breaks a bond in the polymer backbone (Sinha; Patel; Patel, 2010).
2. Saponification reaction, where the charged metal attaches to the heteroatom X (in this case, oxygen), cleaving the polymer chain bond. Given the basic reaction mechanism, it is necessary to use an intermediary acid treatment to precipitate the corresponding diacid, as it is previously a carboxylate salt in the reaction medium (Rabello et al., 2024).

This process offers better conditions for industrial operation compared to neutral hydrolysis, but the additional treatment and subsequent separations are the main challenges to its feasibility.

Acid hydrolysis occurs at lower pH and with the use of a strong acid catalyst. Unlike alkaline hydrolysis, the additional step of acidification to precipitate the monomer, which is initially in the form of a salt, is not required, as the monomer is formed immediately as a product of the reaction. Although this route does not require additional purification steps, it uses large amounts of acid catalyst (Abedsoltan, 2023).

The enzymatic hydrolysis is aimed at developing a milder form of depolymerization that uses lower reaction temperatures, mostly because of the thermolability of enzymes, which are also known as bio-based, non-toxic catalysts. The enzymes used for these processes are usually lipases, cutinases, esterases, and hydrolases (Lai et al., 2023). Dutra et al. investigated PBS degradation with various enzymes and found lipases and cutinases to provide an intensified polymer degradation, with cutinases showing a higher net conversion (Dutra et al., 2011). However, the low temperatures of enzyme activity can represent a disadvantage for polyesters with high melting temperatures. In this case, the enzymatic hydrolysis occurs under solid-state depolymerization conditions, which can result in very low reaction rates. Therefore, the use of a proper solvent or suspension agent is required to improve the enzymatic hydrolysis rates. In homogeneous processes, the presence of a solvent improves the segmental mobility of polymer chains, and a suspension agent can increase the available interfacial area for reaction in heterogeneous processes (Dutra et al., 2022).

2.3.2.4 Glycolysis

Glycolysis is a chemical recycling method that uses glycols for the fragmentation of a polymer through the transesterification reaction. Its mechanism is based on the substitution of the polarized group in C-X bonds by the glycol element, resulting in chain cleavage in a single step. Through successive nucleophilic attacks by the glycol, it is possible to obtain oligomers and ultimately monomers for potential repolymerization (Clark; Shaver, 2024). The product of this reaction is a diester-diol comprising two repeating groups (ester group) linked to two diols.

Primarily for PET degradation, glycolysis serves as a method for high-efficiency chemical recycling with reduced environmental impact. In particular, it allows for easier recovery of the components involved and uses a glycol, a solvent with high boiling point, such as ethylene glycol (197.3°C). Therefore, this method is highly attractive for chemically recycling polyesters with high melting temperatures, as it allows the chemical reactions between the polymer and the glycol to occur in the molten state.

Studies have shown that, for this transesterification reaction to succeed, the use of catalysts is essential as low or no conversion at all, or even extensively long reaction times, have been observed for the non-catalyzed reactions (Wang et al., 2022).

A series of catalysts are being studied to make the process more efficient and environmentally friendly. Studies indicate that organocatalysts, metal acetates, ionic liquids, deep eu-

tectic solvents (DES), and metal nanoparticles can be used. Zinc acetate is the most established catalyst for PET glycolysis.

Due to the low solubility of some polymers (particularly those bearing medium to high degrees of crystallinity) at low temperatures, the addition of cosolvents to facilitate the cleavage of polymer chains by improving their diffusion within the reaction medium have been used, enabling high-efficiency reactions as far as shorter times and/or lower temperatures (Liu et al., 2018; Le et al., 2022).

The separation processes vary due to the specific composition of a given glycolysis compounds. For PET glycolysis, the separation process for its products is established within the following steps (Duque-Ingunza et al., 2014):

1. **Post-Reaction:** The reaction mixture is cooled to room temperature.
2. **Solubilization:** Boiling water (100 °C) is added to the medium for BHET extraction.
3. **Filtration:** The hot mixture is filtered immediately.
4. **Crystallization:** The filtered product is refrigerated at 4 °C for BHET crystallization.
5. **Washing and drying:** The BHET crystals are washed with cold water and then dried for 24 hours at 60 °C.
6. **Purification:** Steps 2-5 can be repeated for higher purity if necessary.
7. **Glycol recovery:** The remaining mixture on each filtration, composed of a water/glycol mixture, can be separated by nanofiltration, multi-stage distillation, vacuum distillation etc.

2.3.2.5 Alcoholysis

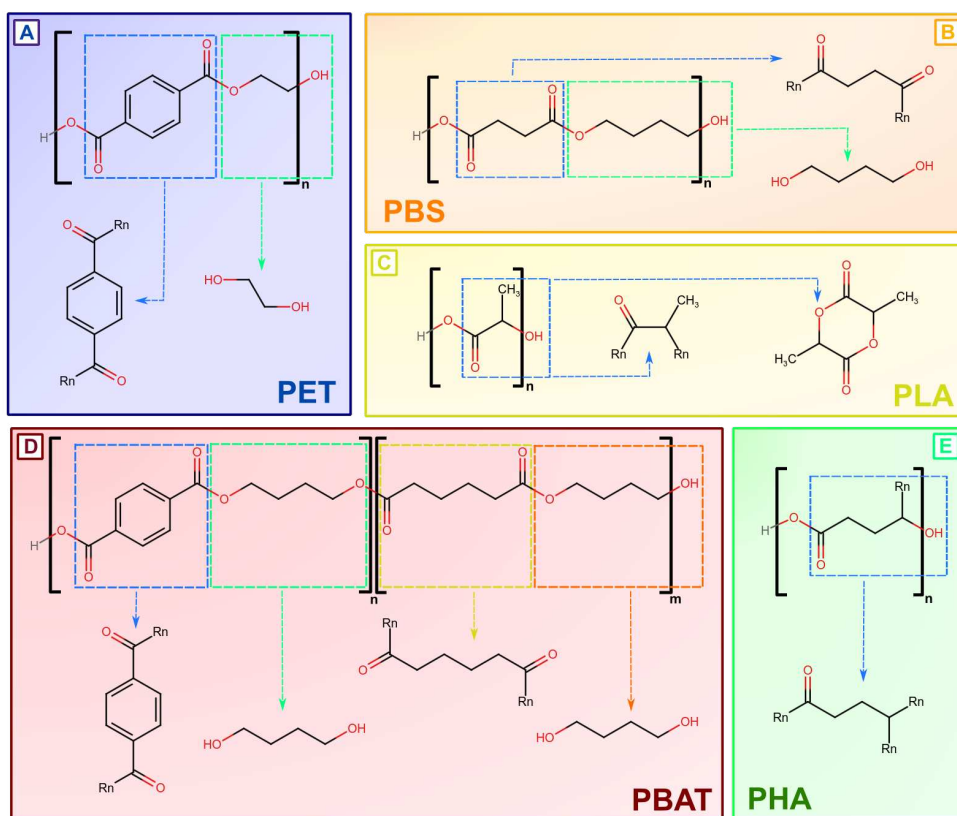
Alcoholysis is a selective depolymerization that uses an alcohol as reactant for chain cleavage. The most common reaction uses methanol, often referred to as methanolysis. The alcoholysis products are generally dialkyl esters of monomers, and a possible by-product according to the polymer structure, e.g. a glycol. Methanolysis, along with glycolysis, is one of the most promising depolymerization processes for polyesters. As an example, the products of PET methanolysis includes dimethyl terephthalate and ethylene glycol, since the repeating unit

has two cleavable C-X bonds. The reaction is usually conducted on liquid phase, but some investigations also deal with gas-phase methanolysis and supercritical methanolysis (Muszyński et al., 2023).

2.3.3 Solvolysis for Polyesters

As discussed, polyesters, and its general recycling capabilities, are presented as one of the most promising families of polymers. In this section, it will discuss the solvolysis method for some of the most important polyesters of market and research. Figure 2.3.3 shows the main polyesters on market and its expected depolymerization products

Figure 2.3.3: Chemical structures of different polyesters and of their depolymerization products. Rn is a giving carbon chain for each specific case of study.



Source: The author (2024).

2.3.4 Poly(ethylene terephthalate) (PET)

PET is the most widely produced polyester globally (Duan et al., 2024), prized for its versatility in applications ranging from automotive components and textiles to bottles, bags, and household items. Its current global production is around 25.5 million tons by 2022 (Our World

in Data, 2025). Additionally, PET stands for most of the global fiber production, accounting for more than 50% of its market by 2021 (Andini et al., 2024).

Its synthesis is based on three main stages: pre-polymerization, polycondensation, and SSP. The raw materials used are terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG). Pre-polymerization occurs to obtain the primary repeating unit of the polymer chain, which is achieved through the esterification of TPA with EG or by the transesterification of DMT with EG, resulting in bis(2-hydroxyethyl) terephthalate (BHET) as the repeating unit. Polycondensation then proceeds by propagating the BHET chain to form a long PET chain. Finally, solid-state polymerization takes place when a significant increase in the molar mass is required. As chemical kinetics in the reaction medium is no longer favorable due to high viscosity and diffusion limitations, this step occurs at very low reaction rates. All steps require the continuous removal of by-product, typically water (for direct esterification) or alcohol (for transesterification), so the reaction equilibrium favors the high-molar mass product (i.e., PET) (Romão; Spinacé; Paoli, 2009).

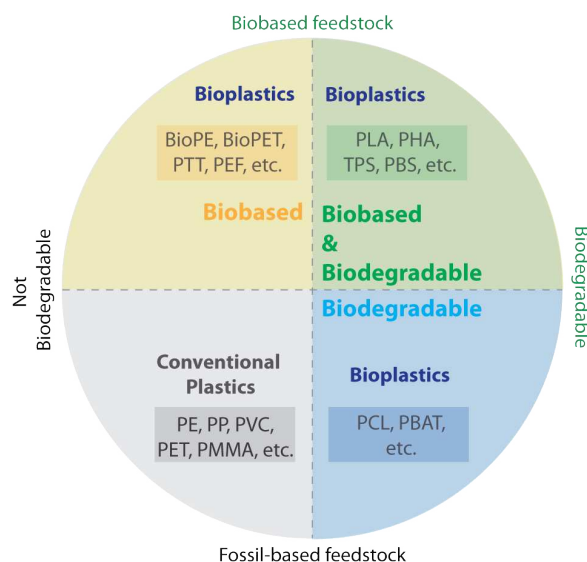
Given its extensive production, there is a subsequent need to properly dispose of its waste. As discussed, the preferred options from the circularity standpoint are reusing and recycling, usually mechanically, as lower-impact solutions; however, in broader contexts, chemical recycling should play a key role in keeping PET within a cycle that is as close as possible. Selective depolymerization of PET is a well-established field of research. Current efforts are primarily focused on developing new catalysts to achieve greater efficiency, reduced costs, and enhanced sustainability. These advancements, aimed to make this process industrially viable and competitive, should involve chemists, chemical engineers, materials scientists, and other skills able to tackle current technical, logistic, and economic challenges.

Many methods for PET solvolysis have been studied, such as hydrolysis, alcoholysis, glycolysis, and aminolysis. The main depolymerization techniques in both academic and industrial processes are glycolysis and hydrolysis. Microwave- and cosolvent-assisted technologies are also well explored for PET, delivering a wide range of results and applications (Chaudhary et al., 2013; Yang; Odelius; Hakkarainen, 2014; Selvam et al., 2023; Muszyński et al., 2023; Le et al., 2022).

2.3.5 Biopolymers

Bioplastics have been defined as those made of polymers from biological and renewable origin, those that are biodegradable or compostable, besides the special group that merges both characteristics (Figure 2.3.4) (European Bioplastics, 2024). Among commercially relevant biopolymers, the most produced polyesters include PLA, PBAT, PHA, and PBS. These polyesters account for 37.1%, 4.6%, 4.1%, and 1.3% of the production in 2024, respectively. The forecasts for 2029 project production levels of 42.3%, 2%, 17%, and 0.6%, respectively, within an expected growth of 132% in production capacity of biopolymers over five years (Ishimwe, 2024).

Figure 2.3.4: Bioplastic definition based on European Bioplastics.



Source: Adapted from (European Bioplastics, 2024).

2.3.5.1 Poly(lactic acid)

PLA can be produced through a variety of synthetic routes depending on its raw materials. In general, its primary variation arises from the stereoisomers L-lactic acid and D-lactic acid, which respectively produce L-lactide and D-lactide, and ultimately, through their combinations, poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA) (Jiménez; Peltzer; Ruseckaite, 2014). Primary applications of PLA include packaging, medical materials, and biocomposites, which generally require high polymer purity for safety and regulatory compliance (Jiménez; Peltzer; Ruseckaite, 2014).

PLA is typically synthesized through one of two traditional synthetic routes. Direct esterification of lactic acid can lead to the production of a polymer with lower molar mass under optimal conditions. The second route involves polycondensation, followed by depolymerization to obtain L/D-lactide, which is then again polymerized through ring opening to form poly(lactide) (Jin; Tian; Wang, 2010).

The procedure of ring-opening polymerization (ROP) is consistently adopted industrially to achieve high molar masses (Yu; Storti; Morbidelli, 2011). A polycondensation reaction occurs with lactic acid to obtain oligo(lactic acid) in a step known as oligomerization. This step is followed by depolymerization of oligomers into lactide through a back-biting mechanism, and, lastly, the lactide is polymerized into PLA by ROP (Masutani; Kimura, 2014).

As an aliphatic polyester with compostable characteristics, PLA tends to degrade in the presence of water by hydrolysis at elevated temperatures. Therefore, mechanical recycling of this polymer may be complicated without specific technological treatments. In particular, the mechanical properties of PLA, such as Young's modulus, impact resistance, and tensile strength, can diminish by about 50% in the first reprocessing stages after drying and extrusion (Zhang et al., 2024). This process still requires substantial research to develop new technologies and evaluate the characteristics of mechanical recycling as a secondary method for material reuse.

Thus, PLA shows potential for chemical recycling, given its relatively easy degradation. Among biopolymers, PLA is by far the most studied polymer in the field of chemical recycling. Published works have focused on alcoholysis (e.g. methanolysis, ethanolysis) and hydrolysis processes, as shown in Table 2.3.1. However, some procedures, such as aminolysis (Liu et al., 2024b) and ring-opening depolymerization (Cederholm et al., 2022; Alberti; Enthaler, 2020), have also been applied for chemically recycling PLA. The heating system is strategic, since microwave-assisted process achieved 99% conversion in 10 minutes for PLA methanolysis at 140 °C, catalyzed by zinc acetate, with a 67.5:1 molar ratio of methanol to monomer units (Cheung; Alberti; Enthaler, 2020).

PLA hydrolysis could be reached in an ionic liquid system using 50 wt% ionic liquid and 150 wt% water, proportional to polymer mass, at 150 °C, resulting in 93% of polymer degradation after 120 minutes of reaction (Cháfer et al., 2024).

Table 2.3.1: Chemical recycling techniques (alcoholysis and hydrolysis) applied for PLA in literature. ^atetrahydrofuran, ^bdichloromethane, ^c1,5,7-triazabicyclo[4.4.0]dec-5-en, ^dtetramethylammonium fluoride, ^ediphenyl phosphate.

Technique	Solvent	Catalyst	Temperature (°C)	Time (min)	Reference
Microwave-Assisted Alcoholysis	None	None	180–210	10	(Hirao; Nakatsuchi; Ohara, 2010)
Hydrolysis	Toluene	Montmorillonite K5	100	60	(Tsuneizumi et al., 2010)
Microwave-Assisted Methanolysis	None	Bismuth salts	160	10	(Alberti; Kricheldorf; Enthaler, 2020)
Microwave-Assisted Methanolysis	None	Zn(OAc) ₂ and Zn(OTf) ₂	100–160	10	(Cheung; Alberti; Enthaler, 2020)
Microwave-Assisted Alcoholysis	None	Sn(Oct) ₂	100–160	1–20	(Hofmann et al., 2020)
Methanolysis	THF ^a	Zn(1Et) ₂ , Zn(1Pr) ₂ , and Zn(2Pr) ₂	50–110	60–360	(Román-Ramírez et al., 2020)
Ethanolysis	Acetone	TBD ^c	50	90	(Majgaonkar et al., 2021)
Methanolysis	None	TMAF ^d	110	60	(Xie et al., 2021)
Methanolysis	DCM ^b /THF ^a	Zn Complex 5	40	5–60	(D’Alterio et al., 2022)
Methanolysis	DCM ^b	Zn(HMDS) ₂	210	180	(Yang et al., 2022a)
Methanolysis	DCM ^b	Mg(HMDS) ₂	25	120	(Zhou et al., 2023c)
Methanolysis	DCM ^b	LiHMDS	25	2	(Liu et al., 2024a)
Methanolysis	THF ^a	Zn[(R,R)-DMEG ₂ -(1,2)ch] ₂	60	120	(Liu et al., 2024b)
Hydrolysis	None	DPP ^e	160	90	(Wu et al., 2024)

Source: The author (2024).

2.3.5.2 Polyhydroxyalkanoates

PHAs are a group of polymers naturally produced by bacteria, which can be extracted to produce plastic products. The main characteristic of these polymers is their complete biodegradability in reasonable periods. The variety of monomer components in PHAs, as well as their resulting properties and characteristic applications, depends on the strains of microorganisms used. With continuous research and improvement, more than 150 polymer variants are currently available (Bano et al., 2024).

Their production occurs through the metabolic synthesis of bacteria with specific genes, resulting in the generation of micro-granules in the bacterial cytoplasm. The process is thus based on the treatment and availability of sugars and fatty acids, bacterial fermentation, and the subsequent extraction of the polymeric material from the cytoplasm (Zytner et al., 2023).

Although PHAs include a large variety of polymers, poly(3-hydroxybutyrate) (PHB) was the first industrially produced and is still the most common homopolymeric PHA. From a copolymer perspective, it is worth highlighting the following polymers: poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHX) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) (Zhou et al., 2023a).

Lee et al. (Lee et al., 2000) investigated an alcoholysis catalyzed by strong acids. The alcoholysis was performed using 1,2-dichloroethane as cosolvent, alcohols (methanol, ethanol, or n-propanol), and hydrochloric acid. The (R)-(2)-3-hydroxybutyrate products resulted in an optical purity close to commercial grade (Lee et al., 2000).

The hydrolysis of PHB with deionized water can happen under various reaction conditions. A systematic study of PHB hydrolysis included the effect of temperature (175 to 220 °C), PHB loading (0.1-1 Mol/L, monomer unit basis), and catalyst addition (3-hydroxybutyric acid (3HBA), crotonic acid (CA), sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), and sodium salts). Among the main results, PHB hydrolysis presented considerable yield at temperatures of at least 215 °C. In addition, PHB loading did not show high influence on the polymer conversion, but higher loading resulted in a higher monomer yield. Regarding the types of catalysts, both acid and alkaline hydrolyses showed higher yields under high loading (Li; Strathmann, 2019).

The microwave-assisted hydrolysis of PHB was performed using methanol and ethanol as solvents at 110 °C and 140 °C respectively, both under neutral and alkaline conditions. The microwave alkaline process was fast and efficient as far as depolymerization, with a further

degradation with increasing NaOH concentrations. However, prolonged processes under microwave can turn 3-methoxybutanoic acid into 3-hydroxybutanoic acid due to its reaction with methanol (Yang; Odelius; Hakkarainen, 2014).

Under the PHA copolymer depolymerization perspective, studies have shown that the products of hydrolysis are several, because of the multiple ester linkages. Alkaline hydrolysis of the PHBV co-polymer presented five possible products: 3-hydroxybutyrate (3HB), crotonate, 3-hydroxyvalerate (3HV), 2-pentenoate, and 3-pentenoate (Myung et al., 2014).

2.3.5.3 Poly(butylene-adipate-co-terephthalate)

PBAT is a polyester derived from fossil-based raw materials with biodegradable characteristics. Its synthesis occurs via polycondensation of 1,4-butanediol, adipic acid (AA), and TPA, typically catalyzed by metals such as zinc, tin, or titanium. Similarly to PET, PBAT requires several steps to achieve successive increases in molar mass, generally involving pre-processing, intermediate synthesis in an inert environment, and vacuum polycondensation with by-product removal (Jian; Xiangbin; Xianbo, 2020).

The aromatic portion renders PBAT recalcitrant against biodegradation. Therefore, there is a specific composition range of the terephthalic group in the copolymer chain that ensures commercially proper mechanical and thermal properties without impairing the biodegradation rate. This range is a key parameter for making this polymer suitable for the intended applications (primarily films for bags, packaging, and mulching) while degrading under the usual composting conditions (Ismail et al., 2024; Witt; Müller; Deckwer, 1997).

Despite its compostability, the gain of industrial relevance of PBAT has stimulated the investigation of chemical recycling approaches. Researchers have explored the chemical recycling of this polymer through different techniques, such as enzymatic (Ismail et al., 2024) and DPP-catalyzed (Wu et al., 2024) hydrolysis, and alcoholysis catalyzed by different metal-based catalysts (Parodi et al., 2023).

PBAT methanolysis at 140 °C allows for high conversions depending on the catalyst type and concentration, being (But)₂SnO and Sn(But)₂(OAc)₂ more efficient in comparison to traditional chemical recycling catalysts such as Zn(OAc)₂, since the accomplishment of conversion above 94% was obtained using six times less mols of the former catalysts (Parodi et al., 2023).

2.3.5.4 Poly(butylene succinate)

PBS is a compostable and biocompatible aliphatic polyester with properties similar to polypropylene (PP) and low-density polyethylene (LDPE), with applications in food packaging, biomedical devices, agricultural composites, and electronics. (Rajgond et al., 2024)

Its synthesis can be achieved through fossil-based or renewable sources, such as by direct esterification of succinic acid and 1,4-butanediol in an inert environment or through transesterification of a succinate diester (dimethyl succinate or diethyl succinate) and 1,4-butanediol, followed by a vacuum polycondensation step. In particular, all steps require the continuous removal of by-products to increase the molar mass (Peñas et al., 2022). As a greener alternative for bio-PBS production, enzymatic synthesis can be used, often involving the *Candida antarctica* lipase B (CALB) enzyme or its immobilized form (N435), at low temperatures and with the use of a non-toxic, bio-based catalyst (Elias Guckert et al., 2023).

Studies have shown a medium capacity for mechanical recycling of PBS. Under strict pretreatment, a series of characteristics of an extruded mechanically recycled PBS were analyzed. PBS presented stable tensile strength, and an important decrease in the strain at break after 3 cycles. In addition, the recycled polymer presented a continuous decrease in the impact strength over recycling cycles, as well as a fair increase in the mass flow rate in the extruder, suggesting depolymerization due to hydrolysis (Nomadolo et al., 2024).

Although PBS presents better performance when mechanically recycled in comparison to PLA, it is still far from the stability of PET in conventional mechanical recycling (Zhang et al., 2024). Therefore, the recovery of its monomers through chemical recycling processes is promising. With all those considerations, few studies have been devoted to the chemical recycling of PBS to date, with few investigations on methanolysis, aminolysis, and hydrolysis.

A methanolysis process of PBS with a cosolvent, such as dichloromethane(DCM) or toluene, in presence of a bis(trimethylsilyl)amides Zinc complex ($\text{Zn}(\text{HMDS})_2$) as catalyst, showed reaction times of 96 (at room temperature) and 34 h (at 50 °C) with DCM as cosolvent and 9 h at 100 °C using toluene as cosolvent, yielding, respectively, 0.54, 0.77, and 0.83 of dimethyl succinate, showing the possibility of PBS depolymerization under relatively low temperatures (Yang et al., 2022b). In particular, PBS is a semicrystalline polyester with melting temperatures around 110 °C, which explains the moderate temperatures used in chemical recycling. However, the use of expensive and environmentally damaging materials, such as the cosolvents selected and the metallic complex catalyst, is a disadvantage considering the

moderately successful results.

Hydrolysis can be performed using acid, enzyme, or alkaline catalysts. The enzymatic hydrolysis of PBS has been investigated in the open literature, and the product of hydrolysis was a mixture of 1,4-butanediol and PBS oligomers. The analysis only considered a strain of cutinase for PBS, reaching 100% of PBS conversion after around 2-4 hours (Rosato et al., 2022).

The acid hydrolysis of PBS was conducted with the use of its own monomer, succinic acid, as an acid catalyst at 150 °C. This process showed a yield of 0.79 of succinic acid after 5 h. It is an interesting approach to address the problem with acid catalysts and their effects. Conversely, the excess succinic acid in the reaction medium limits the process feasibility, since this compound works both as a reaction catalyst and a hydrolysis product. As hydrolysis is a reversible reaction, a progressive reduction in the reaction rate occurs due to the cumulative excess of product in the reaction medium (Zheng et al., 2024).

Aminolysis, in turn, achieved fairly good results under a non-catalyzed bulk process, using only ethanolamine at a 7:1 molar ratio to the monomer unit of PBS. This process reached a 98% yield of bis(2-hydroxyethyl)succinimide in 5 h (Zhou et al., 2023b).

2.3.5.5 Others

Many other biopolymers have been produced, as this has become an evolving industrial trend. The increase in production of these polymers has also intensified investigation into their degradation and depolymerization.

Polycaprolactone (PCL) is a biodegradable polymer bearing interesting properties. As its production increases, recycling processes must be considered. Thermal decomposition of PCL occurs at high temperature (430 °C) without any catalysts. Nelisen et al. reported a yield of 82% in the ring-closing depolymerization of polycaprolactone using $\text{Bu}_2\text{Sn}(\text{OMe})_2$ as catalyst in toluene under vacuum at 260 °C (Nelißen; Keul; Höcker, 1995).

Poly(alkylene xylosediglyoxylate) (PAX) is a polyester derived from a diol and dimethylglyoxylate xylose (DMGX), which is a diester obtained from xylose and lignocellulosic biomass. This polymer is a bio-based material, and exhibits features such as degradability in water, high T_g , high mechanical strength, good gas barrier properties, and proper processability, besides being chemically recyclable by methanolysis (Manker et al., 2022).

Finally, poly(ethylene furanoate) (PEF) stands out as a promising bio-based alternative

to PET. It is synthesized from ethylene glycol and 2,5-furandicarboxylic acid (FDCA). Besides being fully bio-based, it delivers better gas barrier properties and thermal stability compared to PET. Despite the greater T_g and aromaticity of PEF over PET, the depolymerization of the former can also be achieved via alcoholysis or hydrolysis, but studies on selective solvolysis are still limited (Kumar et al., 2024).

2.3.6 Mixtures and blends

A major advantage of chemical recycling over other available recycling approaches is the possibility of using unsorted, complex compositions, such as recovering derivatives from polymer blends or even composites, which in other cases would be difficult or unfeasible. Also important are multilayer films and coated packaging, which have important obstacle against mechanical recycling. Solvolysis offers the potential to separate and recover components, provided the depolymerization is selective to specific layers or components.

Regarding the presence of additives and fillers in polyester matrices, Parodi et al. compared two techniques to separate PBAT from a composite that also contained a plasticizer and starch. The composite was first solubilized in dichloromethane, but an efficient separation of starch and PBAT was not possible. Conversely, the alcoholysis of PBAT was carried out to produce oligomers soluble in methanol, enabling their separation from the starch fraction. Particularly, this procedure was successful for some catalysts, allowing for the subsequent purification of each monomer (Parodi et al., 2023).

In the literature, the application of chemical recycling for the recovery of a polymer from a mixture or blend of polymers may be carried out for diverse types of polymers and blends, additionally different techniques seem to be effective as will be presented below.

A microwave-assisted process is an interesting heating system to accelerate chemical recycling even in blends. Cheung et al. tested the chemical recycling of PCL in the presence of other polymers – such as Nylon 6, poly(phenylene sulfide), polyethylene, polystyrene, poly(vinyl chloride), and poly(ethylene glycol) methyl ether – using microwave-assisted methanolysis at 160 °C for 30 minutes. The addition of another polymer had no significant effect on the process, yielding methyl 6-hydroxyhexanoate at levels higher than 90% during PCL depolymerization (Cheung et al., 2021). Cheung et al. carried out a microwave-assisted methanolysis of PLA in the presence of several polymers such as PET, PCL, poly((R)-hydroxybutyric acid), poly(bisphenol A carbonate), poly(phenylene sulfide), polyethylene, polystyrene, poly(vinyl

chloride), poly(vinyl alcohol), poly(ethylene glycol) methyl ether, epoxy resin, and polydimethylsiloxane. In particular, the methanolysis tests showed selectivity for almost all polymers, except for poly(bisphenol A carbonate), with 99% of yield considering methyl lactate as a product. The methanolysis procedure involved using 1 mol% of $\text{Zn}(\text{OAc})_2$ (as catalyst) at 160°C for 5 min (Cheung; Alberti; Enthaler, 2020).

Tsuneizumi et al. investigated the separation of PLA from a blend with poly(ethylene) through dissolution in toluene and addition of montmorillonite K5 as catalyst to conduct the hydrolysis of PLA. In order to separate the poly(ethylene) and montmorillonite K5, acetonitrile was added to precipitate the polymer, and these compounds were collected by filtration. Next, the evaporation of filtrate yielded oligo(lactic acid), a hydrolysis product. Demonstrating the potential of a process with multiple steps of separation, these authors also tested the separation of PLA from a blend with PBS, starting by dissolution of PLA and PBS blend in toluene, allowing for the separation of PLA from PBS, to the following chemical recycling by hydrolysis using montmorillonite K5 and lipase as catalysts, respectively (Tsuneizumi et al., 2010).

Wu et al. investigated the selective degradation of PLA by hydrolysis in a mixture of plastics, including including PET, polypropylene and polyethylene in the presence of diphenyl phosphate (DPP) as catalyst. The hydrolysis conditions were 1.5 hours and 160°C , resulting in similar quality of the PLA degradation product, while the thermal properties of non-hydrolyzable plastics were not compromised, being these materials recovered by filtration (Wu et al., 2024).

Manker et al. synthesized poly (hexylene xylosediglyoxylate) (PHX), a poly (alkylenexylosediglyoxylate) (PAX) from xylose. This polymer was mixed with PET, high density poly (ethylene), polyamide 6,10, polypropylene and polycarbonate and the mixture was submitted to the acid methanolysis, resulting in the yield of 91.5%, similar compared to the procedure without the simulated mixed plastics (94.9%) (Manker et al., 2022).

Yang et al. investigated the depolymerization of complex polymers mixtures under two different configurations: sequential depolymerization and simultaneous depolymerization. The sequential configuration involved the depolymerization of only one polymer type at each step, with successive separations of products and reactants. Conversely, the simultaneous configuration involved the simultaneous depolymerization of the entire polymer mixture, with successive separations of all monomer products after the single reaction step. These reactions were conducted under cosolvent toluene assisted methanolysis, with the use of the catalyst

Zn(HMDS)₂. The polymer mixtures investigated were the post-consumer products composed of BPA-PC/PET, PLA/PBS and PLA/PBAT. The results showed similar yields for both procedures at the final recovery of monomers, with reaction times of 14 to 16 h for successive depolymerization and 9 to 15 h for simultaneous depolymerization (Yang et al., 2022b).

2.3.7 Intentionally Added Substances

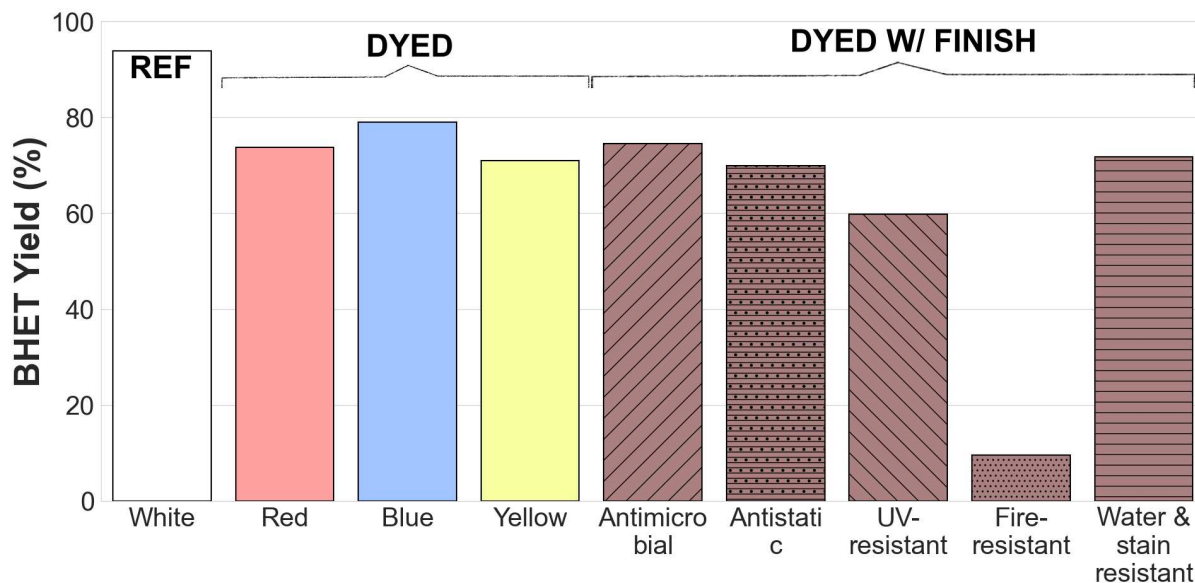
Chemical recycling is an interesting solution to provide a separation of impurities and additives as well as a selective separation of different polymers from mixed plastic waste. However, it is still important to consider the effect of common intentionally added substances (IAS) as additives and impurities on the depolymerization reactions, as their presence can affect the degradation rates in several ways. Additives may include dyes, UV stabilizers, flame retardants, antimicrobials, among others. Few studies have analyzed the impact of various additives and contaminants in post-consumer plastics, but this is an important step to develop high-performance recycling.

A recent investigation focused on the impact of some additives on the yield of glycolysis depolymerization. In particular, the use of colorants significantly reduced conversion by acting as impurities in the reaction medium. Among the colors blue, yellow, and red, blue showed the least impact (Andini et al., 2024). Additives such as UV-resistant and flame retardants lead to reduced yields mainly due to increased hydrophobicity in polymer chains, which reduces diffusion and molecular adhesion, affecting the glycol-promoted heterolytic cleavage (UV-resistant) and the presence of phosphorus with char formation, which in turn is characterized by deactivation of catalysts and substrates (flame retardants) Figure 2.3.5 shows the impact on yield for all additives considered in the study (Andini et al., 2024).

2.3.8 Upcycling

Beyond the concept of chemical recycling, the circular economy principle requires the continuous use of these raw materials to produce regenerated resins or new products. The term currently used for this step is “upcycling”, which is defined as the process to obtain higher-valued products from recovered raw materials (Rorrer et al., 2019). The main advantages include the fact that these upcycled products are believed to result in lower energy consumption and GHG emission, two important parameters for life-cycle assessment (Rorrer et al., 2019).

Figure 2.3.5: BHET yield from 100% dyed textiles (with and without finishes).



Source: Adapted from (Andini et al., 2024).

2.3.8.1 Closed-Loop Chemical Recycling

The first application of this concept is related to the chemical recycling of a polymer to produce the original resin, keeping the same technical features or even enhancing them.

As expected, an increasing number of papers are focused on chemical recycling of PET by glycolysis and subsequent repolymerization to produce r-PET (recycled or regenerated PET), but not restricted to this. In terms of color, PET waste could present a mixture of different pigments, which cause downcycling of r-PET. The glycolysis of PET allowed the development of a discoloration method based on dye adsorption with ion-exchange resin, making this process suitable for producing monomer BHET with a discoloration rate of 99% (Huang et al., 2021). Subsequent polymerization (using ethylene glycol antimony as a catalyst) resulted in r-PET with good chromaticity (Huang et al., 2021). Polyester textile waste is a difficult residue to recycle mechanically, so glycolysis appears as an interesting alternative to turn waste PET fiber into its monomers, allowing the repolymerization by polycondensation at 260 to 280 °C and 100 Pa (Hu et al., 2020). The intrinsic viscosity of r-PET is comparable to that of a virgin resin synthesized by the same procedure (0.58 dL/g); in addition, the thermal properties are comparable in terms of T_m , while T_g was higher for r-PET (Hu et al., 2020). In similar conditions of repolymerization (Sb_2O_3 as catalyst at 280 °C for four hours), the intrinsic viscosity of r-PET obtained from the polycondensation of glycolysis product was 0.67 dL/g, comparable with the

value of a fiber grade virgin resin (0.64 dL/g). After fiber spinning, the physical and mechanical properties in terms of titer, tenacity, and elongation were quite similar (Guo et al., 2021).

These reactions are so versatile that it is possible, in some cases, to apply the same catalyst both for chemical recycling and repolymerization. A synthetic Ti/Si-EG catalyst was successfully applied to obtain BHET from PET and perform its repolymerization in r-PET, applying the pressure of -0.1 MPa at 260 to 280 °C for the polycondensation reaction (Yu et al., 2023). The polymer synthesized from the glycolysis product showed a similar chromaticity and up to 10% lower molar mass compared to that synthesized by the reference method (using commercial monomer) (Yu et al., 2023).

The importance of PLA in the productive chain has grown in the last decades, and some procedures to chemically recycle this polymer and polymerize it once again into recycled PLA (r-PLA) have been applied. Nowadays, there are three main strategies to obtain r-PLA from PLA, including depolymerization-repolymerization (RE-DE polymerization or polymer to new polymer), polymer to monomer (lactide), and polymer to chemical (lactate esters) (Yang et al., 2022a; Zhou et al., 2023c). Through the DE-RE polymerization strategy, the polymer is depolymerized into oligomers using a solvent such as dichloromethane and a certain quantity of methanol. Then, lactide is added to produce new PLA, at room temperature and employing a versatile catalyst, such as $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (Yang et al., 2022a) or $\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$ (Zhou et al., 2023c), to increase the molar mass of the polymer under most reaction conditions, achieving conversions higher than 90%. This resulted in a significant rise in the original M_n of PLA, from 17.8 kDa to 26.1 kDa and from 14.4 kDa to 21.3 kDa, respectively.

As mentioned before, ROP is the strategy applied to obtain high-molar mass PLA, since there is no water in the reaction system. Considering the polymer-to-monomer strategy, during the chemical recycling of PLA under high temperature and vacuum conditions, simulating the conditions seen in the depolymerization step of the PLA synthesis, lactide may be produced with an unavoidable racemization process, with a purification step being needed to conduct the repolymerization (Yang et al., 2022a). Wu et al. synthesized r-PLA with high M_w (505.3 kDa) through the hydrolysis of commercial PLA (M_w of 199.7 kDa) in the presence of diphenyl phosphate as a catalyst. The upcycling process included the production of lactide and its ROP, using $\text{Sn}(\text{Oct})_2$ as catalyst, and anhydrous DCM as solvent, at 140 °C for 8 hours under vacuum (Wu et al., 2024). In a polymer-to-chemical strategy, the microwave-assisted methanolysis of PLA was carried out to obtain methyl lactate, which was submitted to polymerization with

catalytic zinc salts during 24 hours at 130 °C to result in PLA with M_n up to 8.97 kDa (Cheung; Alberti; Enthaler, 2020).

Other techniques could be applied in PLA upcycling. The selective ring-closing polymerization of PLA was feasible to produce L-lactide, which was repolymerized by ROP into a polymer with M_n of 17.2 kDa, in the presence of benzyl alcohol and the catalyst $\text{Sn}(\text{Oct})_2$ (1 mol%), at 100 °C for 1 hour (Cederholm et al., 2022). The polymerization of oligo(lactic acid), using $\text{SnCl}_2/\text{p-toluenesulfonic acid}$ as catalyst, at 175 °C for 6 hours under vacuum, applying a route based on melt- and solid-polymerization resulted in r-PLA with M_w of 173 kDa (Tsuneizumi et al., 2010).

Literature also presents examples of upcycling of other bioplastics. PBAT was chemically upcycled through enzymatic hydrolysis followed by monomer purification, allowing the esterification of terephthalic acid with methanol as an ester precursor of polymerization by the sequential transesterification in the presence of 1,4-butanediol and adipic acid, catalyzed by dibutyltin oxide (Ismail et al., 2024). PHBV was submitted to an alkaline hydrolysis followed by an intracellular biotic repolymerization procedure without any subsequent energy-intensive purification step, resulting in a polymer with a doubled molar mass compared to the commercial material (Myung et al., 2014). The chemical recycling of PCL through hydrogenative depolymerization was performed to obtain 1,6-hexanediol, followed by the upcycling of PCL through dehydrogenative polymerization of 1,6-hexanediol with a catalytic complex at 130 °C during 24 hours, resulting in new PCL (Alberti; Enthaler, 2021). The microwave-assisted methanolysis of PCL with the subsequent polymerization of methyl 6-hydroxyhexanoate at 130 °C for 48 hours also achieved new PCL (Cheung et al., 2021). Both works resulted in PCL with lower molar masses compared to the original polymer, likely due to the differences between the ROP of caprolactone (original) in comparison to the polymerization of a linear monomer.

Upcycling has been such an important theme that new polymers are currently being produced and tested by chemical recycling and repolymerization approaches to highlight the circularity of the material. Poly(hexylene xylosediglyoxylate) (PHX) was synthesized from xylose, and its depolymerization products after acid methanolysis were polymerized into recycled PHX with M_w of 53.4 kDa (Manker et al., 2022). A polymer was produced from spiro-diol V, dimethyl terephthalate and neopentyl glycol, namely PNV, which was chemically recycled by acidic hydrolysis, followed by the repolymerization to obtain the polymer with an estimated M_w of until 36.1 kDa (Mankar et al., 2023).

Even polymers in blends can return as new polymers. The PLA/PBS blend separation were successful by selective chemical recycling using a lipase in a solution of toluene, removing PLA by precipitation, while the cyclic butylene succinate oligomer was recovered and repolymerized through enzymatic ROP in toluene at 100 °C during 24 hours, producing recycled PBS with M_w of 68 kDa (Tsuneizumi et al., 2010). Parodi et al. demonstrated that PBAT could be recovered by previous separation from starch and plasticizer through the alcoholysis of PBAT, followed by repolymerization of oligomers into new PBAT, using the same catalyst added during the chemical recycling step (Parodi et al., 2023) .

2.3.8.2 Production of Copolymers

The second application of upcycling is wide and involves the degradation of a polymer to obtain building blocks to produce copolymers, blends or other compounds. This concept is one of the strongest features of chemical recycling in comparison with mechanical recycling and is explored here and in the next subsection.

Copolymers are defined as polymers produced with more than one type of monomer, reflecting in a backbone with different repeating unit combinations to modify physical-chemical features. Copolymer synthesis also finds potential for the chemical recycling and upcycling of PET. Through the DE-RE polymerization strategy, it was possible to carry out the glycolysis of PET from bottles, films and pellets, followed by the polycondensation of these precursors with cyclohexane-1,4-dimethanol to produce PETG/PCTG copolymers. The copolymerization step was conducted by a pre-polycondensation at 250 to 260 °C under vacuum (0.01 MPa) during 45 min to withdraw part of ethylene glycol, followed by a polycondensation step at 280 to 285 °C for 2 hours, under 300 Pa, producing copolyesters with intrinsic viscosity up to 0.73 dL/g, which was similar to the intrinsic viscosity of plastic bottles used as raw material (Wei et al., 2024). This means that the same processing techniques likely applies to the new copolyesters, favoring a closed-loop chemical recycling approach. In another strategy, segmented thermoplastic copolyesters were produced by the glycolysis reaction of PET followed by the direct esterification of BHET with a bio-based dimer fatty acid, being ethylene glycol continuously removed by distillation at 250 °C under a high vacuum of 0.28 mbar, resulting in a material with mechanical properties comparable with other commercial thermoplastic elastomers in terms of stress and elongation (Karanastasis; Safin; Pitet, 2022). Using a similar concept, the PET waste bottle was converted into poly(ethylene hydrogenated dimerate-*co*-terephthalate) by a thermal

copolymerization reaction at 280 °C under 100 Pa for 8 hours involving carboxyl-ester transesterification process to partially substitute terephthalic acid by adding a bio-based hydrogenated dimer acid, resulting in the production of TPA, which was recovered by sublimation, and conferring a biodegradability feature to this new copolymer (Fang et al., 2024).

One of the main aspects of polymer chemistry is the functionalization process that changes polymer features through the addition of functional groups. Rubes et al. carried out the glycolysis of flakes from post-consumer bottles of PET with ethylene glycol and diethylene glycol, followed by the direct esterification between the glycolized products and itaconic acid to convert these raw materials into unsaturated polyesters. In the last step, these polymers were post-cured through crosslinking reactions in methacrylates and itaconates, resulting in a high gel content (Rubes et al., 2024).

The principle of producing a biodegradable copolyester from a petroleum-based polyester is not restricted to PET. PBT, which is a polycondensation product from terephthalic acid and 1,4-butanediol was depolymerized by alcoholysis (1,4-butanediol) into bishydroxybutyl terephthalate, which acted as building block through reaction with bis(4-hydroxybutyl) adipate to produce PBAT by catalytic polycondensation by some increasing temperature steps until 260 °C and vacuum (Jiang et al., 2024). The cyclodepolymerization is a chemical recycling approach capable to produce oligo(butylene terephthalate) from PBT, which allows the subsequent addition of other monomers as ethylene brassylate (Bian et al., 2024) and poly(butylene adipate) diol (Yan et al., 2024) to perform ROP into poly(ethylene brassylate-*co*-butylene terephthalate) and PBAT, respectively. Cyclodepolymerization may be applied in PEF to obtain cyclic oligo(ethylene 2,5-furandicarboxylate) and converted into bio-based poly(ethylene-*co*-isosorbide furanoate) (PEIF) by ROP in the presence of isosorbide (Li et al., 2023a). $\text{Ti}(\text{OBu})_4$ seems an interesting catalyst for the ROP of these cyclic oligomers, since it was applied in all these studies.

PLA is also an interesting platform to produce other copolymers. The aminolysis of PLA in the presence of different amines resulted in diols with amide bonds instead of ester bonds, being these precursors capable to polymerize into poly(ester-amide) when in contact with dicarboxylic acids through esterification reactions, using $\text{Ti}(\text{OBu})_4$ as catalyst (Liu et al., 2024b). In this procedure, the polycondensation process involves two steps: a vacuum pre-esterification followed by an increase of temperature, allowing the production of polymers with M_n up to 29.8 kDa, while the original PLA had a M_n of 41 kDa. (Liu et al., 2024b).

2.3.8.3 Open-Loop Chemical Recycling

Fermentative processes are capable of biosynthesizing new compounds using products from chemical recycling of polymers as carbon sources. PET were successfully bioconverted into cathecol (Kim et al., 2021) and lycopene (Diao et al., 2023) from glycolysis and alkaline hydrolysis products, respectively. In these studies, *Escherichia coli* (Kim et al., 2021) and *Rhodococcus jostii* (Diao et al., 2023) strains were able to produce that compounds.

Despite the use of chemical recycling to return to polymer or copolymer, there are also other applications. The aminolysis of PLA with diamines as N,N-dimethylethylenediamine, N,N-dimethylpropylenediamine and 3-aminopropylimidazole allowed obtaining organic salts with behavior of ionic liquids after alkylation of lactamides (Majgaonkar et al., 2021). The ethanolysis of PLA using triazabicyclodecene as catalyst resulted in ethyl lactate at mild temperature (50 °C), with this compound being treated as a highly valued bio-based solvent (Majgaonkar et al., 2021). The methanolysis of PCL resulted in oligomers with plasticizing behavior in PVC (Dong et al., 2024).

Some products from chemical recycling are suitable to act as new monomers to produce other classes of polymers after chemical modifications. Acid alcoholysis was applied to depolymerize poly(3-hydroxybutyrate) (P3HB) into methyl and ethyl 3-hydroxybutyrate (Li; Shen; Li, 2022), and R-methyl 3-hydroxybutyrate (Li et al., 2023b), which were converted into bicyclic ether-ester monomers by reaction with cyclohexene oxide and properly polymerized into a poly(ether ester) by ROP reactions.

2.3.9 Environmental and economics assessments

Life cycle assessment (LCA) and the techno-economic analysis (TEA) are two of the most important metrics for assessing the feasibility of an industrial project. LCA evaluates the environmental impact during the life cycle of a product, whether complete or partial, while TEA analyzes its commercial feasibility aspect, addressing its market competitiveness. This section will discuss both aspects from the perspective of academic evaluations of various depolymerization processes configurations. Below, one can see the main definitions about this theme in accordance with ISO 14040:2006 and the US Department of Energy:

- Life Cycle Assessment (LCA): "addresses the environmental aspects and potential environmental impacts (e.g. use of resources and the environmental consequences of releases)

Table 2.3.2: LCA Metrics recommendations accordingly to the European commission (European Union, 2021).

EF impact category	Impact category indicator	unit
Climate change	Global warming potential (GWP ₁₀₀)	kg CO ₂ eq.
Ozone depletion	Ozone depletion potential (ODP)	kg CFC-11 eq
Human toxicity, cancer	Comparative toxic unit for humans (CTU h)	CTUh
Human toxicity, noncancer	Comparative toxic unit for humans (CTU h)	CTUh
Particulate matter	Impact on human health	Disease incidence
Ionising radiation, human health	Human exposure efficiency relative to U ₂₃₅	kBq U ₂₃₅ eq
Photochemical ozone formation, human health	Tropospheric ozone concentration increase	kg NMVOC eq
Acidification	Accumulated exceedance (AE)	mol H ⁺ eq
Eutrophication, terrestrial	Accumulated exceedance (AE)	mol N eq
Eutrophication, freshwater	Fraction of nutrients reaching freshwater end compartment (P)	kg P eq
Eutrophication, marine	Fraction of nutrients reaching marine end compartment (N)	kg N eq
Land use	Soil quality index	Dimensionless (pt)
Water use	User deprivation potential (deprivationweighted water consumption)	m ³ water eq of deprived water
Resource use, minerals and metals	Abiotic resource depletion (ADP ultimate reserves)	kg Sb eq
Resource use, fossils	Abiotic resource depletion – fossil fuels (ADP-fossil)	MJ

Source: The author (2024).

throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal." (International Organization for Standardization, 2025).

- Techno-Economic Analysis (TEA): "a method for evaluating the economic performance of a technology." (U.S. Department of Energy, 2025).

2.3.10 Life cycle assessment

The LCA framework is the most used systematic method to analyze the environmental impact of a production roadmap (Frehner et al., 2020). It is a combination of many environmental footprint (EF) metrics, listed in Table 2.3.2 with their respective measurement units, according to the European Commission recommendations (European Union, 2021).

Among these metrics, the most analyzed is the global warming potential (GWP), which is defined by the effect of GHG emissions (CO₂, CH₃, N₂O, etc.) by the life cycle under analysis. Specifically, it measures how much energy the emission of 1 ton of a gas will absorb

over a given period. Most analyses convert the emissions to the corresponding CO₂ equivalent. Therefore, the LCA discussion will be mainly over the GWP data analysis provided by the literature for polyesters' solvolysis method (US EPA, 2016).

Another important aspect to run a proper LCA is defining its boundaries, limiting what kind of data will be analyzed. For example, a facility may produce an LCA of a product only at the mark of its release for market, not considering its impact after sales and consumption. It is important to interpret LCA outcomes in light of system boundaries, as cradle-to-gate analyses often omit downstream emissions and end-of-life burdens.

The most common boundaries used are defined below (US EPA, 2016):

- **Cradle-to-Gate** - An assessment that covers the production from the sourcing of raw materials (cradle) to the impact of the final product, i.e factory gate.
- **Cradle-to-Customer** - This assessment takes the previous perspective and considers the supply distribution to the customer's availability.
- **Cradle-to-Shelf** - This assessment covers the impact from the raw material to the market availability for the customer.
- **Cradle-to-Fork** - This term is usually used only on food or related assessments; it covers preparation for use, such as food preparation for consumption.
- **Cradle-to-Grave** - Finally, this assessment covers the full product life cycle, analyzing the impact from the raw material for production to the disposal or treatment of the waste related to the product.

The solvolysis' LCA review is defined under the available literature for glycolysis, hydrolysis and alcoholysis. The data available provide an analysis for PET and PLA (only for hydrolysis and alcoholysis).

2.3.10.1 Glycolysis

The glycolysis process is one of the most promising processes for solvolysis of polyesters. Although this recycling method has mainly been studied for PET depolymerization, there is considerable LCA data analysis and commercial operations.

The published works focused on glycolysis show a considerable variance on the LCA data for its various processes conditions. GWP values change from 0.437 to 91.285 kg·CO₂ eq.

Table 2.3.3: Global Warming Potential for glycolysis of various polymers and its comparison for virgin and recycled polymers (Arifuzzaman et al., 2023).

Polymer	Monomer	Global Warming Potential (kg·CO ₂ eq)		
		Chemical Recycling	Repolymerization	Virgin
PET	BHET	0.437	0.54	2.17
PU	MDA	0.364	0.88	5.04
PA	CL	0.235	0.34	6.51
PC	BPA	1.02	1.41	7.76

Source: The author (2024).

(Arifuzzaman et al., 2023; Iturrondobeitia; Alonso; Lizundia, 2023; Shen; Worrell; Patel, 2010; Ao et al., 2024; Schwarz et al., 2021; Luo et al., 2023; Selvam et al., 2023; Troev et al., 2003; Abdelaal; Sobahi; Makki, 2011; Uekert et al., 2023).

An LCA of the glycolysis process is considered neutral with regard to the use of waste PET, therefore, the use of waste had no positive impact on the metrics. The process was catalyzed with ZnO nanoparticles, with and without surfactants. The results for both processes were, respectively, 14.2 and 11.5 kg·CO₂ eq./kg (Ao et al., 2024). The analysis also demonstrates how every LCA metric is reduced by around 20% with the use of a surfactant-free nanoparticle, showing the importance of an efficient and eco-friendly process design.

An investigation for the glycolysis process over various waste polymer products, including polyurethane, polyester (PET), polyamide, and polycarbonate, showed results that both the glycolysis process and the entire recycling process have considerable low GHG emissions. Table 2.3.3 shows the GWP for both the monomer production through glycolysis processes and the upcycled polymer production, compared to the virgin route (Arifuzzaman et al., 2023). It demonstrates that glycolysis can be a very efficient pathway to deal with mixed plastics, whereas the LCA of those compounds on a mixed matrix shows around a 51% reduction on fossil energy consumption and less GHG emissions, which provides both the possibility of a mechanical recycling logistic problem and the possibility of an efficient compound separation.

Another study on the LCA of chemical recycling technologies shows GWP values of 1.6 and 1.3 kg·CO₂ eq/kg for PA and PET glycolysis, respectively (Schwarz et al., 2021). Although it surpasses the polyester review theme, it is important to highlight the high efficiency of glycolysis processes to other complex polymers, offering potential for the degradation of mixtures and blends.

A very important approach for the glycolysis process is the microwave-assisted glycolysis. The LCAs for the microwave heating glycolysis of PET under ZnO catalyst, the most common catalyst used for this process, for virgin grade, colored bottles, fibers and fabrics demonstrated a low GWP, ranging from 0.636 to 0.793 kg·CO₂ eq/kg (Luo et al., 2023; Selvam et al., 2023). The studies show an important contribution of a microwave-assisted technology for lowering most LCA metrics under an efficient process.

It is also worth mentioning that ethylene glycol is the main reactant used in the glycolysis process of PET. However, other dialcohols can be also utilized as reactants, such as diethylene glycol, propylene glycol and 1,4-butanediol (Iturrondobeitia; Alonso; Lizundia, 2023; Troev et al., 2003; Abdelaal; Sobahi; Makki, 2011). Few studies defined the best diol for glycolysis processes, but the use of other reactants, such as propylene glycol, has shown a similar impact for the PET depolymerization, with a GWP of around 4.64 kg·CO₂ eq/kg (Iturrondobeitia; Alonso; Lizundia, 2023).

As investigations proceed, a pattern shows that every aspect of the solvolysis processes significantly affects the LCA impact metrics. For instance, many analyses shows a GWP for glycolysis of PET with ethylene glycol of around the range of 0.5 kg·CO₂ eq. for a low-emission process to 12 kg·CO₂ eq. for a high-emission process (Ao et al., 2024; Arifuzzaman et al., 2023; Luo et al., 2023; Selvam et al., 2023; Shen; Worrell; Patel, 2010). Conversely, complex systems that use many compounds, such as cosolvents, can present higher values of GWP, such as 91.285 kg·CO₂ eq. (Iturrondobeitia; Alonso; Lizundia, 2023).

PET glycolysis using ethylene glycol (EG) and propylene glycol (PG) was compared to evaluate their respective environmental impact under complex composition reactions. In particular, the glycolysis reaction with EF had a much higher GWP value, due to the use of many damaging reaction compounds, such as cosolvents (Iturrondobeitia; Alonso; Lizundia, 2023).

Although the use of cosolvent is not a conventional process, these results highlight the importance of evaluating other alternatives for this process, with less environmental impact. In addition, as an important perspective of process design, the method of purification of the monomer is greatly important on the environmental impact. The typical batch purification uses high amounts of water for separation, requiring multiple distillation steps of water to recover the glycol. In contrast, direct crystallization through temperature reduction can offer significant benefits. The use of a combined process, such as a preheated microwave glycolysis with a direct

crystallization, can reach up to 85% decrease on the GWP (Luo et al., 2023).

2.3.10.2 Hydrolysis

Hydrolysis presents literature data available for both PET and PLA depolymerization technologies. Enzymatic hydrolysis studies for PET highlight some important aspects of the environmental analysis, presenting high GHG emission, water usage and toxicity.

LCA of hydrolysis processes taken into account several conditions, such as yield, enzyme loading, pH, recoveries and process variables (e.g. temperature, residence time, plant area). Enzymatic hydrolysis of PET shows a GWP value in the range of 2.13-6.05 kg·CO₂ eq/kg and on the range of 2.36-8.05 kg·CO₂ eq/kg. For the complete PET recycling processes, the GWP changed between 2.36-8.05 kg·CO₂ eq/kg (Uekert et al., 2023, 2022).

The LCAs for the neutral (autocatalytic) hydrolysis of PLA show a GWP range from around 0.9 to 1.697 kg·CO₂ eq/kg PLA. It was also stated that, if it is taking accountable the biogenic carbon contribution, the GWP emission would be of a negative value (Cosate De Andrade et al., 2016; Aryan et al., 2021).

2.3.10.3 Alcoholysis

LCA of alcoholysis processes shows available data for PET methanolysis and PLA methanolysis and ethanolysis. The cradle-to-gate analysis for methanolysis shows high GHG emission, water usage, toxicity, and GWP ranging from 1.79 to 4.2 kg·CO₂eq/kg (Cao et al., 2024; Uekert et al., 2023; Shen; Worrell; Patel, 2010).

Taking the repolymerization step into consideration, the GWP emission can reach 2.15 to 2.76 kg·CO₂eq/kg for production in Europe and China, respectively. Therefore, the plant region is also a very important consideration. In particular, the depolymerization and repolymerization processes of PET in Europe and China show a reduction in energy consumption of 40.9-56% and a GWP reduction of 1.8-44.5% referred to the virgin production (Cao et al., 2024).

A comparison for LCA of PLA methanolysis and ethanolysis processes, catalyzed by Sn(Oct)₂ and TBD, respectively. The results show a GWP, including and excluding the biogenic carbon contribution, respectively, of -1.387 and 1.389 kg·CO₂ eq/kg PLA for methanolysis and -1.23 and -2.91 kg·CO₂ eq/kg PLA for ethanolysis (Aryan et al., 2021).

2.3.11 Comparative analysis

A comparative study of the LCA for PLA recycling showed a GWP of 1.2 kg·CO₂ eq/kg PLA and around 0.9 eq/kg PLA and 0.3 kg·CO₂ eq/kg PLA for hydrolysis and mechanical recycling, respectively. The comparison of these results with PLA composting disposal shows that, in general, most of the LCA metrics are much higher for composting. In particular, the relative GWP of composting was 30% higher than that of hydrolysis and 10% higher than that of mechanical recycling (Cosate De Andrade et al., 2016). Most of the metrics show slightly higher values for hydrolysis compared to mechanical recycling. Specifically, mechanical recycling shows a tendency for lower product quality, while chemical recycling presents an important and complementary alternative for waste recycling.

An LCA was performed for neutral hydrolysis, Sn(Oct)₂ catalyzed methanolysis, TBD catalyzed ethanolysis, and incineration for comparison purposes. The results show GWP, including and excluding the biogenic carbon, respectively, of -0.059 and 1.697 kg·CO₂ eq/kg PLA for neutral hydrolysis, -1.387 eq/kg PLA and 1.389 kg·CO₂ eq/kg PLA for methanolysis, -1.23 eq/kg PLA and -2.91 kg·CO₂ eq/kg PLA for ethanolysis, and -0.552 eq/kg PLA and 1.250 kg·CO₂ eq/kg PLA for incineration (Aryan et al., 2021).

A cradle-to-gate LCA of PET fiber production through mechanical, semi-mechanical (a flake-pellet-fiber process route), glycolysis, and methanolysis processes was also presented in the literature. The results showed a GWP of 0.96 kg·CO₂ eq/kg for mechanical recycling, 1.88 kg·CO₂ eq/kg for semi-mechanical recycling, 2.59 kg·CO₂ eq/kg for glycolysis, 3.08 kg·CO₂ eq/kg for methanolysis, and 4.06 kg·CO₂ eq/kg for virgin fiber production within the European context. An expansion for a successive cradle-to-grave LCA leads to a closed parametrization for the GWP of recycling methods, presenting values of 1.33 kg·CO₂ eq/kg for mechanical recycling, 2.21 kg·CO₂ eq/kg for semi-mechanical recycling 2.82 kg·CO₂ eq/kg for glycolysis, and 5.54 kg·CO₂ eq/kg for the virgin production (Shen; Worrell; Patel, 2010). The results demonstrate that although the mechanical processes show generally better LCA metrics, glycolysis results are also considerably better than virgin production, highlighting the benefits of a solvolysis process for virgin quality recycling.

Schwarz et al. conducted an LCA of 25 different polymers. LCA for chemical recycling was analyzed for PA, PET, and PLA, and the GWP values were 1.6 kg·CO₂ eq/kg for PA glycolysis, 1.3 kg·CO₂ eq/kg for PET glycolysis, and 1.3 kg·CO₂ eq/kg for PLA hydrolysis (Schwarz et al., 2021).

In another study, several recycling processes of HDPE, LDPE, PP, and PET were compared. For PET, the only polyester analyzed, environmental metrics data for dissolution, enzymatic hydrolysis, methanolysis, glycolysis, mechanical recycling, and virgin production were presented. Some important aspects presented in this analysis are the high energy consumption for virgin polymer, the lower energy consumption and GHG emission for mechanical recycling, and glycolysis. High GHG emission, water usage and toxicity are presented for enzymatic hydrolysis and methanolysis, and dissolution presents the highest land use and GHG emissions (Uekert et al., 2023).

A comparison between PET methanolysis depolymerization and repolymerization processes with the virgin production in Europe and China showed a reduction in the energy consumption of 40.9%-56% and a kg·CO₂ eq reduction of 1.8%-44.5% (Cao et al., 2024).

In summary, mechanical recycling of polyesters, in particular PET, is widely implemented owing to its low energy requirements and simple infrastructural demands. However, mechanically recycling polyesters typically leads to polymer degradation. Chemical recycling, in turn, enables depolymerization into monomers that can then be re-polymerized with virgin-like properties. Yet, chemical recycling requires more energy and emits more GHG than mechanical recycling, making the latter more suitable for contaminated, colors, and mixed-materials streams, while the former is preferred for clean, single-stream waste.

The Table 2.3.4 summarizes the main discussion points comparing the technologies impacts.

2.3.12 Techno-economic assessment

A TEA from 2023 analyzed the minimal selling prices (MSP) for PET production under mechanical recycling, glycolysis, enzymatic hydrolysis, methanolysis and dissolution compared to the virgin MSP. Cost definitions were evaluated over a range of optimistic and pessimistic perspectives. The enzymatic hydrolysis, glycolysis and methanolysis processes, respectively, showed an MSP in the range of 1.83-2.47, 0.84-1.16 and 0.94-1.22 \$/kg. The comparative values in this scenario were 1.19 \$/kg for virgin PET, 0.87 \$/kg for dissolution and 0.54 \$/kg for mechanical recycled PET (Uekert et al., 2023).

The modular MW-ZnO plant with five identical production lines and one backbone facility, after capacity expansion, significantly reduced the MSP to \$1350/t, by 2023 standard, due to operating cost reduction. In contrast, the conventional MW-ZnO plant with a 100-kW mi-

Table 2.3.4: Solvolysis summary on the environmental impact over the methods analyzed (Based on (Uekert et al., 2023)).

Method	Pros	Cons	Observations
Hydrolysis	• Greener solvent/reactant • Low land use	• High Water usage • High toxicity • High GWP • High waste generation • High energy consumption	Althought it uses an abundant neutral solvent, it shows a high energy consumption, mainly due to efficiency and high water content.
Glycolysis	• Low energy consumption • Low water consumption • Low GWP		It does not show a relatable high demand for most of the indicators, being on the middle zone for most of the metrics.
Alcoholysis	• Low water consumption • Low waste generation • Low GWP	• High land use • High energy consumption	Presented mainly by its high energy consumption and high GWP emission due to the material needed

Source: The author (2024).

crowave reactor only performs slightly better than the modular plants at the same scale because of its lower capital cost. Owing to its simple plant configuration and efficient glycolysis chemistry by the heterogeneous ZnO catalyst, the microwave-assisted PET glycolysis is more cost effective. Overall, conventional size and modular MW-ZnO processes with 837 kg BHET/h capacity have lower BHET MSPs than the DMT-based process at a much larger scale (14,600 kg BHET/h). With a slightly higher (\$130/t) production cost, the modular plant could have 36% lower initial investment and faster start-up, which could be favored by investors (Luo et al., 2023).

On another assessment from 2024, a thermal catalyzed glycolysis of PET using a LiCoO₂ waste showed an MSP for BHET in the range of 0.9-1.7 \$/kg. The TEA showed that the main factor to the cost of the recycled product was the PET waste material source, with around 44%

of the MSP contribution. The operational analysis, under the considered scenario, showed a requirement of a flow rate of around 15.000 t/year of consumed PET, for a virgin BHET under the cost of 1.35 \$/kg (Lou et al., 2024).

Despite promising LCA results, the economic feasibility of solvolysis is highly sensitive to feedstock quality, product purity requirements, solvent recovery costs, and catalyst lifetime. Current techno-economic models suggest that policy incentives, such as Extended Producer Responsibility (EPR) or carbon credits, are critical to bridge the cost gap between recycled and virgin polyesters.

2.3.13 Industrial scenario

Although chemical recycling is in a very important stage, with considerable research interest to continuously enable a more efficient and commercially feasible process, its market still lacks significant industrial demonstration. Yet, few industrial companies are already working in this field, as summarized in Table 2.3.5.

Table 2.3.5: Companies in the chemical recycling market and their respective processes

Company	Process	Polymer	Country	Ref.
Commercial				
Revalyu	Glycolysis	PET	India	(Heraeus, 2025)
Carbios	Enzymatic Hydrolysis	PET	France	(Branson et al., 2023)
Eastman	Methanolysis	Polyester	United States	(Eastman, 2024)
BASF (loopamide)	-	Polyamide 6	-	(Loop amid, 2024)
TotalEnergies Corbion	Hydrolysis	PLA	Thailand	(TotalEnergies Corbion, 2025; Bie et al., 2025)
Samsara Eco	Enzymatic Hydrolysis	Polyester fiber	Australia	(Samsara Eco, 2025)
EVRNU	Soluble purification	Cotton	United States	(Evrnu, 2024)
Infinited Fiber	Soluble purification	Cotton	Finland	(Infinited Fiber, 2020)

Continued from previous page				
JEPLAN	Glycolysis	PET	Japan	(JEPLAN, 2020)
Ioniqa	Glycolysis	PET	Netherlands	(Ioniqa, 2024; Braglia, 2024)
Syre	Glycolysis	Polyester fiber	Sweden	(syre)
Pilot				
Cure	Partial Glycolysis	PET	Netherlands	(CuRe, 2024)
Depoly	Alkaline Hydrolysis	PET	Switzerland	(Depoly, 2024; AN-DEPERSON; IRELAND; HLAIEM, 2024)
G3EN	Alkaline Hydrolysis	PET	Italy	(GR3N, 2024)
SK Chemicals	Glycolysis	PET	South Korea	(Sk Chemicals, 2025)
Project				
Ioniqa/KOCH	Glycolysis	PET	Netherlands	(Denua, 2024)
Research				
Garbo (Chempet)	Glycolysis	PET	Italy	(Garbo, 2024)
Recyc'elit	Alcoholysis	PET	France	(Mcube, 2024; MAHDI; Medimagh; FOURDIN, 2023)
Plast Nordic	Alkaline Hydrolysis	PET	Nordic region	(Sustainable Plastics, 2024)
Syntetica	-	Nylon	France	(Syntetica, 2025)
Macrocycle	Cyclic Depolymerization	PET	United States	(MacroCycle Technologies, 2025)
Epoch	Enzymatic Depolymerization	Nylon and Polyester	United Kingdom	(Epoch BioDesign, 2025)
Protein Evolution	Enzymatic Hydrolysis	Polyester	United States	(Taylor et al., 2025)
Birch Biosciences	Enzymatic Depolymerization	PET	United States	(Birch Biosciences, 2025)

Continued from previous page

Source: The author (2024).

Operationally, it is worth mentioning the projects of Eastman, (Eastman, 2024), with a process of polyester depolymerization through methanolysis, and of BASF, with a non-publicly specified process for polyamide chemical recycling known as “loopamide project” (Loop amid, 2024).

Revalyu is an Indian recycling company for PET glycolysis that was acquired by the German company Heraeus (Heraeus, 2025). It is one of largest selective depolymerization companies, with two operating units in India, one plant planned for 2025 in India, and another estimated for 2026 in the USA (Duffler, 2024). This project aims to implement a demonstrator capable to process 100 t of waste annually by 2025 (Mcube, 2024).

On the bioplastic scenario, advanced recycling of pre- and post-consumer PLA are already operative, through the hydrolysis depolymerization process by TotalEnergies Corbion, major global PLA producer, integrating its Thailand’s commercial plant for the production of recycled PLA with recycled content of 30% and 100% (TotalEnergies Corbion, 2025). It shows great progress, as an argued potential polymer for circular production, demonstrating that even a considerably low volume of polymer production can have an integrated depolymerization process, showing a properly accountable end-of-life policy (Bie et al., 2025).

There are also independent companies such as Carbios and Samsara Eco, which developed an enzymatic depolymerization process for polyesters. In addition, Infinited fiber (Infinited Fiber, 2020) and EVRNU (Evrnu, 2024) are also focused on advanced recycling based on purification technology solutions for cotton recycling. This is an important step for textile and fiber recycling that needs to be addressed (Branson et al., 2023). Moreover, in an advanced research step, Garbo, with a ChemPET project which would be a productive demonstration unit by 2020, but it was delayed due to the SARS-CoV-2 pandemics (Garbo, 2024).

Following Carbios’ and Samsara’s processes, many startups are developing pathways toward sustainable enzymatic degradation. Companies such as Epoch, Protein Evolution and BirchBiosciences are on the enzymatic efficiency research and possibly on a commercial production plant planning (Epoch BioDesign, 2025; Taylor et al., 2025; Birch Biosciences, 2025).

Syntetic and Epoch also play an important role with technologies for nylon depolymerization, important fraction of a fiber economy. Epoch, working on a biotechnology perspective, provide research both on nylon and polyesters (Syntetica, 2025; Epoch BioDesign, 2025).

Another important initiative is the T-REX project, which is a 3-year long consortium of 13 companies (Addidas, Ioniqa, Infinited Fiber, Aalto University, Arapaha, BASF, CURE, Fashion for Good,

FAU University, Fulgar, INDORAMA, LinzTextil, Quantis, and VEOLIA). Each player contributes with its expertise to develop efficient solutions for cloth and fiber recycling (Studio, 2024).

CURE, Depoly and Gr3en are in a demonstration/pilot step of their own projects, which could be the most promising chemical recycling processes of recent industrial projects. CURE, Depoly and Gr3en are in a demonstration/pilot step of their own projects, which could be the most promising chemical recycling processes of recent industrial projects. CURE, in particular, is enabling a close-loop recycling of PET through partial glycolysis, which means that it does not directly produce the BHET monomer, but its oligomers. Because PET production also requires a pre-polymerization to produce oligomers, the direct close-loop recycling reduces both the costs for depolymerization process and for repolymerization with an already pre-polymerized product (Depoly, 2024).

Depoly, a recent award-winning startup, shows an interesting alkaline hydrolysis process under room pressure and temperature. This mild conditioning reaction enables a low-cost process and promises future market feasibility (Depoly, 2024).

GR3N is a Swiss company and is not yet in operation. This process will operate using a microwave-hydrolysis technology called Microwave Assisted Depolymerization (MADE). GR3N announced a demonstration plant on a venture with the engineering company Intecsa, with a capacity to produce 40,000 t of PET, expected to be operational until 2027. Its technology is also planned to be used by other industrial plants, such as Plast Nordic company, which has announced the interest in PET recycling units in the Nordic region using the MADE technology (Sustainable Plastics, 2024).

Sk Chemical is also with a new depolymerization project for a operating pilot plant planned to 2026. It will perform under a annual capacity of 50 tons of waste of PET bottles, fibers, films and automotive parts (Sk Chemicals, 2025).

Ioniqa (Ioniqa, 2024) is a company that had filed for bankruptcy in October of 2024 (Victory, 2024) and declared its restructuring for a smaller operation (Laird, 2024) in December of 2024. Its bankruptcy resulted from issues with competitive viability, particularly the challenge of competing with the prices of oil-based companies for the some grade products. In addition, there was the need for regulation to enable a truly sustainable circular economy, with less reliance on 1st generation production (Braglia, 2024). Ioniqa also has an interesting project with KOCH (Denua) (Denua, 2024), for PET glycolysis.

As a token of potential scalability and projection for the depolymerization market, Jan Van Kisfeld, managing director of Revalyu Group, states that, along with the operating plants in India, the new projected plants demonstrate the feasibility of chemical recycling projects from both economic and environmental perspectives (Taylor, 2024).

The commercial potential of chemical recycling can be also found indirectly. The enterprise

Biosolvit, which was created from the patent developed by Vale and Federal University of Espírito Santo (UFES, Brazil), since June 2024, have produced an ore dust suppressor resin from the alkaline hydrolysis of transparent and green PET bottles in the presence of a cationic surfactant (Melo; Silva; Vasconcelos, 2016). The production of alkyd resins by chemical recycling of PET bottles is currently a commercial reality. BASF, through its decorative paint brand Suvinil, have already recycled PET to manufacture enamels and varnishes, substituting petroleum-based raw materials (Silva, 2021).

2.3.14 Perspectives

This section aims to further discuss the recycling market, highlighting the regulatory and political discussion required to promote and engage a highly circular economy. It also proposes a scenario analysis for potential improvements. In addition, the requirements of the industrial ecosystem for sustainable global plastic production will be discussed, followed by an analysis of the available data on process variables to enhance the effectiveness and efficiency of depolymerization processes.

2.3.15 Regulatory Framework

Some regulatory measures, governmental policies, and global/regional development acts will be essential for a sustainable circular economy. As previously discussed, the Ioniqa company recently declared bankruptcy due to a lack of incentives for the chemical recycling business. In particular, the main drawback is the direct competition with fossil-based products, which are typically much cheaper. A common solution to this problem would be to provide solid incentives for advanced recycling solutions, such as financing and lower taxes, or an intense penalization for using virgin oil-based polymers for short-term applications. This approach is because, regardless of their end-of-life, petrochemical polymers do not incorporate their environmental damages into their cost, in addition to the heavy subsidies that this industry commonly receives.

Besides that, most of the world's governments were not yet properly interested in a comprehensive solution for plastic waste. However, this scenario is changing, as the market faces the demand for environmentally better solutions and ways to address plastic pollution, in addition to the currently negotiated intergovernmental instrument against plastic pollution, under the guidance of the UN Environmental Programme (UNEP) (United Nations, 2021). Driven by this demand, Europe is pushing intense regulatory frameworks for a future redefinition of plastic waste. A proposal for regulation of the European Parliament and of the Council emphasized the need for reuse and recycling processes in the entire plastic products supply chain by 2030 in an economically feasible way (Directorate-General for Environment, 2025).

This is part of the DIRECTIVE (EU) 2019/904 OF THE EUROPEAN PARLIAMENT AND

OF THE COUNCIL, aimed at developing an effective circular economy (EUROPEAN PARLIAMENT, 2024). With this regulatory framework, the market and legislation will eventually lead to an indubitably demand for advanced and chemical recycling solutions, as even mechanical recycling solutions are not entirely recyclable, being limited to only a few recycling cycles. Although it still is a bold proposal, it shows a state vision for an advanced plastic waste solution (European Parliament, 2025).

The earliest update release for this directive by the amending of Regulation (EU) 2019/1020 and Directive (EU) 2019/904, and repealing Directive 94/62/EC, which show an important amendment on advanced recycling systems, stating that it will be needed to have a well-established recycling ecosystem with sustainable virgin grade quality recycled polymer, which came into force in February 11th of 2025. It is an interesting perspective that solvolysis technologies can explore to resolve sustainably (European Parliament, 2025).

The European Commission also has the “Circular Economy Action Plan”, as a part of the European Green Deal and its “strategy for sustainable and circular textiles” and “Plastics strategy” policies. The strategy for sustainable and circular textiles aims for a straightforward regulatory development of the textile market. It states the definition to require minimal composition of recycled content on fibers, being applied to all products on the market, both European and imported products, and the implementation of singular collection systems for textile wastes (European Commission, 2024). A recent proposal is undergoing discussion for a mandatory ban on the destruction of unsold consumer goods, among other important decisions. Also, it defines the producer’s responsibility for the whole life cycle of textile products, defining a fee according to the product’s destinations. These action plans should be implemented no later than 2027 (Directorate-General for Environment, 2025).

Another field of regulation shows a perspective of a possible legislative deflection towards fossil-based materials. On December 26th, 2024, the New York governor, Kathy Hochul, passed a law that held large oil and fossil fuel companies responsible for climate change effects, designing a payment of a ‘Climate Superfund’ of USD 75 billion over twenty-five years to support New York-based projects that bolster New York’s resiliency to dangerous climate impacts like flooding and extreme heat. This landmark resolves the burden of the common citizen to pay for environmental disaster, to the designated polluting companies (Liz Krueger, 2025). It is important for one of the wealthiest states in the US to proceed with this approach. Besides a projected responsibility for climate change over polluting companies, the climate levy provides a higher competitiveness for innovative technologies over the conventional fossil-based economy. Although not yet directed to polymers, it opens the possibility to other markets, such as the petrochemical plastic industry.

With India’s waste generation growth, government initiatives like EPR (Extended Producer Responsibility) policies are currently being strongly developed. The Indian government has set a mandate

for a minimum of 30% recycled plastic content in rigid packaging by April 1st, 2025 (Deccan Herald, 2025), with an ambitious target of 60% by 2028-29 (Bora, 2025), providing a stronger scenario for circular production globally.

2.3.16 Process variables analysis

To ensure its feasibility, analyzing the effects of process variables on recycling efficiency and product yield is critical for optimizing methods like glycolysis, hydrolysis, and methanolysis. Analyzing process variables, such as temperature, reaction time, catalyst type, and reactant concentration, allows for understanding which factors have the greatest influence on the yield of the recovered monomers.

This analysis integrates graphical data representations, charts, and statistical tools, such as analysis of variance (ANOVA) and correlational analysis, to systematically evaluate the effects and interactions between variables across the solvolysis methods. The ANOVA provides a statistical analysis of all the reaction results datasets, under their own conditions, to determine which variables and interactions have a significant statistical impact on the reaction yield. The correlational visualizations give the perspective of how strong the influence of each continuous variable is, including the yield, under a correlational relationship with each other.

2.3.16.1 PET Glycolysis

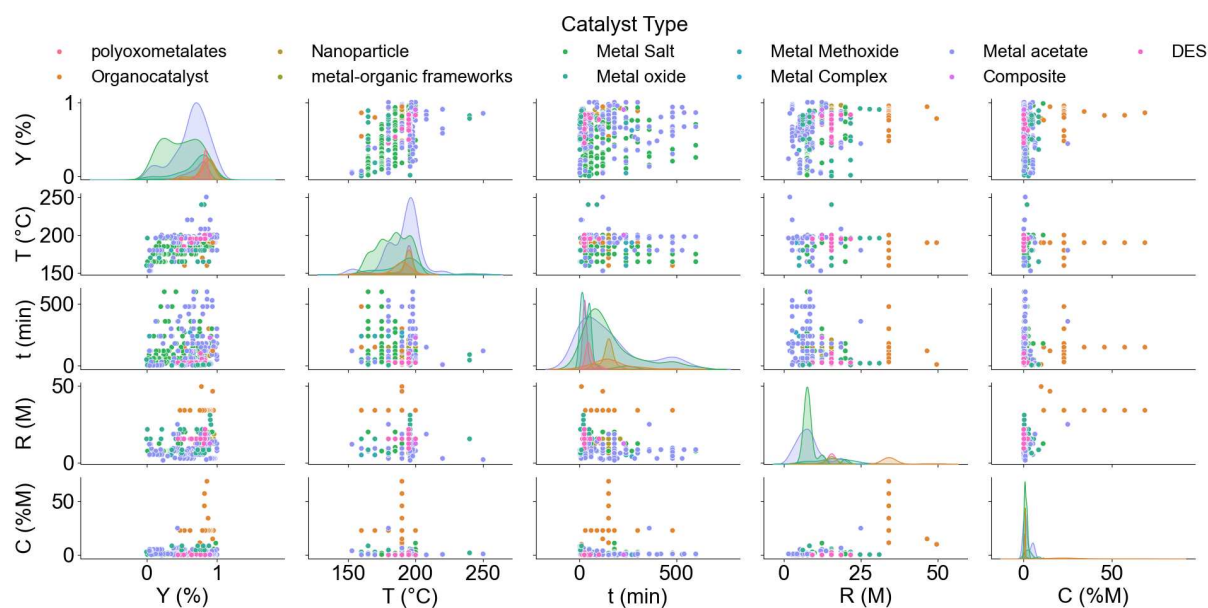
As the primary object of study in selective depolymerization, PET serves as a valuable model, providing insights from its successes and challenges, and enabling the extension of research to a wider variety of polymers. The focus of this analysis was PET glycolysis, which has been considered one of the most effective available methods, and, according to the previous discussion, stands out as a promising method for PET depolymerization under the environmental and economic aspects.

In total, 419 PET glycolysis reaction results from the literature were collected for the data analysis. The Figure 2.3.6 illustrates the complete data set distribution utilized in the analysis.

The ANOVA and correlational analysis were performed on a Python script, using the libraries statsmodel, with the ANOVA model type 3 (since it is an unbalanced interdependent dataset), and pandas respectively.

The correlation of the process variables was analyzed under nine assumptions (Figure 2.3.7). The analysis considered (1) the complete data set without the use of a cosolvent, (2) a complete data set with the use of a cosolvent and, under the system without cosolvent, the following groups: origin of the polymer ((3) bottle, (4) fiber, and (5) virgin) and type of catalyst ((6) metal acetate, (7) metal salt, (8) organocatalyst, and (9) metal oxide). Among the main results of Figure 2.3.7, one can highlight:

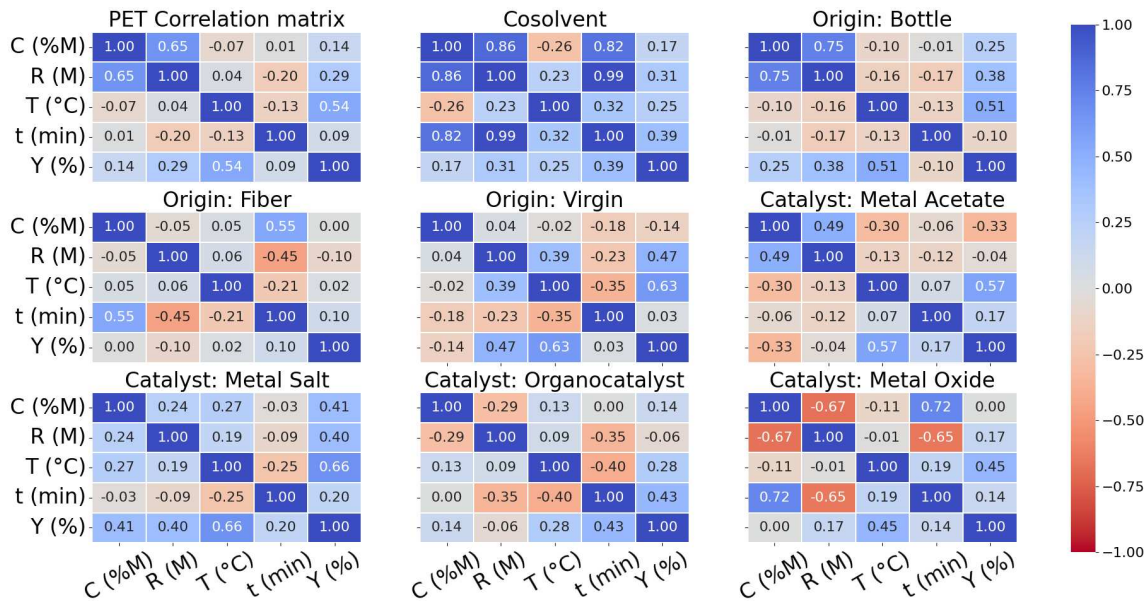
Figure 2.3.6: Operational range between process variables according to the conversion of PET to BHET. Variables: Y = Yield; T = Temperature; t = reaction time; R = Ethylene glycol ratio; C = Catalyst ratio (Aguado et al., 2014; Chen et al., 2013, 2015; Fang et al., 2018; Fukushima et al., 2011; Troev et al., 2003; Xi; Lu; Sun, 2005; Najafi-Shoa et al., 2021; Nifant'ev et al., 2023; Alzuhairi; Khalil; Hadi, 2017; Wang et al., 2021a; Wang et al., 2021c,b; Wang et al., 2023; Chaudhary et al., 2013; Guo et al., 2021; Wang et al., 2022; Nica et al., 2018; McKeown et al., 2020; Karayannidis et al., 2006; Karanastasis; Safin; Pitet, 2022; López-Fonseca et al., 2011; Le et al., 2022; Lee et al., 2023; Yao et al., 2022; Chen et al., 2022; Ghaemy; Mossaddegh, 2005; Asueta et al., 2023; Hu et al., 2020; Liu et al., 2018; Shukla; Kulkarni, 2002; Sangalang; Bartolome; Kim, 2015; Pardal; Tersac, 2007, 2006; Chen; Chen; Cheng, 1999; Kirshanov et al., 2023; Achilias et al., 2010; Huang et al., 2021; Colomines et al., 2006; Javed; Fisse; Vogt, 2023; Kim et al., 2021; Al-Sabagh et al., 2014; Andini et al., 2024; El Mejjatti et al., 2014; Rubes et al., 2024; Yu et al., 2023; Wei et al., 2024; Yang et al., 2023).



Source: The author (2024).

- Matrix 1 shows a strong correlation between the catalyst and the reactant ratios, which can be explained by the fact that, in general, the glycolysis reaction follows the mechanistic ratio of the reactant and its catalyst in the molecular cleavage action. Temperature also plays an important role in the reaction yield, which is expected because kinetic parameters depend on such a variable. The moderate correlation can be explained by the range of temperatures in the reported studies, typically close to the melting temperature. Most of the other correlations show a nearly neutral value, which can be due to the high variation under different catalysts, origins, and other conditions. The difficulty in depolymerizing PET in bulk conditions due to its high degree of crystallinity can also be an important issue. In addition, the low linear correlation with time can suggest the absence of systematic research work focused on the kinetic evaluation of glycolysis processes.
- Matrix 2 for the cosolvent-assisted general dataset shows a strong or moderate positive correlation for most of the variables, which shows the high influence of the use of a cosolvent, providing a much faster and more effective reaction, although it often requires the use of less environmentally

Figure 2.3.7: Correlation matrix for PET glycolysis. Variables: Y = Yield; T = Temperature; t = reaction time; R = Ethylene glycol ratio; C = Catalyst ratio. (Aguado et al., 2014; Chen et al., 2013, 2015; Fang et al., 2018; Fukushima et al., 2011; Troev et al., 2003; Xi; Lu; Sun, 2005; Najafi-Shoa et al., 2021; Nifant'ev et al., 2023; Alzuhairi; Khalil; Hadi, 2017; Wang et al., 2021a; Wang et al., 2021c,b; Wang et al., 2023; Chaudhary et al., 2013; Guo et al., 2021; Wang et al., 2022; Nica et al., 2018; McKeown et al., 2020; Karayannidis et al., 2006; Karanastasis; Safin; Pitet, 2022; López-Fonseca et al., 2011; Le et al., 2022; Lee et al., 2023; Yao et al., 2022; Chen et al., 2022; Ghaemy; Mossaddegh, 2005; Asueta et al., 2023; Hu et al., 2020; Liu et al., 2018; Shukla; Kulkarni, 2002; Sangalang; Bartolome; Kim, 2015; Pardal; Tersac, 2007, 2006; Chen; Chen; Cheng, 1999; Kirshanov et al., 2023; Achilias et al., 2010; Huang et al., 2021; Colomines et al., 2006; Javed; Fisse; Vogt, 2023; Kim et al., 2021; Al-Sabagh et al., 2014; Andini et al., 2024; El Mejjatti et al., 2014; Rubes et al., 2024; Yu et al., 2023; Wei et al., 2024; Yang et al., 2023).



Source: The author (2024).

neutral compounds. Some important metrics are the high influence of the ratio of catalyst and reactant, and the general impact of the reaction time. In addition, the high correlation between the ratios of catalyst and time suggests the benefits of catalyst addition in solution glycolysis processes. A similar result was observed regarding the correlation between the ratio of reactant and time.

- The origin perspective shows that the bottle (3) has an important correlation for the catalyst and reactant ratios and the moderate effect that the reaction temperature exerts over the product yield. In particular, the correlation matrix for bottles was very similar to PET. For the fiber (4), most variables show a neutral correlation, except for the reaction time, which shows a strong positive correlation for the catalyst ratio and negative for the reactant ratio, which could be due to the general higher surface area of a fiber, providing a higher diffusion and a lower amount of reactant. The virgin dataset (5) shows, respectively, a strong positive correlation of temperature and a moderate correlation of reactant ratio with yield. In addition, a moderate positive correlation of temperature to reactant ratio and a negative correlation of reaction temperature to time were also observed. At higher purity, the main effects can be demonstrated: temperature (energy) required for the bond cleavage, amount of reactant to improve the kinetics, and temperature that provides a faster reaction, as expected.
- The metal acetate catalysts (6) show a possible need for higher temperatures for an efficient reaction, but the amount of catalyst used could decrease that need; it makes evident the need for a kinetic study for such a process. The metal salt (7) shows a good interaction for the augmentation of most parameters towards higher yield, particularly the catalyst and reactant ratio and the temperature. Organocatalysts (8) show a higher necessity for reaction time, but also demonstrate that with higher reactant ratios, the reaction time and the catalyst ratio can be lowered. Lastly, the metal oxide(9) shows an interesting data pattern, suggesting the necessity of much less reactant under the high catalyst load and, at the same time, a longer reaction time. This can provide an insight that, although the reaction ratio does not provide a direct yield increase, it can show a lower need for catalyst load and still work on lower reaction times.

Under the ANOVA analysis of the whole reaction samples, considering the statistical significance of 0.05, excluding cosolvent systems, the main factors for efficient depolymerization through glycolysis of PET are highlighted in Table 2.3.6. The reactant ratio plays a major role in glycolysis processes, as shown in the correlational analysis, being a significant variable both by itself and by its impact on the other variables for an effective process.

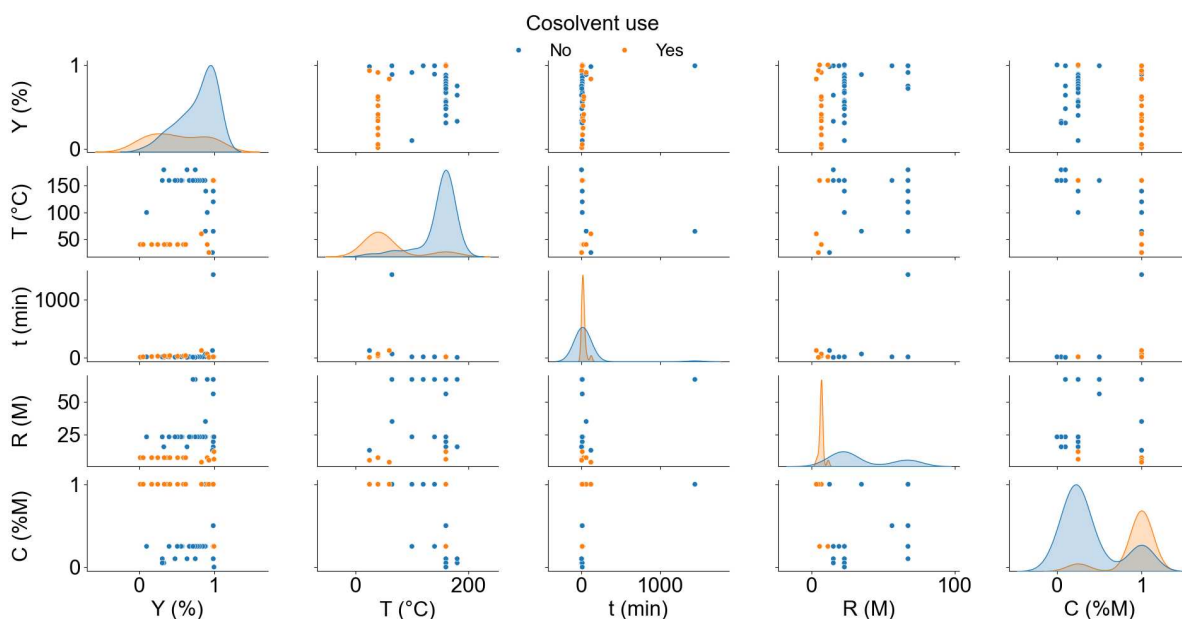
These results show that, while catalyst design remains a crucial area of investigation, the process

Table 2.3.6: ANOVA on literature PET glycolysis studies on main variables. Categorical: Reactant, Origin and Catalyst. Continuous: Reactant ratio, catalyst ratio, temperature and time (Aguado et al., 2014; Chen et al., 2013, 2015; Fang et al., 2018; Fukushima et al., 2011; Troev et al., 2003; Xi; Lu; Sun, 2005; Najafi-Shoa et al., 2021; Nifant'ev et al., 2023; Alzuhairi; Khalil; Hadi, 2017; Wang et al., 2021a; Wang et al., 2021c,b; Wang et al., 2023; Chaudhary et al., 2013; Guo et al., 2021; Wang et al., 2022; Nica et al., 2018; McKeown et al., 2020; Karayannidis et al., 2006; Karanastasis; Safin; Pitet, 2022; López-Fonseca et al., 2011; Le et al., 2022; Lee et al., 2023; Yao et al., 2022; Chen et al., 2022; Ghaemy; Mossaddegh, 2005; Asueta et al., 2023; Hu et al., 2020; Liu et al., 2018; Shukla; Kulkarni, 2002; Sangalang; Bartolome; Kim, 2015; Pardal; Tersac, 2007, 2006; Chen; Chen; Cheng, 1999; Kirshanov et al., 2023; Achilias et al., 2010; Huang et al., 2021; Colomines et al., 2006; Javed; Fisse; Vogt, 2023; Kim et al., 2021; Al-Sabagh et al., 2014; Andini et al., 2024; El Mejjatti et al., 2014; Rubes et al., 2024; Yu et al., 2023; Wei et al., 2024; Yang et al., 2023).

	p-value		p-value
Intercept	9.76E-01		
Reactant	9.99E-01	ReactantRatio *	4.17E-17
		CatalystRatio	
Origin	1.00E+00	Temperature	9.42E-01
Catalyst	2.47E-01	Reactant * Temperature	3.41E-08
ReactantRatio	4.54E-31	Origin * Temperature	1.00E+00
Reactant * Origin	1.00E+00	Catalyst * Temperature	9.52E-01
Reactant * Catalyst	6.26E-01	ReactantRatio * Temperature	5.06E-12
Reactant * ReactantRatio	6.00E-17	Time	5.58E-01
Origin * Catalyst	1.00E+00	Reactant * Time	5.53E-01
Origin * ReactantRatio	2.53E-35	Origin * Time	1.00E+00
Catalyst * ReactantRatio	9.85E-29	Catalyst * Time	2.13E-17
CatalystRatio	9.92E-01	ReactantRatio * Time	8.29E-54
Reactant * CatalystRatio	1.00E+00	CatalystRatio * Temperature	1.00E+00
Origin * CatalystRatio	1.00E+00	CatalystRatio * Time	7.24E-01
Catalyst * CatalystRatio	1.88E-01	Temperature * Time	1.00E+00

Source: The author (2024).

Figure 2.3.8: Operational range between process variables according to the conversion of PLA. Variables: Y = Yield; T = Temperature; t = reaction time; R = Ethylene glycol ratio; C = Catalyst ratio (hofmann_tin_2020; Cheung; Alberti; Enthaler, 2020; Xie et al., 2021; D'Alterio et al., 2022; Liu et al., 2024a; Liu et al., 2024b; Alberti; Kricheldorf; Enthaler, 2020; Zhou et al., 2023c).



Source: The author (2024).

conditions are equally essential for designing an effective depolymerization system. Future research should focus on a complementary investigation of these process variables to achieve optimal efficiency.

The importance of polymer origin underscores a critical aspect of solvolysis processes, particularly since the primary feedstock comprises PCW. Additionally, the observed influence of additives on reaction efficiency suggests that this variable could significantly impact the process, especially in correlation with temperature (energy) management.

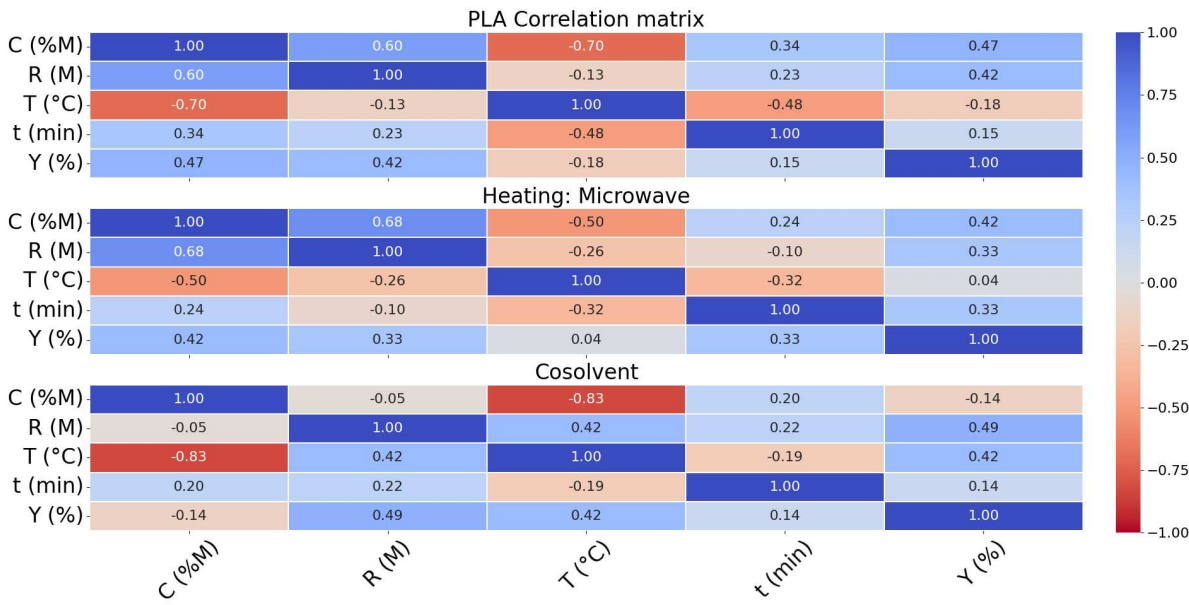
Furthermore, the catalyst type and its interaction with the reactant ratios are key factors. This suggests a promising direction for future research: the development of catalyst systems that minimize the use of both reactant and catalyst while maintaining optimal reaction conditions, especially since achieving a lower effective reactant load can significantly impact the subsequent process variables.

2.3.16.2 PLA Methanolysis

On another perspective, as the only biopolyester with considerable depolymerization data, the secondary matter of analysis was the PLA methanolysis, with 58 entries (Figure 2.3.8).

The analyses were conducted under similar conditions to those of PET glycolysis. The ANOVA at 0.05 significance considered all PLA methanolysis (without cosolvent) data acquired, and the correlation matrix considered the limitation to microwave methanolysis (heating method) and cosolvent system

Figure 2.3.9: Correlation matrix for PLA depolymerization. Variables: Y = Yield; T = Temperature; t = reaction time; R = Methanol ratio; C = Catalyst ratio (hofmann_tin_2020; Cheung; Alberti; Enthaler, 2020; Xie et al., 2021; D'Alterio et al., 2022; Liu et al., 2024a; Liu et al., 2024b; Alberti; Kricheldorf; Enthaler, 2020; Zhou et al., 2023c).



Source: The author (2024).

entries due to the much fewer results in the literature.

Under the correlation matrix (Figure 2.3.9) system, the main factors highlighted for an efficient PLA depolymerization by methanolysis are the moderate positive correlation of methanol and catalyst ratios to the yield and each other. Temperature also shows an important impact on a lower reaction time and catalyst load, which can be considered the other way around.

Considering the microwave-heated systems, there is a similar pattern to the general results, but with a slightly lower temperature and a higher reaction time to yield a correlation. This agrees with the expected results already discussed on the motivation for using microwave, that is, lowering the energy use and reaction times for an efficient process. Considering its results reported in the literature, it generally presents very low reaction times, putting in perspective that the reaction time considered could have a much lower correlation value towards the yield, since it became a very fast reaction.

From the cosolvent systems perspective, a strong negative correlation of temperature to catalyst ratio shows the possibility of working at much lower temperatures under the right catalyst load. This is an important advantage of solution depolymerization processes, in which the solvent addition can decrease the viscosity of the reaction medium and control the reaction rates by diffusive effects. Other important correlations are the positive influence of temperature on reaction rate and on yield, as expected.

An ANOVA was used to analyze the main effects on the collected results data for PLA methanolysis, considering all reaction samples except for cosolvent systems.

Table 2.3.7: ANOVA on literature PLA methanolysis studies on main variables (hofmann_tin_2020; Cheung; Alberti; Enthaler, 2020; Xie et al., 2021; D'Alterio et al., 2022; Liu et al., 2024a; Liu et al., 2024b; Alberti; Kricheldorf; Enthaler, 2020; Zhou et al., 2023c)

	P-value		P-value
Intercept	3.50E-13	Temperature	2.72E-01
Origin	1.69E-09	Origin * Temperature	3.48E-06
Catalyst	4.01E-12	Catalyst * Temperature	3.98E-06
ReactantPerPol	2.36E-15	ReactantRatio * Temperature	3.98E-06
Origin * Catalyst	1.66E-09	Time	4.75E-01
Origin * ReactantRatio	2.61E-13	Origin * Time	6.69E-05
Catalyst * ReactantRatio	2.36E-15	Catalyst * Time	7.26E-02
CatalystPerPol	1.15E-14	ReactantRatio * Time	3.89E-04
Origin * CatalystRatio	5.15E-12	CatalystRatio * Temperature	2.48E-06
Catalyst * CatalystRatio	1.05E-14	CatalystRatio * Time	1.03E-01
ReactantRatio * CatalystRatio	2.36E-15	Temperature * Time	4.87E-01

Source: The author (2024).

Most factors show a significant impact on the reaction yield (highlighted in Table 2.3.7). The only variables that were not statistically significant were temperature, reaction time, and interactions of time with type of catalyst, the catalyst ratio, and the temperature. The higher number of statistically significant variables can be due to the smaller dataset studied, showing fewer entries for each condition. Furthermore, a smaller range of data related to important variables, such as temperature, could impact its level of significance.

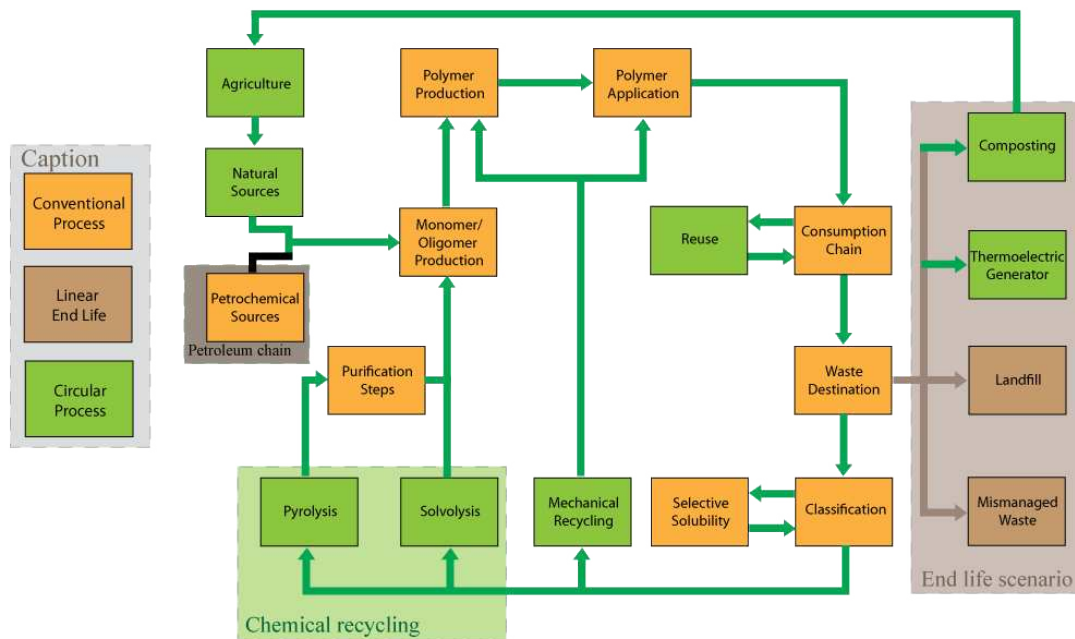
Further studies on the highlighted parameters, such as temperature to catalyst and reactant load for optimal yield, can allow more effective future analyses and a more precise statistical definition.

2.3.17 Integrating technologies

As discussed before, there is no unique solution for a sustainable production. The need for a systematic industrial complex is a key factor for achieving effective circular production. The need to combine recycling technologies arises from processes involved in the post-consumer collection and sorting of the plastics industry, which play a crucial role in recycling effectiveness. Some initiatives to provide dynamic integration between the technologies are described below:

- **Combination of Mechanical and Chemical Recycling:** The need to establish the combination of mechanical and chemical recycling processes as a complementary development of the market, not a direct competitive market.
- **Synergies and Limitations:** Identify the numerous recycling technologies and where each is well-suited according to its limitations and definitions.

Figure 2.3.10: Roadmap proposal for a plastic full life cycle industrial ecosystem.



Source: The author (2024).

- **Examples of Integrated Recycling Systems:** Propose a systemic development of a possible or/and viable recycling ecosystem, denominating, internal or external (other companies), complementing the recycling ecosystem from the effective collection of post-consumer waste to the effective reprocessing or disposal.

An important aspect of impactful change that is needed in a sustainable plastic ecosystem is the capacity for the industries to design processes that are tailored for recycling and reuse processes, and which can be applied in many aspects. The polymer used can be either a polyester or a biopolyester, facilitating the recycling processes in case it is not reusable or not possible to reuse anymore. In addition, it is worth mentioning the following important features:

- Products with no or less colors have a higher effectiveness in the recycling processes;
- Avoiding multilayer packaging is an important step since it makes sorting much more difficult and can promote product mismanagement.

The origin of the waste is also an interesting perspective for a plastic recycling roadmap. In general, there is pre-consumer and post-consumer plastic waste; the former consists of waste generated within the production facility, while the latter is generated by household consumption. Although most discussion seeks to intervene in post-consumer waste disposal, pre-consumer waste is also of interest.

Because there are fewer contaminants and mixtures in pre-consumer waste, it makes it more susceptible to mechanical or, if needed, chemical recycling technologies. Another important factor for

the feasibility of a complete industrial recycling ecosystem is the necessity for an efficient collection and sorting process. A promising facility for plastic sorting is the site zero of Svensk Plaståtervinning, a Swedish plastic recycling company. It is a 60,000 m² plant equipped with 60 near-infrared (NIR) sensors and an approximately 5-km conveyor belt, which processes 40 t of mixed plastic waste per hour (Svensk Plaståtervinning, 2024).

This process has a 95% sorting effectiveness, and any fragment of plastic remaining after the sorting process is separated and sent for chemical recycling, turned into new composite products, or used for energy recovery with carbon capture and storage. In addition, today this plant can sort efficiently a variety of 12 types of plastics, covering a wide range of plastics needed for a circular economy. By 2025, the plant is expected to have a washing and granulation station (Svensk Plaståtervinning, 2024). As the biggest plastic sorting facility, it sets an example for the future circular ecosystem.

Figure 2.3.10 displays a proposal for a systematic recycling ecosystem for an efficient circular economy approach. This diagram reinforces the importance of integrating chemical recycling technologies into the usual process flow, as these processes can be incorporated for the raw material production of monomers and oligomers. The purification and separation processes for monomers obtained via solvolysis could enable their reintegration into 1st-generation production lines (closed-loop), replacing virgin feedstocks or into other production lines for new product processing, on an open-loop, enhancing circularity of the plastic industry.

The use of bio-based materials and the increase of the importance given to the end-of-life scenarios with circular approaches could result in lower waste generation and destination to landfills and, mainly, to less mismanagement. When reuse, mechanical and chemical recycling are not possible, the application of composting and thermoelectric facilities contributes to the carbon and energy recovery, respectively, which could strengthen the circularity principles.

From the monomer production perspective, either bio-based or petrochemical-based, polymer production and application play a major role in the efficient design of a circular ecosystem. Polymer pellets and products with fewer additives and colors can be obtained to produce a product designed to recycle and/or degrade, e.g., a product designed to recycle and/or degrade. The minimal standard involves using easily recyclable polymer formulations, such as polyester, and compostable polymers to address potential leakage in the collecting and sorting chain.

Due to its post-consumer condition, plastic waste must be properly collected through a highly efficient system. Although this theme is not a focus of this review, it requires intense studies and adaptation. The sorting system should be able to properly separate each type of polymer and the multilayer separations as much as possible.

All properly separated plastic should primarily undergo preferential reuse and mechanical re-

cycling. Currently, low systematic industrial reuse is placed, but it is the most environmentally neutral process. From that perspective, mechanical recycling closes the loop for a more sustainable transformation of the same material, enabling a new life cycle for the material, mostly on a lower grade quality, however.

On the other hand, the materials that are not well suited for those processes, or those that degrade due to mechanical recycling processes, need depolymerization methods through chemical recycling technology. Solvolysis methods should be prioritized for their lower LCA, energy consumption, and specific product formation, utilizing all the C-X polymers unsuitable for mechanical recycling and the possible waste stream from a mechanical recycling process.

Hard-to-separate materials are also of singular interest since solvolysis methods can provide systematic separation through sequential depolymerization, with separation steps between each reaction, and simultaneous depolymerization, with a series of separation methods at the end of the reaction process (Yang et al., 2022b). These methods can be incorporated into a more advanced systematic recycling route.

The waste stream of all those processes could be processed by a thermochemical method, resulting in a final mixture of products or energy without the need for sorting and selecting plastic material.

In the common scenario of waste destination worldwide, single-use plastics should be preferably biodegradable or compostable. If a plastic waste stream is mismanaged and ends in environmental leakage, it would be possible to have a lower impact due to lower degradation times or possibly full biodegradation. However, the insertion of chemical recycling as a viable and integrated technology allows the recovery of monomers of these polymers to minimize the wastage of resources and the emission of CO₂ and CH₄ to the atmosphere.

As presented before, the global index of plastic recycling is below 10% (OECD, 2024b), making conventional processes incapable of handling plastic waste problems today. Integrating systems with chemical recycling and applying more robust legislation could increase this index, reducing the percentage of non-recovered plastics, and turning industries into agents of change by contributing to a more circular economy.

2.3.18 Concluding remarks

Chemical recycling via selective depolymerization, such as hydrolysis, glycolysis, alcoholysis, emerges from this review as a pivotal strategy for enhancing polyester circularity, recovering virgin-like monomers/oligomers from contaminated, mixed, or degraded post-consumer waste (PCW) streams unsuitable for mechanical recycling.

For polyesters, solvolysis selectively cleaves ester bonds, enabling efficient separation of in-

tentionally added substances (IAS), fillers, dyes, and copolymers, providing high-purity feedstocks for direct repolymerization or innovative green technologies.

The industrial PET landscape demonstrates scalability, with cases of industrial plants employing various technology specialties. Studies on bioplastics extend these benefits, improving LCA by averting landfilling and composting defaults. Although the cost challenges remain, the technology shows a promising future market.

Statistical analyses identified catalyst efficiency, reaction kinetics, PCW composition, crystallinity, and IAS as dominant factors through correlational and ANOVA methods, underscoring gaps in robust, reproducible protocols for process intensification and further academic research.

In summary, economic hurdles still persist, but integration via continuous-flow systems, multi-feedstock hubs, renewable energy coupling, solvent recovery, design-for-recycling principles, policy incentives (e.g., EPR), and public-private partnerships can elevate chemical recycling from niche to cornerstone of sustainable polyester economies, complementing reuse and mechanical recycling routes in a holistic circular ecosystem.

Chapter 3

Mechanism study of Simultaneous ring opening polymerization of lactones and polycondensation of diethyl succinate and 1,4-butanediol

3.1 Introduction

Poly(butylene succinate) (PBS) is a biodegradable aliphatic polyester that has gained increasing attention. Its popularity stems from its favorable mechanical properties, which are comparable to several polyolefins, as well as its biodegradability, and its potential for bio-based synthesis. Conventionally, PBS is synthesized through stepwise esterification or transesterification reactions followed by polycondensation, typically in the presence of metallic catalysts such as titanium or tin alkoxides. Although effective, these processes often suffer from operational and environmental drawbacks, including catalyst toxicity, high energy demand associated with the high required temperatures, and limited control over polymer microstructure (Adamopoulou, 2012; Dixon et al., 2025; Armani; Petri, 2023).

In the same perspective, polylactones have been synthesized under ring-opening polymerization processes, exhibiting interesting properties, such as high polymerization rates and ability to reach high molar masses even under mild conditions. These lactone-derived polyesters have been used mainly for medical applications, such as controlled drug delivery. However, these polymers most often present thermal and mechanical properties suited to specific application, such as low melting (T_m) and glass-transition (T_g) temperatures (Sartori; Diaz; Diaz-Muñoz, 2021; Guindani et al., 2017).

Poly(ϵ -caprolactone) (PCL) and Poly(Globalide) (PGL) are promising materials for the bioplas-

tic industry. PCL, despite not being a bio-derived material, is a polylactone widely recognized in industry and literature due to its attractive biodegradation properties. Conversely, PGL is relatively new in academic and industrial research, but it shows interesting properties for polymerization purposes, such as its unsaturated chain, allowing post-functionalization (Guindani et al., 2017; Piotrowska et al., 2025; Guindani et al., 2020; Dixon et al., 2025; Mahapatro et al., 2003).

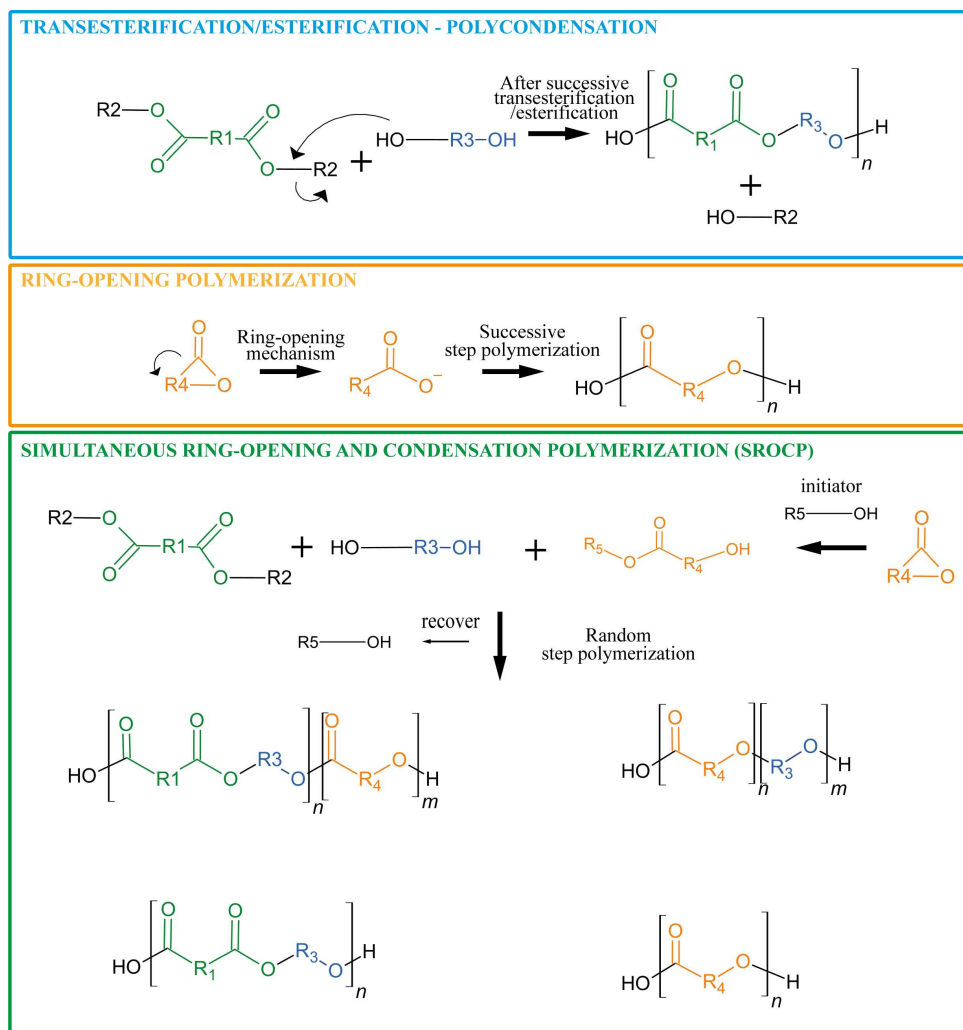
In this context, enzymatic catalysis has emerged as a promising alternative for polyester synthesis. Lipases, particularly *Candida antarctica* lipase B (CALB), have demonstrated high catalytic efficiency in esterification, transesterification, and ring-opening polymerization reactions under milder conditions. The use of biocatalysts enables improved selectivity, reduced energy consumption, and compatibility with bio-based monomers, aligning polymer synthesis with green chemistry principles and sustainable process development (Jiang; Loos, 2016; Elias Guckert et al., 2023; Kobayashi, 2015; Champagne; Strandman; Zhu, 2016; Kundys et al., 2018; Sena et al., 2023).

Beyond conventional step-growth or chain-growth polymerization routes, hybrid strategies capable of combining multiple mechanisms within a single system have been proposed. Among them, the Simultaneous Ring Opening and Condensation Polymerization (SROCP) method integrates step-growth condensation between diesters (or diacids) and diols, with the ring-opening polymerization of cyclic esters, such as lactones or macrolactones. The concurrent activation of these pathways may result in copolymers with distinct microstructures and property profiles, including improved thermal behavior, mechanical performance, and biodegradability (Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021; Kobayashi, 2015; Atta et al., 2021; Punyodom et al., 2021).

This pathway is based on step growth polymerization, in which all reactive species exhibit significant reactivity, allowing multiple and statistically random propagation events in the presence of different monomeric units. Upon ring opening, the generated reactive chain ends can interact with terminal groups formed during step growth reactions, promoting chain rearrangement and yielding polymers with predominantly random compositions (Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021; Safari et al., 2021).

The proposed reaction mechanism for the SROCP system is detailed in Figure ??, where R_1 to R_3 define the structural form of the polymer chain. For transesterification reactions, R_4 has $C > 0$, with an alcohol as a byproduct, whereas for esterification reactions $R_4 = H$, leading to H_2O formation. The ring-opening reaction starts with an initiation step involving a R_5-OH group, which can be an activated-enzyme molecule. The resulting initiation product is a bifunctional monomer, which can react subsequently through transesterification or esterification reactions (Johnson; Kundu; Beers, 2011). This mechanistic framework highlights how condensation and ring-opening reactions can coexist within the same system, enabling complex polymer architectures (Hu et al., 2016; Appavoo et al., 2021; Krichel-

Figure 3.1.1: Main polyester synthesis pathway and the proposal for SROCP mechanism.



Source: The author (2024).

dorf; Weidner, 2020).

This study details an experimental investigation into the enzymatic polymerization of diethyl succinate and 1,4-butanediol, the classical PBS precursors, simultaneously combined with selected lactones, specifically ϵ -caprolactone and globalide, in the presence of immobilized *Candida antarctica* lipase B (CALB). The effects of temperature, reaction time, and monomer ratio on polymer formation and copolymer composition are systematically evaluated. The resulting materials are characterized using Gel Permeation Chromatography (GPC), C^{13} and H^1 Nuclear Magnetic Resonance (NMR) to assess molecular mass distribution, and polymer composition.

The published studies for the copolymerization system presented on Figure 3.1.1 are few, when involving PBS monomers the ϵ -caprolactone is the only registered on literature. The study mainly analysed the effect of copolymer structure on thermal properties. The main findings demonstrated the effective copolymerization either through a SROCP or cyclization of the butylene succinate segment followed

by a double ring-opening polymerization. In particular, it has been demonstrated that two distinct units crystallize in different crystal lattices, providing the possibility for a designed crystallinity on an isodimorphic behavior (Ciulik et al., 2017; Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021; Safari et al., 2018, 2019, 2021; Zeng et al., 2012).

Overall, this work reports the synthesis and characterization of a novel PBS–PGL copolymer that has not yet been systematically analyzed on available literature. The materials obtained are compared with the corresponding homopolymers and with a copolymer composed of PBS and PCL repeating units, available on literature, which is used as a reference system. The results provide new insights into enzymatically driven hybrid polymerization routes and demonstrate the potential of SROCP as a sustainable strategy for the design of advanced biodegradable polyesters.

3.2 Material and methods

3.2.1 Materials

Novozym 435 immobilized lipase from *Candida antarctica* was kindly donated by Novozymes. Globalide (GL, purity 99%) was kindly donated by Symrise. Diethyl succinate (DS, purity 99%), 1,4-butanediol (BDO, purity 99%), ϵ -Caprolactone (CL, purity 99%) and deuterated chloroform anhydrous (99.8 atom 2%D, with purity 99%) were purchased from Sigma-Aldrich. Chloroform (minimum content of 99.8%) was acquired from Dinâmica. Chloroform (HPLC grade, 99.8% purity) was bought from J.T.Baker. All components were used as received without further purification or modification.

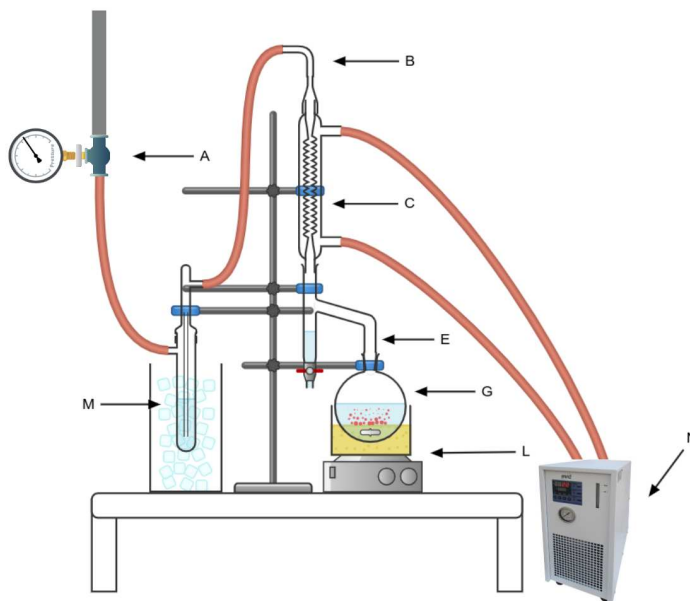
3.2.2 Experimental unit

The experimental unit used for the simultaneous polycondensation and ring-opening polymerization runs is composed of a heating and magnetic stirring plate (C-MAG HS 7, IKA), an oil bath, a reaction flask (100ml), a magnetic stirrer, a Dean-Stark trap (25ml), an elliptical condenser, a thermocryostatic bath, MQBTC99-2, Microquímica), a vacuum output, a vacuum trap on an ice bath and a vacuum pump, composed according to the Figure 3.2.1.

3.2.3 Enzymatic condensation and ring-opening polymerization

The polymerization processes were conducted in bulk conditions using an equimolar proportion of monomers. The reactions were catalyzed enzymatically at a concentration of 10% w/w (based on total monomer mass). For each reaction, 0.1 mol of monomers (17.42 g of DS, 9.01 g of BDO, and 23.8 g of GL or 11.4 g of CL) were weighed and added to the reaction medium, along with the respective enzyme amount. The enzyme was dried at 40 °C on a vacuum stove for 24 h for water removal before its addition

Figure 3.2.1: Experimental unit for simultaneous polycondensation and ring-opening polymerization.



(A) Vacuum pump (B) Vacuum connector (C) Elliptical shaped condenser (E) Dean-Stark trap (G) Round bottom flask with a magnetic stirrer (L) Heating magnetic (N) Thermocryostatic (M) Vacuum Trap in a ice bath.
Source: The author (2024).

to the flask with the reactants (Elias Guckert et al., 2022, 2023; Núñez; Muñoz-Guerra; Martínez De Ilarduya, 2021).

The reaction medium containing the reactants underwent three successive cycles of nitrogen gas (N_2) purge, followed by vacuum application. The system was then heated in an oil bath to 90 °C with magnetic stirring at 200 rpm. In addition, vacuum was applied to remove the polycondensation by-product (ethanol), while the condenser fluid (water) was maintained at 2.5 °C. The reaction was maintained under vacuum (-700mmHg) for each specified condition, as described on Table 3.2.1.

Each compositional structure was analyzed, including the synthesis of P(BS), P(GL), P(CL), P(BSCL), P(BS-GL), and P(BS-CL-GL). The reactions were carried out under the following temperature conditions for each polymerization system: 90 °C for 24 h; 90 °C for 4 h followed by 150 °C for 20 h; and 90 °C for 24 h.

The condensed mass of the by-product (ethanol) over time was collected for each reaction in the Dean-Stark trap. The reaction condition for the standardized PBS was conducted in triplicate to provide the experimental errors associated with the reaction system. The total mass of the flask with its contents was measured before and after the reaction to acquire the mass loss associated with ethanol condensation.

The experimental errors were estimated (Equation 3.2.1) for each reaction proportionally to its measured mass sampled over the time, and the mean mass loss of ethanol was distributed equally to the

Table 3.2.1: Reaction conditions.

	Monomers	Step 1		Step 2		Product
		Time (h)	Temperature (°C)	Time (h)	Temperature (°C)	
1	DS +BDO	4	90	-	-	P(BS)
2	CL	4	90	-	-	P(CL)
3	GL	4	90	-	-	P(GL)
4	BS + BDO + CL	4	90	-	-	P(BS-CL)
5	BS + BDO + GL	4	90	-	-	P(BS-GL)
6	BS + BDO + CL + GL	4	90	-	-	P(BS-CL-GL)
7	BS + BDO + CL	24	90	-	-	P(BS-CL)
8	BS + BDO + GL	24	90	-	-	P(BS-GL)
9	BS + BDO + CL + GL	24	90	-	-	P(BS-CL-GL)
10	DS +BDO	4	90	20	150	P(BS)
11	CL	4	90	20	150	P(CL)
12	GL	4	90	20	150	P(GL)
13	BS + BDO + CL	4	90	20	150	P(BS-CL)
14	BS + BDO + GL	4	90	20	150	P(BS-GL)
15	BS + BDO + CL + GL	4	90	20	150	P(BS-CL-GL)

Source: The author (2024).

ethanol collected masses. σ_{ref} and $\bar{m}_{\text{ref}}$ are the standard deviation and mean mass, respectively, of the collected condensate from the PBS triplicate reaction, while m_i is the mass of the condensate collected from the reaction system.

$$Error = \frac{\sigma_{\text{ref}}}{\bar{m}_{\text{ref}}} \frac{m_i}{\bar{m}_{\text{ref}}} \quad (3.2.1)$$

The reaction yield was calculated using Equation 3.2.2, where m_{pp} is the mass of precipitated polymer, m_{m} is the total mass of monomers and m_{se} is the stoichiometric mass of ethanol for the reaction.

$$Yield = \frac{m_{\text{pp}}}{m_{\text{m}} - m_{\text{se}}} \quad (3.2.2)$$

3.2.4 Purification

When the reaction was finished, the reaction medium was cooled until room temperature. Next, chloroform was added for polymer dissolution and enzyme separation. The polymer solution was stirred under 2000 rpm at 50 °C until full dissolution, using a water bath heated by a magnetic stirring heating plate

The mixture was then filtered for enzyme separation, and ice cold methanol was added to the dissolved polymer to allow the product precipitation. The mixture was then left overnight at -4 °C for complete precipitation and finally the polymer was separated by vacuum filtration and dried on a convection stove under 60 °C for 24 h.

3.2.5 Material characterization

3.2.5.1 Molar mass distributions and copolymer composition

Number (M_n) and weight average average molar mass (M_w), as well as the dispersity index ($\mathcal{D}$) (calculated as the ratio M_w/M_n) and molar mass distributions were measured by GPC. The equipment used was SHIMADZUL's LC-20AD, equipped with a RID-10A refractive index detector, a SIL-20A auto sampler, a SHODEX pre-column KF-G 4A (8 μm , 4.6 x 10 mm) followed by two SHODEX KF-405LHQ (3 μm , 4.6 x 150 mm) columns arranged in series.

Each sample was prepared by the dissolution of 20 mg of each polymer in 4 mL of chloroform and subsequent filtration with a 0.22 μm PTFE membrane, with pore size of 0.45 μm . All analyses were conducted under 40°C, with chloroform (HPLC grade), as eluent, and flow rate of 0.3 mL.min⁻¹. The molecular masses were determined based on a calibration curve prepared with polystyrene (with molecular masses ranging from 580 g.mol⁻¹ to 6.035x10⁶ g.mol⁻¹).

For validation purposes, the GPC analysis was compared to the subsequent H¹ NMR analysis, with the calculation of M_n according to the method detailed by Hou and Pearce (Hou; Pearce, 2021). Additionally, compositional distributions of the copolymers were investigated through the C¹³ and H¹ NMR. Sample preparation consisted of dissolving 5 mg of the polymer in 0.5 mL of deuterated chloroform.

All spectrophotometers analysis were conducted on a Bruker Avance 500 spectrometer operating at 500 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent peak 7.26 ppm for CDCl₃ as an internal reference. Data processing was performed using Mestrenova.

For each segment of the polymer, a monomer characteristic signal was detected, enabling the identification of copolymer composition. For clarity in the subsequent discussion, the following spectral assignments in H¹ NMR are noted:

- The peak at 2.6 ppm is characteristic of the succinate group within the PBS segment.
- The peak at 2.3 ppm is a characteristic peak for PCL.
- The peak at 3.5 ppm represents a terminal group.
- The peaks at 5.3 and 5.4 ppm correspond to the hydrogen atoms of PGL's unsaturated carbon bond.

Therefore, the peaks from NMR analysis were integrated and used to calculate the M_n for each sample. For this, a characteristic signal, isolated peak from other segments, was identified and integrated for each polymer or copolymer segment, and a terminal group was also identified and integrated.

Equation 3.2.3 details how the repetition number of each segment can be calculated, related to the terminal signal value, where: n_a and n_b are the repetition number on the polymer chain; a_a and a_b is the integral value; m_a and m_b are the molar mass of the molecule measured on NMR (since it is a hydrogen analysis, it can be translated to the number of hydrogen measured on each peak) on the peak “a” and “b”, respectively, where “a” and “b” can be any elected characteristic signal, in this case “a” is the polymer segment on analysis and “b” is the terminal bond (hence, n_b is generally 1) (Hou; Pearce, 2021).

$$n_a = \frac{a_a n_b m_b}{a_b m_a} \quad (3.2.3)$$

With these given values, and the understanding of each molar mass segment, it is possible to calculate the molar mass of each polymer and the fraction of each polymer segment on a copolymer distribution (Equation 3.2.4).

$$Mn = n_{PBS}M_{DS} + n_{PCL}M_{CL} + n_{PGL}M_{GL} + M_{Terminal} \quad (3.2.4)$$

3.3 Results and discussion

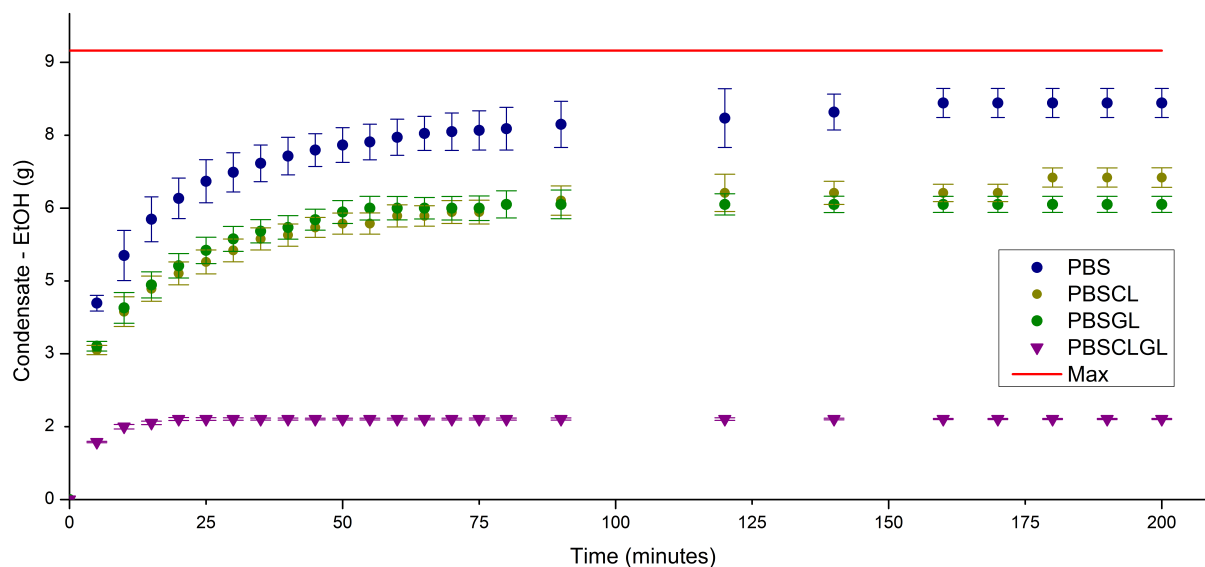
3.3.1 Copolymer synthesis

Reactions were conducted according to the initial planning detailed on Table 3.2.1, where the expected reactions for the homopolymers under 90°C for 24h were not completed due to solidification of the medium after 4 h.

The total amount of condensate collected was slightly lower during the copolymerization runs. An exception was the P(BS-CL-GL) reaction, which presented a significantly reduced condensate profile (Figure 3.3.1), potentially due to high ring-opening polymerization rate and subsequent reduced diffusivity associated with high reaction medium viscosity at low temperature.

Table 3.3.1 presents the yield and polycondensation conversion, measured through the weight of ethanol collected over the reaction time. In particular, the insertion of the macrolactones under the established conditions leads to a lower polycondensation rate, which, by hypothesis, could be caused by the following reasons. Firstly, the formation of PBS in homopolymerization decreases the diffusion rates and, therefore, the transesterification reaction between 1,4-butanediol and diethyl succinate becomes controlled by diffusion effects. In particular, enzymatic PBS polycondensation occurs in the solid state, due to the high melting temperature of PBS, when compared with the reaction medium temperature (Elias Guckert et al., 2023). Secondly, the higher reaction rates of ring-opening polymerization (ROP) of macrolactones leads to a high viscous medium. The increased viscosity restricts diffusion, consequently,

Figure 3.3.1: Condensate profile for each copolymer and PBS homopolymer runs.



Source: The author (2024).

lowering the rate of the transesterification reaction. Lastly, 1,4-butanediol can act as an initiator in the macrolactone ROP, generating bi-functional species which can subsequently react by transesterification reactions. In this case, it also presents the possibility of generating isolated and opened macrolactones molecules (Johnson; Kundu; Beers, 2011).

Polymer	Entry	Conversion (%) ^a	Yield (%) ^b	Polymer	Entry	Conversion (%) ^a	Yield (%) ^b
P(BS)	1	81.40	59.44	P(BS-CL)	4	66.63	46.04
	10	89.12	58.81		7	72.84	39.73
P(CL)	2	-*	67.03		13	79.69	38.73
	11	-*	66.18	P(BS-GL)	5	35.99	37.22
P(GL)	3	-*	73.77		8	47.99	27.59
	12	-*	72.43		14	78.83	34.44
P(BS-CL-GL)	6	12.85	13.22	P(BS-CL-GL)	6	12.85	13.22
	9	12.85	15.72		9	12.85	15.72
	15	20.57	6.33		15	20.57	6.33

Table 3.3.1: (a) Condensate collected referenced to the stoichiometric maximum for the reaction and (b) polymer yield. *Not applied

3.3.2 Molar mass

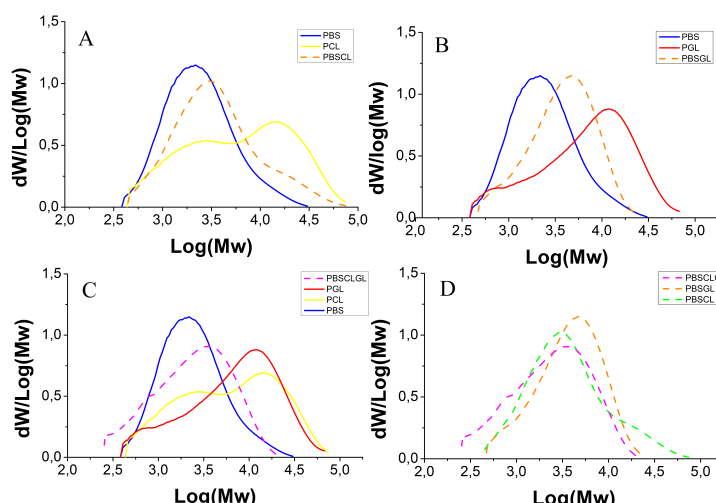
The molar masses of all synthesized polymers, measured by both GPC and NMR (for M_n), are summarized in Table 3.3.2. In general, copolymer samples exhibited intermediate average molar masses compared to their respective homopolymers, which aligns with the expected behavior for partial copolymerization between segments of different reactivity.

Table 3.3.2: Average number and weight molar masses: (a) Mn computed by NMR, (b) Mn and (c) Mw by GPC.

Polymer	Entry	Mn (Da) ^a	Mn (Da) ^b	Mw (Da) ^c	$\bar{D}$
PBS	1	1074	3563	5800	1.63
	10	1906	3196	4954	1.55
PCL	2	611	4767	10640	2.23
	11	2884	6236	18906	3.03
PGL	3	3050	6481	22728	3.51
	12	2554	7615	18688	2.45
P(BS-CL)	4	1614	3025	10567	3.49
	7	1260	2111	3397	1.61
	13	1441	3445	9006	2.61
P(BS-GL)	5	1106	2847	4784	1.68
	8	1068	2747	4481	1.61
	14	2314	3535	5997	1.70
P(BS-CL-GL)	6	1164	2713	4604	1.70
	9	1080	1955	4263	2.18
	15	1567	3683	6682	1.81

Source: The author (2024).

Figure 3.3.2: Molar mass distribution for homopolymers and copolymers under 4 h at 90°C.

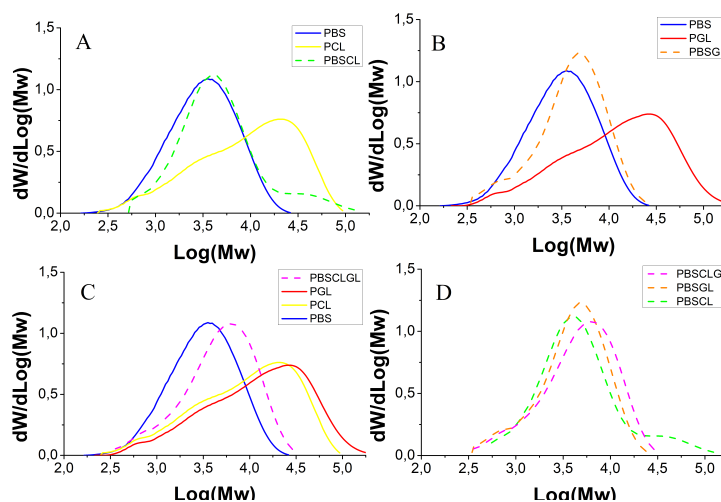


Source: The author (2025).

Figure 3.3.2 presents the molar mass distributions of the samples synthesized at 90 °C for 4 h. Under these conditions, most copolymers display monomodal distributions centered between those of PBS and the corresponding homopolymer of the comonomer (lactone). The main exception is the P(BS-co-CL) sample (Figure 3.3.2.A), which exhibited a bimodal profile — one fraction corresponding to PBS-like molecular weights and another overlapping with the PCL region. This bimodal distribution suggests

that PBS and PCL chains are produced independently, with limited or no copolymerization between the monomer segments under these conditions. Conversely, the P(BS-co-GL) sample displayed a single narrow distribution without bimodality, indicating the formation of a more homogeneous copolymer rather than a blend of homopolymers.

Figure 3.3.3: GPC's molar mass distribution for homopolymers and copolymers under 4 h at 90°C and 20 h at 150°C



Source: The author (2025).

The samples subjected to an additional thermal stage (90 °C for 4 h followed by 150 °C for 20 h) are shown in Figure 3.3.3. A similar profile was observed, with the P(BS-co-GL) sample maintaining a narrow (c.a. same value for $\bar{M}_w$; Table 3.3.2), and unimodal distribution and a slight shift toward higher molar masses compared to samples produced at lower temperature. The wider distribution of the copolymers, when compared to PBS, suggests that the elevated temperature (above the PBS melting point) promoted increased chain mobility and by-product removal, thereby enhancing chain growth and polymer segment diffusion.

Finally, Figure 3.3.5 compares the molar mass distributions of samples synthesized at 90 °C for 24 h. Under these conditions, the molar mass profiles of the copolymers varied only slightly from those observed in shorter reactions, particularly for the P(BS-co-GL) system. Prolonged reaction time did not significantly affect the molar mass distribution, implying that the molecular weight development is mainly governed by the initial prepolymerization step rather than the subsequent thermal stage. Reactions involving homopolymers could not be extended beyond 4 h due to solidification, which halted stirring and further polymer growth. In addition, the enzyme deactivation cannot be disregarded when the catalyst is submitted to high reaction times and temperatures. Immobilized lipases (N435) can present significant activity loss in polycondensation systems after 5 cycles of reuse at 90°C for 4h (Elias Guckert et al., 2022). The use of high temperatures (150°C) affected only the system with both lactones (CL and GL).

Figure 3.3.4: Molar mass distribution for copolymers synthesized at different temperatures and reaction times

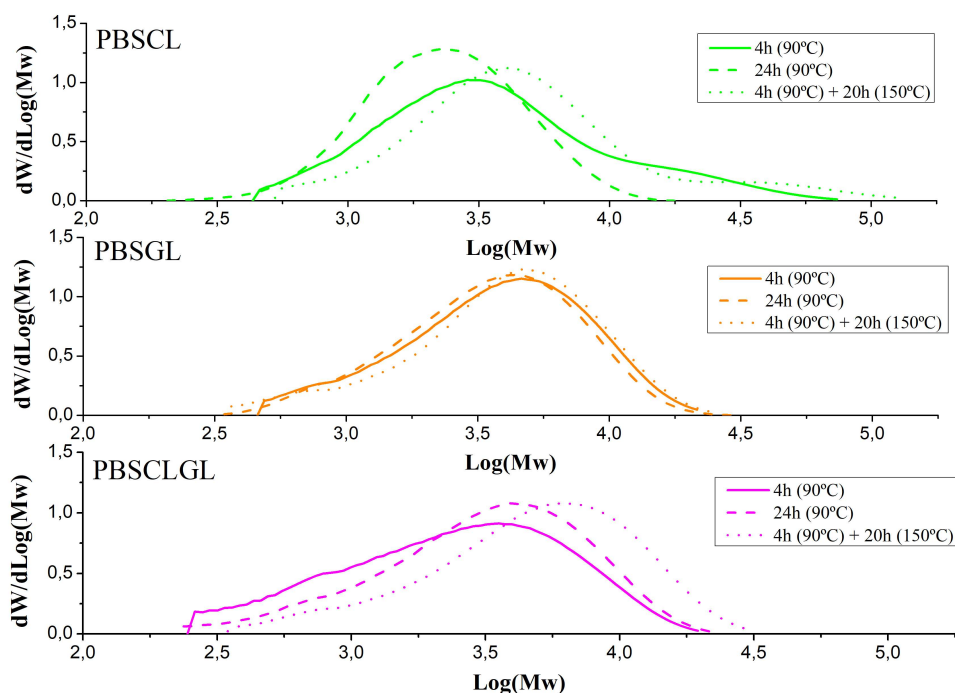


Figure 3.3.5: Molar mass distribution for copolymers synthesized at different temperatures and reaction times

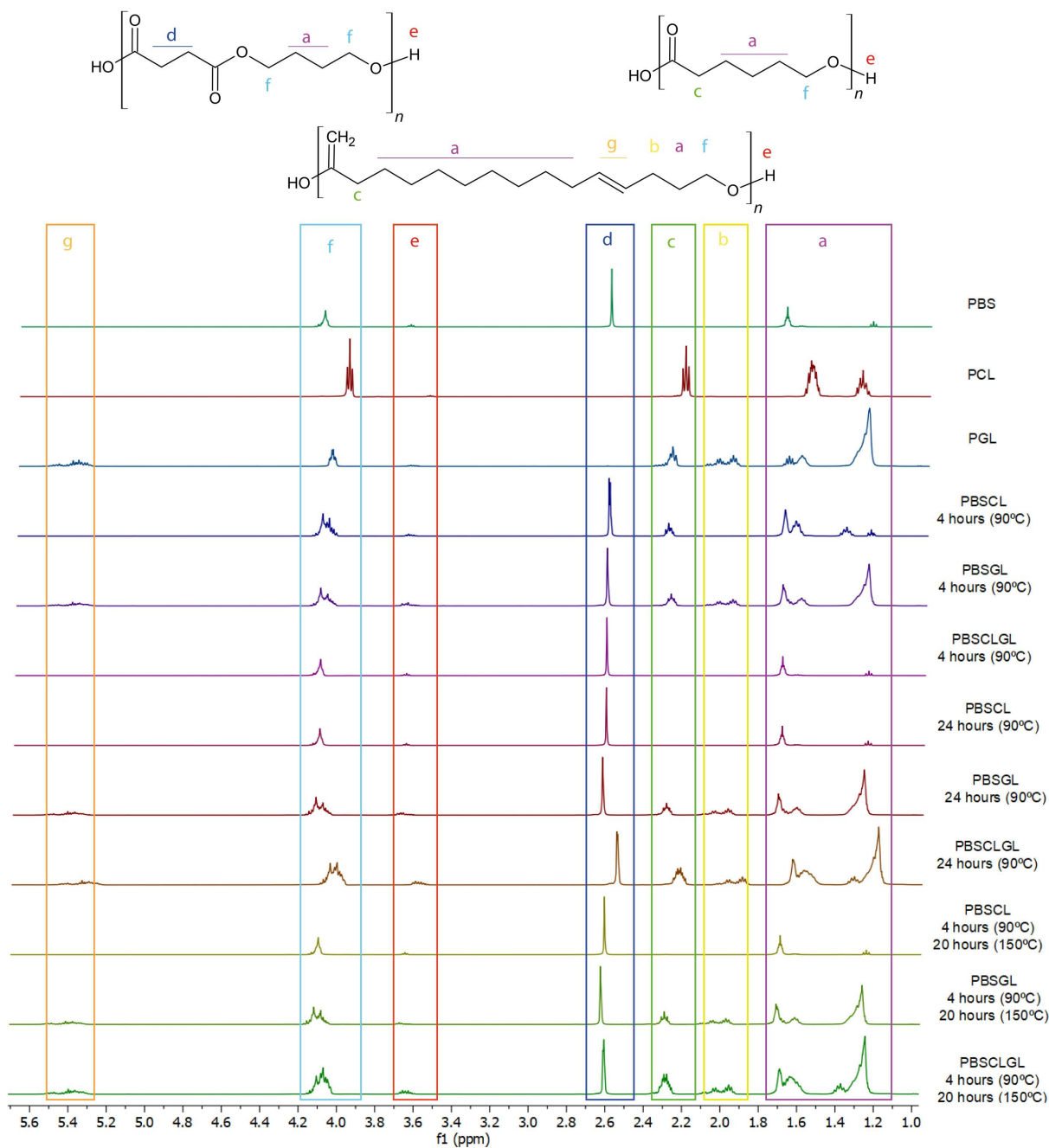
Source: The author (2024).

Overall, GPC and NMR analyses consistently indicate that the introduction of GL into the system promotes uniform chain extension and stable molar mass growth, while CL shows difficult incorporation. These findings support the subsequent NMR structural results, confirming that globalide acts as a more compatible and reactive comonomer under the investigated conditions.

3.3.3 Copolymer composition

^1H NMR analysis enabled the identification and quantification of the different monomeric segments incorporated into the synthesized polymers. Following Equation 3.2.3, the number of repeating units for each segment was calculated from their characteristic isolated signals relative to the terminal group. The main chemical shifts used were 2.6 ppm for the succinate group of PBS, 2.3 ppm for the CL segment, 3.5 ppm for chain-end protons, and 5.3–5.4 ppm for the unsaturated carbons of the GL unit.

Figure 3.3.6 shows the ^1H spectra of all samples, while Table 3.3.3 summarizes the calculated segmental compositions. Data indicate that the caprolactone signal at 2.3 ppm was only clearly detected under specific conditions. Among all the reactions, significant CL incorporation (31.3%) occurred only for the synthesis performed at 90 °C for 4 h. The same reaction followed by a second step at 150 °C for 20 h produced only 2 % CL content, suggesting instability or even cleavage of CL segments at high

Figure 3.3.6: ^1H NMR for all samples

Source: The author (2026).

temperature. The reaction conducted at 90 °C for 24 h exhibited no CL-related signals, indicating that prolonged reaction times favor PBS homopolymer formation and reduce CL incorporation.

In contrast, the P(BS-co-GL) samples displayed consistent signals for both BS and GL segments in all reaction conditions, with nearly equimolar segmental ratios ($\approx 50:50\%$). This uniform composition suggests a more stable and effective copolymerization between the succinate and macrolactone monomers. Likewise, the terpolymeric samples P(BS-co-CL-co-GL) exhibited regular BS and GL incorporation and minor CL content, except for the material obtained after 4 h at 90 °C, which contained

Table 3.3.3: Polymer composition through H^1 NMR according to the repetition unit on the sample.

Run	Sample	%BS	%CL	%GL
1	PBS	100	-	-
2	CL	-	100	-
3	GL	-	-	100
4	P(BS-CL)	69	31	-
5	P(BS-GL)	50	-	49
6	P(BS-CL-GL)	100	0	0
7	P(BS-CL)	100	-	-
8	P(BS-GL)	55	-	44
9	P(BS-CL-GL)	49	7	43
10	PBS	100	-	-
11	CL	-	100	-
12	GL	-	-	100
13	P(BS-CL)	98	2	-
14	P(BS-GL)	53	-	47
15	P(BS-CL-GL)	44	12	44

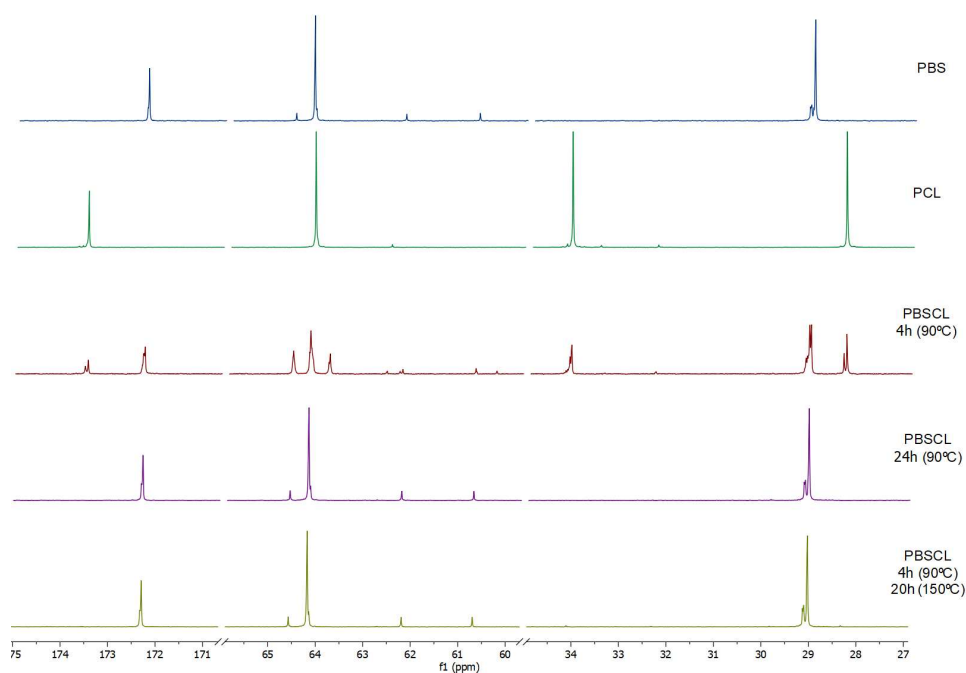
Source: The author (2026).

exclusively PBS domains. The latter reinforces that the presence of GL promotes copolymerization, whereas CL incorporation is both kinetically and thermodynamically limited under similar conditions.

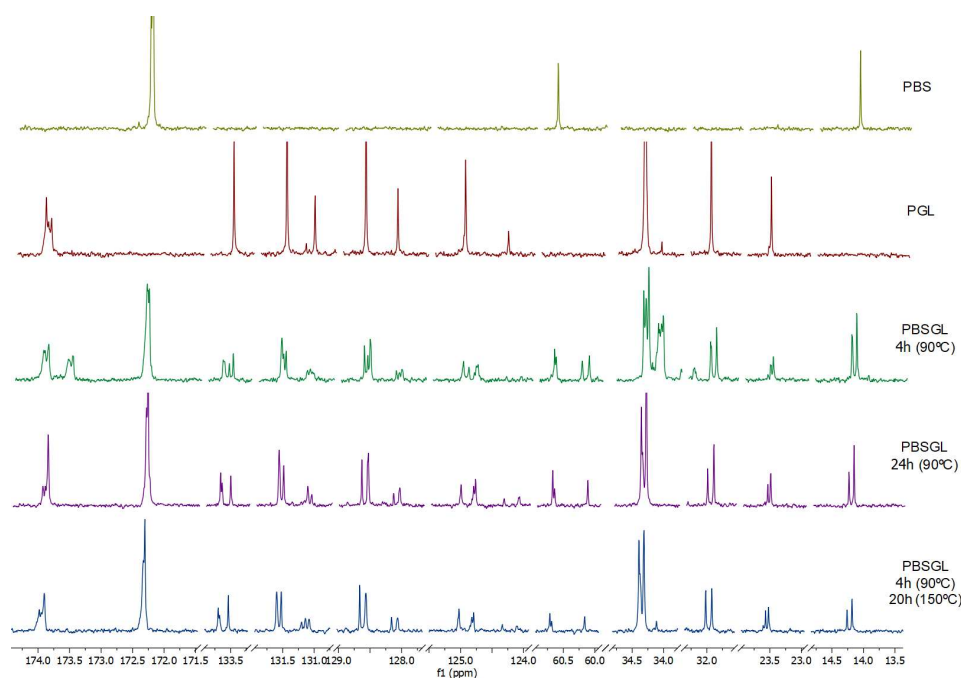
Structural confirmation of copolymerization was provided by C^{13} NMR analysis, which revealed multiplicities and peak distortions in comparison to the homopolymer spectra. For P(BS-co-CL) (Figure 3.3.7), copolymerization evidence was observed only in the sample synthesized at 90 °C for 4 h. The CL carbon signals at 28, 34, and 174 ppm were split into doublets, and the resonance at 64 ppm appeared as a triplet, with additional minor peaks between 60–63 ppm consistent with mixed BS–CL segments.

For P(BS-co-GL) (Figure 3.3.7), however, several characteristic changes were evident across all synthesis conditions, supporting the occurrence of a more homogeneous copolymerization. The BS-related peaks (14, 61, and 172 ppm) and GL peaks (24–35 ppm and 125–133 ppm) appeared broadened or split into multiplets, evidencing random BS–GL arrangements along the polymer backbone. A similar pattern was detected in the terpolymer P(BS-co-CL-co-GL) (Figures 3.3.9) where BS–GL copolymerization was predominant and CL incorporation remained limited.

Overall, both H^1 and C^{13} NMR analyses demonstrate that GL acts as a more reactive and compatible comonomer with PBS than CL under the investigated conditions. The higher copolymerization rates, in this case, is attributed to the structural flexibility and lower ring strain of the macrolactone, which favor ring-opening and subsequent chain growth, leading to random P(BS-co-GL) and P(BS-co-CL-co-GL) copolymers.

Figure 3.3.7: C^{13} NMR for the P(BS-co-CL) samples

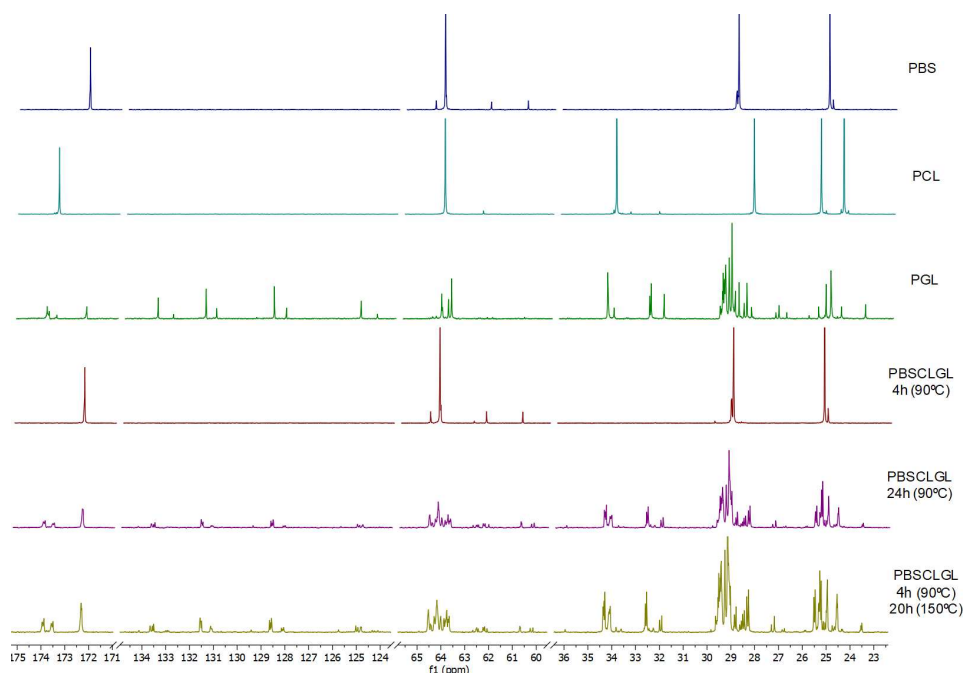
Source: The author (2026).

Figure 3.3.8: C^{13} NMR for the P(BS-co-GL) samples

Source: The author (2026).

3.4 Conclusion

This work has successfully demonstrated the feasibility of Simultaneous Ring-Opening and Condensation Polymerization (SROCP) for synthesizing PBS-based copolymers with ϵ -caprolactone (CL)

Figure 3.3.9: C^{13} NMR for the P(BS-co-CL-co-GL) samples

Source: The author (2026).

and globalide (GL) using immobilized lipase under mild enzymatic conditions.

Key findings reveal that GL exhibits superior reactivity and compatibility with PBS compared to CL across all tested conditions (90 °C for 4–24 h, with or without a 150 °C post-stage). GPC analyses showed monomodal, narrow distributions for P(BS-co-GL) samples, with intermediate molar masses confirming true copolymer formation, whereas P(BS-co-CL) often displayed bimodality indicative of homopolymer blends. Complementary H^1 and C^{13} NMR confirmed copolymerization: GL incorporation reached 50 mol% consistently, evidenced by multiplet distortions in characteristic carbon signals, while CL content remained marginal (≤ 12 mol%) and unstable at elevated temperatures.

These results highlight the mechanistic advantages of macrolactones like GL — lower ring strain and higher chain flexibility — which enable efficient hybrid propagation alongside PBS condensation, yielding random copolymers. In contrast, CL's higher ring strain and polarity mismatch limit its integration, favoring phase separation.

This enzymatic SROCP approach offers a sustainable alternative to metal-catalyzed methods, operating at lower temperatures with reduced energy demands and catalyst toxicity. Future optimization should focus on monomer ratios, use of alternative lipases, and scaling to enhance molar masses (≥ 10 kDa), as well as explore thermal/mechanical properties for bioplastic applications. Overall, these findings advance green polyester synthesis toward circular economy goals, particularly for PBS-GL systems as novel and bio-based materials.

Chapter 4

Chemical recycling of PBS by glycolysis

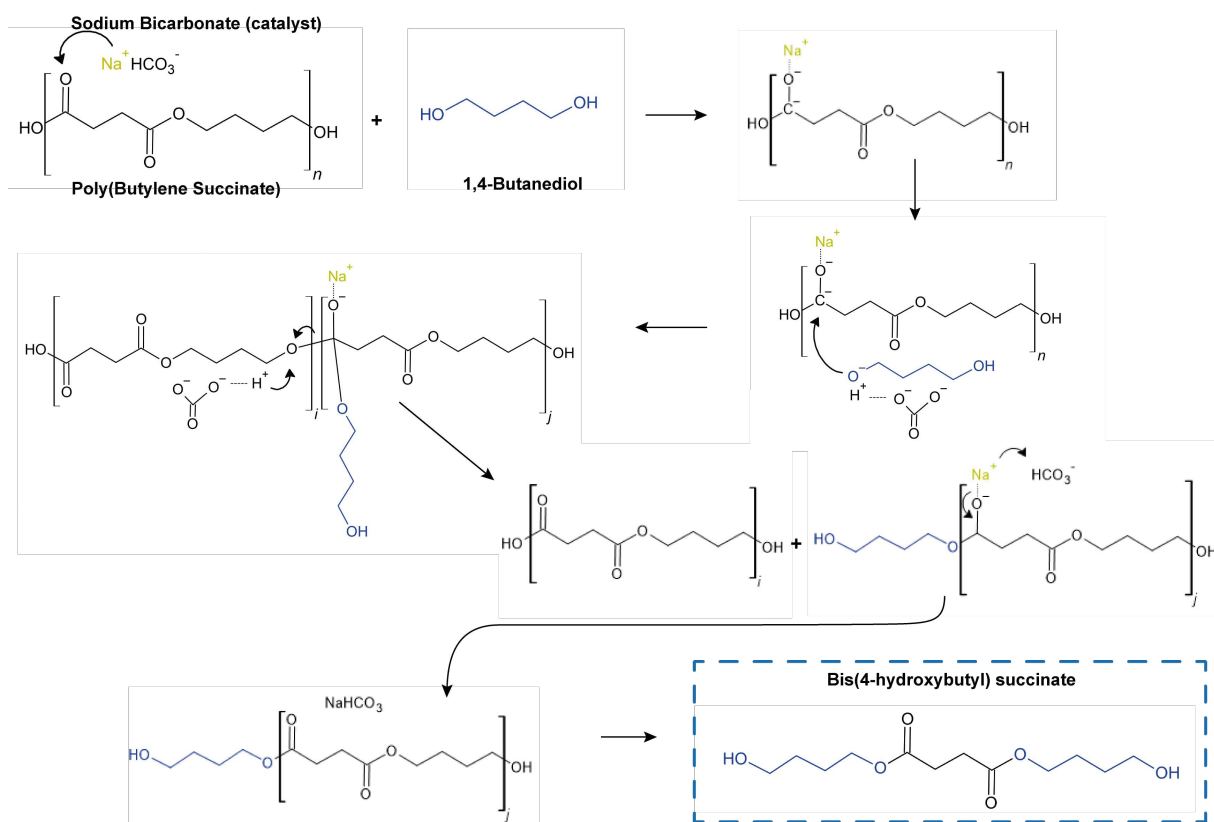
4.1 Introduction

Poly(butylene succinate) is widely recognized for its biodegradability, its potential for production from renewable monomers, and mechanical and thermal properties comparable to conventional polyolefins (Adamopoulou, 2012; Aliotta et al., 2022). Despite its widespread use, mechanical recycling often fails to preserve its properties due to chain scission (induced by hydrolysis reactions)(Zhang et al., 2024; Nomadolo et al., 2024; Resch-Fauster et al., 2017). Chemical recycling methods, such as glycolysis, offer an alternative route capable of depolymerizing PBS into its original monomers or oligomers, which can subsequently be repolymerized into materials of comparable quality. This recycling approach not only minimizes waste accumulation but also reduces the dependency on virgin feedstocks, enhancing the overall sustainability of PBS-based products (Adamopoulou, 2012; Merchan et al., 2022).

The glycolysis reaction involves the transesterification of ester bonds within the polyester backbone using glycols, causing a controlled polymer chain scission into a monomer for further waste valorization (upcycling). Typically, ethylene glycol is used; however, it can be performed with the use of several diols (e.g. 1,3-propanediol, 1,4-butanediol). This reaction has been mostly used on PET depolymerization technologies, hence the general use of ethylene glycol (as a monomer to PET), however, it is a potential technology for other heterogeneous polymers (Clark; Shaver, 2024; Darai et al., 2024). It can be performed without a catalyst, but it shows low yield and very high energy consumption, therefore, many catalyst systems have been analyzed, and the most established are zinc-based catalysts (Asueta et al., 2023; Chen et al., 2013; Darai et al., 2024).

As a PBS monomer, glycolysis in the presence of 1,4-butanediol can be a promising route, when the aim is to promote the PBS upcycling (Clark; Shaver, 2024; Darai et al., 2024). Key process variables such as temperature, reaction time, catalyst concentration, and BDO-to-polymer ratio are prone to have high effects on the glycolysis rate and product distribution.(Aguado et al., 2014) Figure 4.1.1 presents

Figure 4.1.1: PBS' glycolysis mechanism (Based on [(Van Hong Thien et al., 2024)])



Source: The author (2024).

the mechanism involved in the PBS' glycolysis reaction.

In particular, PBS depolymerization via glycolysis offers several advantages over other depolymerization routes, such as hydrolysis or methanolysis, which are the only alternatives consistently reported in the literature so far. The use of a high-boiling glycol, such as 1,4-BDO, enables operation at temperatures above the PBS melting point, improving polymer swelling and mass transfer and thus enhancing depolymerization efficiency. Glycolysis has also been identified as a promising industrial pathway for textile chemical recycling, a waste stream that remains difficult to process in current practices, and was projected to reach Technology Readiness Level (TRL) 9 by 2025 in a 2024 assessment. (Lanz et al., 2024)

Therefore, PBS beads in the molten state present higher swelling rates in the 1,4-BDO, which reduces the mass transfer limitations and enables higher glycolysis rates. In contrast, the swelling rate of PBS in water or methanol is very low, even at high temperatures. In comparison with glycolysis, the depolymerization through hydrolysis or methanolysis occurs predominantly at the beads surface, which increases the mass transfer resistance and results in lower reaction rates than glycolysis, as higher crystallinity inhibits the depolymerization reaction. (Merchan et al., 2022; Clark; Shaver, 2024)

Other process variables which affect glycolysis include the use of an additional solvent, such as

tetrahydrofuran, aniline, nitrobenzene, dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP), based on either the storage of the reaction products, enhancing the reaction kinetics or to improve the intermolecular interactions (Le et al., 2022; Kirshanov et al., 2023). However, the process generally involves the use of harmful material and the need for further separation and recovery processes (Abed-soltan, 2023; Kirshanov et al., 2023; Liu et al., 2018). The use of micro-wave heating provides fast heating and reaction conditions through irradiation (Achilias et al., 2010; Hirao; Nakatsuchi; Ohara, 2010; Shojaei; Abtahi; Najafi, 2020). Lastly, glycolysis reactions can be performed in the presence of catalysts with different specificities, such as metal-based, organocatalysts, metal-framework, liquid-ionic, deep eutectic solvents, salt catalysts, and many others. Particular attention is given to the use of sustainable catalysts, which can replace conventional metal-based systems and align with the green chemistry principles (Li et al., 2024; Sert; Yilmaz; Atalay, 2019; Chen et al., 2022; Wang et al., 2022; Najafi-Shoa et al., 2021; Song et al., 2014; Pham et al., 2024; Nilwanna et al., 2024).

This work addresses the broader implications of PBS glycolysis within the context of chemical recycling technologies, a topic that remains largely unexplored in the literature. A Design of Experiments (DOE) approach was employed to systematically investigate process variables—namely temperature, BDO-to-PBS repeat-unit molar ratio, and catalyst content—and identify their significant interactions on glycolysis yield. Statistical modeling combined with ANOVA provided quantitative understanding of individual and combined effects, enabling optimization of depolymerization yield and generating valuable data for future scale-up and industrial integration. Additionally, the work prioritizes the use of elements of a lower cost and environmental impact, thus, a cheap metal salt, in this case sodium carbonate (NaHCO_3), can be used as a catalyst with prominent mild impact. (Van Hong Thien et al., 2024; Zahova et al., 2023) In addition, the kinetic behaviour of PBS glycolysis reaction was also investigated to address the characteristic time of the depolymerization reaction.

Repolymerization reactions were performed and the products thereof were also analyzed, and compared with those obtained from virgin monomers under the same conditions using both enzyme, Novozym 435, and metal-based catalyst ($\text{Ti}(\text{BuO})_4$). By combining mechanistic and statistical approaches, as well as the repolymerization perspective, this study bridges the conceptual gap between polymer synthesis and chemical recycling. It demonstrates that the same transesterification principles enabling polyester formation can be reversed in a controlled manner, reinforcing the idea that molecular design and process engineering must be co-developed to achieve a truly circular polymer economy.

4.2 Material and methods

4.2.1 Materials

Diethyl succinate (DS, purity 99%), 1,4-butanediol (BDO, purity 99%), Titanium(IV) butoxide ($\text{Ti}(\text{BuO})_4$, 97%), and deuterated chloroform anhydrous (99.8 atom 2%D, with purity 99%) were purchased from Sigma-Aldrich. Poly(butylene succinate) ellipsoidal pellets (5x3x1 mm, Mw = 190kDa, $\bar{D} = 2.74$) were acquired from Mitsubishi Chemicals (kindly donated by Prof. Silvia Bettini from UFSCar). Sodium bicarbonate (NaHCO_3) was acquired from Neon. Nitrogen (N_2) was acquired from Air Liquide. Novozym 435, an immobilized lipase from *Candida Antarctica*, was kindly donated by Novozymes. Chloroform (minimum content of 99.8%) was acquired from Dinâmica. Chloroform (HPLC grade, 99.8% purity) was acquired from J.T.Baker. All components were used as received without further purification or modification.

4.2.2 PBS glycolysis

The glycolysis reactions were carried out in a 100 mL reaction flasks equipped with a magnetic stirring bar and stirred at 2000 rpm on a heating-magnetic stirring plate (C-MAG HS 7, IKA) placed in a sand bath, with temperature monitored using the equipment's ETS-D5 contact thermometer on a BDO-filled glass tube embedded in the sand parallel to the reaction flask to provide a more accurate measurement of the heating conditions. The PBS samples (5 g) were placed in the reaction flask with the respective amount of 1,4-butanediol and the salt sodium bicarbonate (NaHCO_3) as catalyst, and conducted at the respective temperature for 4 h. At the beginning of the reactions, the reaction medium was purged under a nitrogen flow for 1 min (Van Hong Thien et al., 2024; Zahova et al., 2023).

A sequential experimental design was defined, starting with a fractional factorial design with 3 factors at 2 levels and a central point (performed in triplicate for error evaluation), followed by the inclusion of axial points using a Central Composite Rotable (CCR) Design. The selected controlled variables were temperature, BDO/PBS ratio and catalyst/PBS ratio (Table 4.2.1 and Figure 4.2.1). The specific conditions were selected based on general use on most PET depolymerization articles, considering a milder condition (Chen et al., 2013; Al-Sabagh et al., 2014; Chen et al., 2013; Chen; Chen; Cheng, 1999; Asueta et al., 2023).

In addition, the central point was selected for the following additional runs: 1) a 10x scaleup carried out in a 450 mL stainless steel high pressure reactor, Metalquim model RTA-B-450-CM (Figure 4.2.2), equipped with temperature control, a mechanical stirrer (at 3000 rpm), and improved inertization compared with the previously used round bottom flask; 2) a preliminary kinetic evaluation based on destructive depolymerization experiments conducted for 0.5 h, 1 h, 2 h, 3 h and 4 h (whereas the 4 h run

Table 4.2.1: Glycolysis' reaction conditions for PBS depolymerization. ^a Relative to PBS repetition unit. ^b 10x up-scaled.

Run	Duration (h)	Temperature (°C)	BDO/pol (mol/mol) ^a	Cat/pol (%mol/mol) ^a
Full 2 ³ factorial experiments				
1	4	120	6	5
2	4	120	2	5
3	4	120	6	1
4	4	120	2	1
5	4	180	6	5
6	4	180	2	5
7	4	180	6	1
8	4	180	2	1
9 (C)	4	150	4	3
10 (C)	4	150	4	3
11 (C)	4	150	4	3
Central Composite Rotable experiments (CCR)				
12	4	109.41	4	3
13	4	190.59	4	3
14	4	150	1.29	3
15	4	150	6.71	3
16	4	150	4	0.29
17	4	150	4	5.71
Additional experiments				
18 ^b	4	150	4	5
19	0.5	150	4	5
20	1	150	4	5
21	2	150	4	5
22	3	150	4	5
23	4	150	4	0

Source: The author (2025).

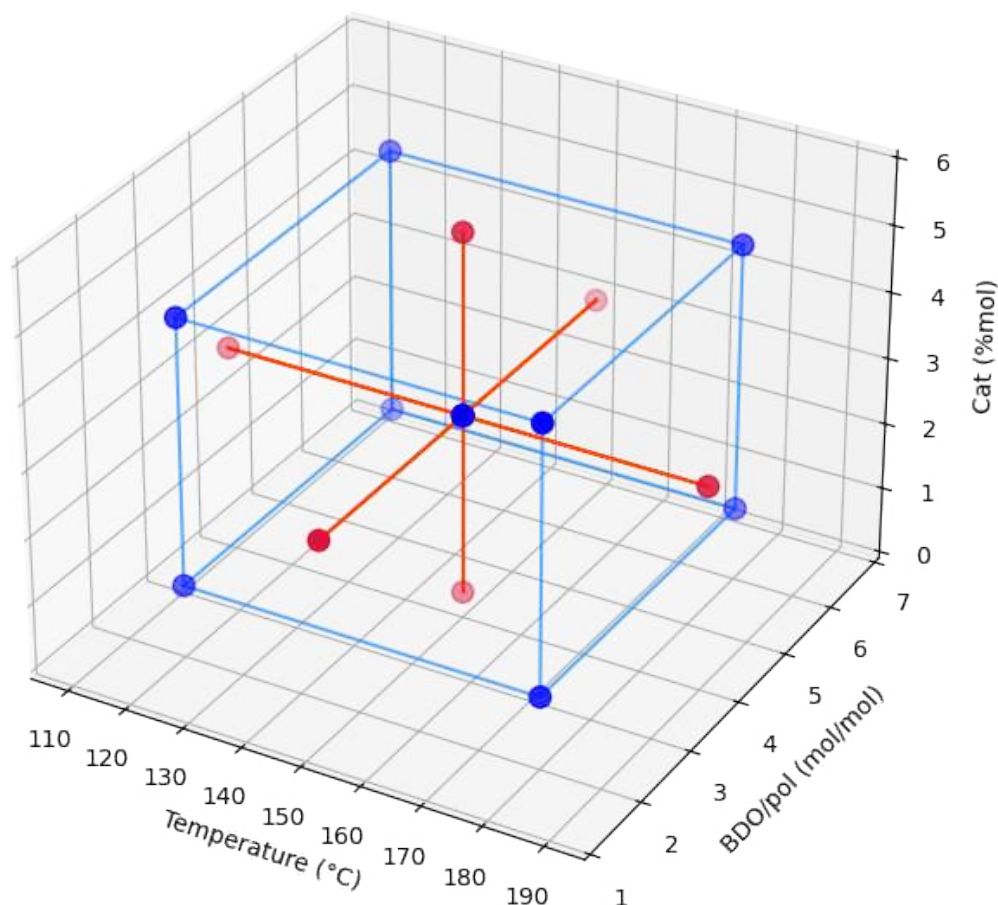
is the DOE's central point); and 3) A glycolysis reaction performed in the absence of catalyst.

4.2.3 Re-polymerization

Based on the depolymerization design results, the central point was selected to perform the repolymerization experiments. The reactions were carried out in the experimental setup shown in Figure 3.2.1, using the same reactor in which depolymerization had been performed (one-pot repolymerization), except for the addition of DS to compensate for the excess BDO used in the depolymerization reaction (Table 4.2.1).

A metal-catalyzed polycondensation was then conducted to evaluate the suitability of the glycolysis product for the synthesis of high-molar-mass PBS. The polymerization was catalyzed by $\text{Ti}(\text{BuO})_4$ at 190°C for 1 h under nitrogen flow (cm³/s), followed by 6 h under vacuum (-700 mmHg). In the repolymerization procedure, DS was added in the repolymerization assays to compensate for the excess BDO introduced during depolymerization (Table 4.2.2). For comparison, a virgin-monomer polymerization

Figure 4.2.1: Graphic representation of the DOE conditions analyzed in this study



Source: The author (2025).

was also carried out under the same conditions, serving as a reference for the use of the depolymerization product (Adamopoulou, 2012).

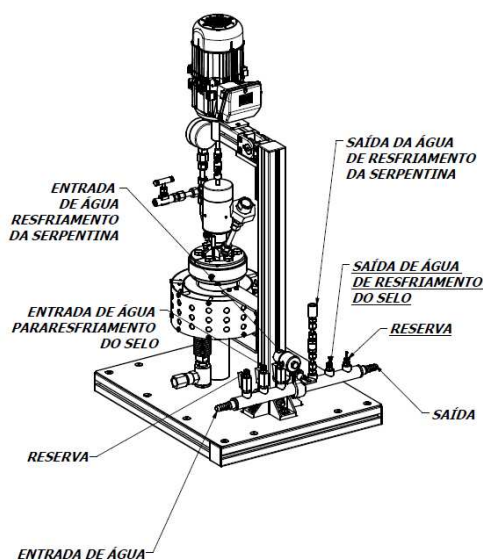
Table 4.2.2: Repolymerization reaction conditions: a) Blank metal-catalyzed polycondensation b) Blank enzyme-catalyzed polycondensation c) BDO amount used on the depolymerization reaction.

Run	BDO (g)	DS (g)	Catalyst (g)	Time under N ₂ (h)	Time under vacuum (h)	Temperature (°C)
1 ^a	9.02	17.42	0.026	1	6	190
2 ^a	10.47 ^c	20.23	0.031	1	6	190
3 ^b	9.02	17.42	3.289	-	4	90
4 ^b	10.47 ^c	20.23	3.570	-	4	90

Source: The author (2026).

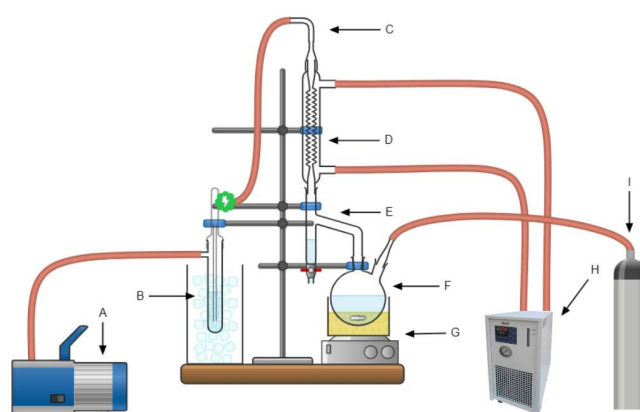
Additionally, an enzymatic repolymerization was carried out directly under vacuum for 4 h, until the medium solidified and could no longer be stirred. It was conducted at a 1:1 BDO:DS molar ratio with

Figure 4.2.2: 450 mL stainless steel high pressure reactor, Metalquim model RTA-B-450-CM.



Source: Metalquim.

Figure 4.2.3: Experimental unit for polycondensation.

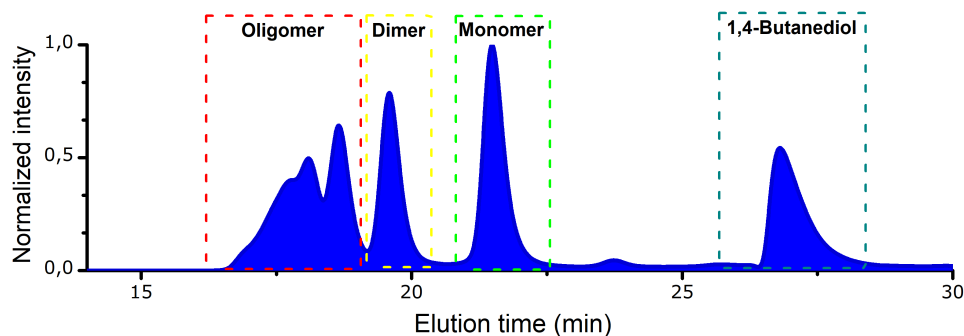


(A) Vacuum pump (B) Vacuum Trap in an ice bath (C) Vacuum connector (D) Elliptical shaped condenser (E) Dean-Stark trap (F) Round bottom flask with a magnetic stirrer (G) Heating magnetic (H) Thermocryostatic (I) N₂ cylinder.

Source: The author (2026).

10 wt% Novozym 435 (N435) as the catalyst. The same experimental setup (Figure 4.2.3) was used, except that nitrogen flow was not applied. The reaction conditions for both virgin polymerization and

Figure 4.2.4: GPC compound identification for monomer, dimer and oligomer on low molar mass column.



Source: The author (2026).

repolymerization are also summarized in Table 4.2.2 and all four reactions were conducted in bulk.

4.2.4 Characterization

4.2.4.1 Molar Mass

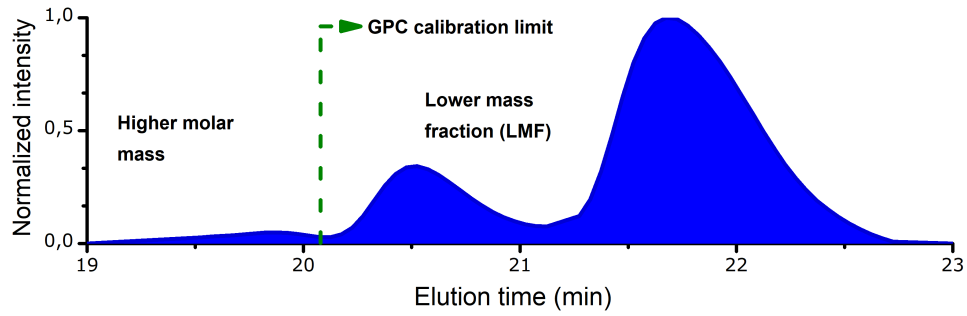
The number-average (M_n) and weight-average (M_w), molar masses, the polydispersity index ($\mathcal{D}$) (calculated as the M_w/M_n ratio) and the molar mass distributions were measured by Gel Permeation Chromatography (GPC). The equipment used was SHIMADZU's LC-20AD, equipped with a RID-10A refractive index detector, a SIL-20A auto sampler, a PL gelMiniMIX pre-column (5 μm , 50 x 4 mm) followed by two PL gelMiniMIX columns (5 μm , 250 x 4.6 mm) arranged in series.

Each sample was prepared by the dissolution of 40 mg in 2 mL of chloroform and subsequent filtration with a 0.22 μm PTFE membrane, with pore size of 0.45 μm . All analyses were conducted under 40 $^{\circ}\text{C}$, using chloroform (HPLC grade) as eluent, at a flow rate of 0.3 $\text{mL}\cdot\text{min}^{-1}$. The molar masses were measured based on a calibration curve prepared with polystyrene (with molar masses ranging from 580 $\text{g}\cdot\text{mol}^{-1}$ to $9.225\cdot 10^6$ $\text{g}\cdot\text{mol}^{-1}$).

Using the same methodology, the samples were analyzed on a Styragel HR 0.5 (50 $\text{\AA}$, 5 μm , 7.8 mm X 300 mm) single column. This column is able to measure low molar mass molecules, designed for molar mass separation in the 0–1000 Da range, according to the manufacturer specifications. The column was calibrated with the use of several PA reactants (1,4-butanediol, stearic acid, Bis(2-hydroxyethyl) terephthalate, dimethyl-itaconate, linseed oil and polystyrene (500, 1000, and 2000 g/mol), providing data for monomer, dimer and oligomer identification and their respective mass fraction measurements on each sample (Figure 4.2.4), as detailed on equations 4.2.1, 4.2.2, and 4.2.3.

$$\text{Monomer}(m/m) = \frac{A_{\text{mon}}}{A_{\text{mon}} + A_{\text{dim}} + A_{\text{olig}}} \quad (4.2.1)$$

Figure 4.2.5: Definition for GPC LMF analysis on high molar mass column.



Source: The author (2026).

$$Dimer(m/m) = \frac{A_{dim}}{A_{mon} + A_{dim} + A_{olig}} \quad (4.2.2)$$

$$Oligomer(m/m) = \frac{A_{olig}}{A_{mon} + A_{dim} + A_{olig}} \quad (4.2.3)$$

In addition to absolute molecular weight determination, the depolymerization extent was also evaluated through the fraction of material eluting below the calibration limit of the polystyrene standards (Figure 4.2.5). This parameter, defined as the Lower Mass Fraction (LMF), represents the cumulative contribution of oligomers and low-molecular-weight species and provides an integrated metric of structural depolymerization. Although less specific than monomer quantification, the LMF captures the global shift of the molecular weight distribution and is therefore suitable for comparative and statistical analyses as a response variable across experimental conditions.

In addition to average molar mass measurement, the depolymerization degree was also evaluated based on the fraction of material eluting below the calibration limit of the polystyrene standards (4.2.5). This parameter, defined in this work as the Lower Mass Fraction (LMF, equation 4.2.4, where A_{LMF} and A_{HMM} are the respective GPC areas of low- and high-molar mass fractions), represents the cumulative contribution of oligomers and low-molar mass species and provides an integrated metric of structural depolymerization. It is measured through a partial integration until the GPC calibration limit and a second integration for the remaining detected signal as a molar mass lower than 500Da (close to the monomer). The value used is the percentage to the total integral given by the LCSolution's GPC postrun software. Although less specific than monomer quantification, the LMF captures the overall shift of the molar mass distribution toward the lower molar masses and is therefore suitable for comparative and statistical analyses as a response variable across experimental conditions.

$$LMF(m/m) = \frac{A_{LMF}}{A_{LMF} + A_{HMM}} \quad (4.2.4)$$

4.2.5 DOE-Based Statistical Model

The experimental results from the proposed design of experiments were analyzed using statistical models to represent the glycolysis process. Statistical models were developed for the monomer fraction and LMF responses using linear models, as shown in Equation 4.2.5, where Y is the predicted response, α represents the regression coefficients, Z denotes the factor (predictor) values, n is the number of factors, and i is the number of interaction terms included in the model. The model coefficients were estimated using the Ordinary Least Squares (OLS) objective function, followed by the subsequent construction of response surface plots following Equation 4.2.5. (Fávero, 2017; Box; Hunter; Hunter, 2005).

$$Y(\alpha, Z) = \alpha_0 + \sum_{k=1}^n \alpha_k Z_k + \sum_{1 \leq j < k} \alpha_{jk} Z_j Z_k + \sum_{k=1}^n \alpha_{kk} Z_k^2 \quad (4.2.5)$$

Two response variables were therefore considered in parallel: (i) the monomer fraction, obtained from low-molar-mass GPC analysis, and (ii) the LMF, derived from the integral of the molar mass distribution below the calibration threshold. While the monomer, and dimer fractions provide high-resolution information on depolymerization products, the LMF offers a robust and instrument-independent descriptor of overall chain scission. Both responses were analyzed under the same experimental design and statistical framework to assess consistency and robustness of the identified effects.

With the model defined, a parity plot comparing experimental and predicted monomer values, together with their corresponding residuals, was employed for validation purposes. Model accuracy was quantified through the Mean Absolute Error (MAE) and the Relative Mean Absolute Error (RMAE), while model reliability was assessed using the OLS-derived effects, standard errors, and confidence intervals. The experimental design was further evaluated using a Type II ANOVA to determine the statistical significance of each variable and interaction based on the associated p-values (Fávero, 2017; Box; Hunter; Hunter, 2005)

Additional diagnostic tests were performed to verify model adequacy: the Omnibus and Jarque–Bera tests to assess the normality of residuals; skewness and kurtosis coefficients to describe residual distribution; the Durbin–Watson statistic to check for autocorrelation; and the condition number (Cond. No.) to examine multicollinearity in the regression matrix. Those tests confirm normality and possible false positives (Fávero, 2017; Box; Hunter; Hunter, 2005) All analyses were performed in Statistica and Python using statsmodels (OLS and ANOVA) and SciPy (residual diagnostics).

4.3 Results and discussion

4.3.1 PBS glycolysis

The reactions were conducted according to the design of experiments (Table 4.2.1). During each respective reaction, a given characteristic appearance of the mixture was observed with different seeming viscosity, due to rigidity and visual flow, proportional to the intensity of each variable considered in the experimental planning. The analysis presented in the following sections shows promising results toward obtaining depolymerization products suitable for recycling the original material.

Compared to PBS hydrolysis processes (Zheng et al., 2024), the present glycolysis reactions showed lower reaction time and reactant use, based on the central point (Table 4.2.1), reaching around 6-12 times lower reactant consumption, on a molar basis. In particular, PBS hydrolysis used a ratio of water of 98.8 mol/mol and succinic acid (catalyst) and 2.5 mol/mol, respectively, related to the PBS repeat-unit at 150°C for 5h, reaching up to 79.0 % yield of succinic acid for 50 g of PBS.

In another work, a metal-catalysed ($\text{Zn}(\text{HMDS})_2$) methanolysis process was carried out for PBS depolymerization, reaching a regular yield of monomers (DS and 1,4-BDO) under lower temperatures than those applied in this study (Yang et al., 2022b). In addition, the required amount of methanol was four times higher than the BDO amount used in this study, based on the central point (Table 1). And, this process presented an extensive use of a co-solvent (dichloromethane), comparable with the methanol amount used in the reactor (same volume). This investigation was run at 50°C for 34h, using 3g of PBS and the ratios of methanol, dichloromethane and catalyst were, respectively, 16.89 mol/mol, 5.08 mol/mol and 2%mol/mol, related to the PBS repeat-unit, reaching a yield of 77% of dimethyl succinate.

4.3.2 Glycolysis product characterization

4.3.2.1 Average Molar Mass and Monomer Fraction

The average molar masses (M_w and M_n), as well as the monomer and dimer fractions and LMF, were measured for each sample in the experimental planning, providing enough data to improve understanding of the feasibility of this reaction and to enable statistical analysis of controlled variables. Table 4.3.1 presents each value for M_n and M_w measured on GPC (based on the higher molar mass fraction), the corresponding LMF measured in the high molar mass GPC column analysis, and the fractions of monomer and dimers (based on measures in the low molar mass GPC column).

Furthermore, besides the standard DOE conditions, a simple kinetic study was performed at the central point to evaluate the process behavior over time using a five-points destructive kinetic approach. Figure 4.3.1 shows the combined monomer and dimer content and LMF in the depolymerized sample

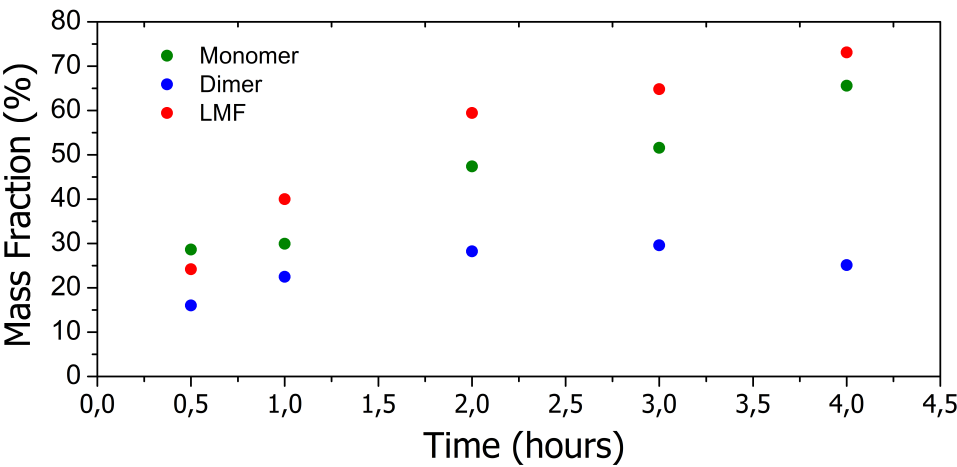
Table 4.3.1: GPC results for Mw, Mn values and LMF for the experimental design. (Commercial-grade PBS: Mw = 190kDa, Đ = 2.74).^a Relative to PBS repetition unit. ^b 10x up-scaled.

Run	Time (h)	Temp (°C)	BDO/pol ^a	Cat/pol (%) ^a	Mw (Da)	Đ	%LMF	%Monomer	%Dimer
Full 2 ³ factorial experiments									
1	4	120	6	5	996	1.2	55.3	28,3	54.1
2	4	120	2	5	856	1.2	48.7	21.5	37.3
3	4	120	6	1	972	1.6	35.6	20.9	27.4
4	4	120	2	1	1931	1.8	14.2	13.0	12.2
5	4	180	6	5	633	1.0	87.6	19.1	63.2
6	4	180	2	5	758	1.4	55	29.1	49.4
7	4	180	6	1	647	1.1	84.3	22.4	68.3
8	4	180	2	1	625	1.2	61.8	29.0	48.6
9	4	150	4	3	-	-	63.21	26.3	59.9
10	4	150	4	3	-	-	73.1	26.0	65.1
11	4	150	4	3	-	-	74.8	25.1	65.6
Central Composite Rotable experiments (CCR)									
12	4	109.4	4	3	190762	2.7	0	0,0	0
13	4	190.6	4	3	-	-	71.3	25.51	67.9
14	4	150	1.3	3	658	519	44.6	26.1	34.1
15	4	150	6.7	3	-	-	77.3	24.0	61.7
16	4	150	4	0.3	892	1.3	41.8	24.4	33.5
17	4	150	4	5.7	615	1.2	70.2	25.3	64.7
Additional experiments									
18 ^b	4	150	4	3	845	1.4	56.9	27.7	52.8
19	0.5	150	4	3	1315	1.6	24.2	16.0	28.6
20	1	150	4	3	998	1.4	40.0	22.5	29.9
21	2	150	4	3	606	1.2	59.4	28.2	47.4
22	3	150	4	3	-	-	64.8	29.6	51.6
23	4	150	4	0	1822	1.9	16.4	14.2	17.3

Source: The author (2026).

over time under the central condition.

Figure 4.3.1: Depolymerization kinetics for the central point on the DOE.



Source: The author (2026).

A non-catalyzed reaction was performed under the central point condition. This reaction presented M_w of 1,822 Da and $\bar{D}$ of 1.93, for the higher molar fraction, and a LMF of 16.43%. Within this LMF, a monomer content of 17.33% from the total sample was measured using the low-molar-mass GPC column. In particular, the occurrence of non-catalyzed glycolysis can be explained by two main reasons. Firstly, the aliphatic ester bonds present in PBS are more easily breakable, which makes the glycolysis reaction prone to depolymerization, even without a catalyst

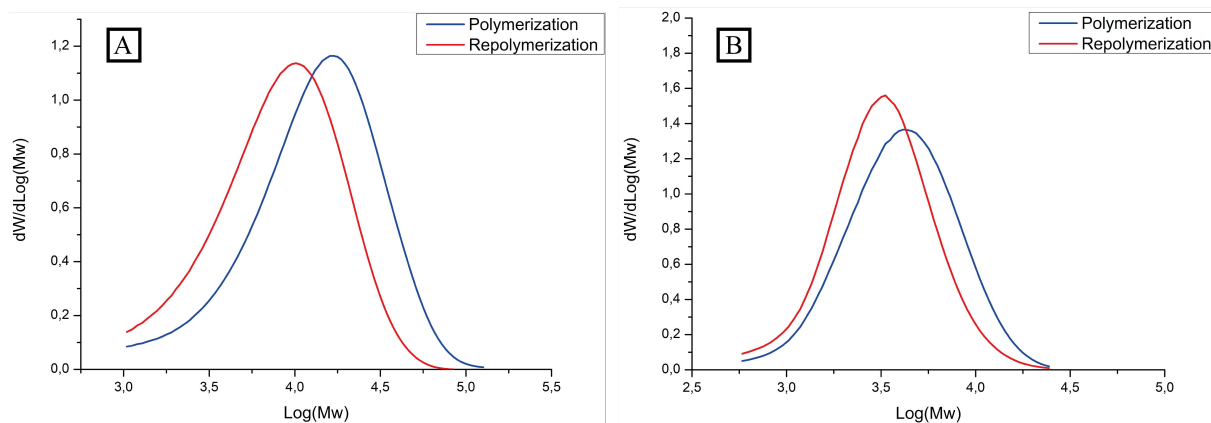
The commercial polymer sample does not have defined intentionally added substances (IAS), which may include residual catalysts (typically used during the polycondensation reaction) that can also induce a depolymerization under the given conditions. In addition, temperatures above the PBS melting temperature improves the PBS swelling in 1,4-BDO and increases the polymer chain segmental mobility, which also improves the glycol diffusion to the ester bounds.(Gabrič et al., 2025; Silva et al., 2018)

Finally, the upscale reaction (Run 18 in Table 4.3.1), carried out at 10-fold higher scale, resulted in only a slight decrease in monomer yield, illustrating the potential for transferring this process toward industrially relevant conditions. However, this result also highlights that scale-up is not a simple matter of increasing reactor volume, since additional variables such as heat transfer and molecular diffusion become more pronounced. In larger volumes, careful reactor and process design are required to achieve a temperature and concentration profile as close as possible to homogeneity.

4.3.3 Re-polymerization

In the metal-catalyzed system, repolymerization of the glycolysis products under the central point conditions (Table 4.2.1) demonstrated the reintroduction of oligomeric PBS obtained from depolymerization into a polycondensation step, yielding materials with relevant molar masses although the full recovery of the original high M_w was not achieved. The weight-average molar mass decreased from 17,788 Da in the polymerization from virgin monomers to 10,835 Da after repolymerization, with a similar polydispersity of 2.25 to 1.93, respectively. This behavior is reflected in the GPC molar mass distribution. Figure 4.3.2.A shows the shift between metal-catalyzed polymerization and repolymerization curves. This result is consistent with the kinetic profile of the system (Figure 4.3.3). In particular, when polycondensation was performed using DS and BDO (virgin monomers), ethanol was fully removed during the first step in the presence of nitrogen flow, indicating the full conversion of DS and BDO at 20 min. In the second step, the presence of a metallic catalyst improved the transesterification between the hydroxybutyl end groups along the polymer chains. Transesterification reaction between terminal hydroxyl groups is expected in polycondensation systems upon addition of a metallic catalyst. In addition, the applied reaction conditions (60 mmHg and 190°C) allowed the removal of 1,4-BDO, which explains the condensate mass above the ethanol stoichiometric amount. This reaction was used as a blank test and

Figure 4.3.2: Weight fraction molar mass distributions. A) metal-catalyzed and B) enzyme-catalyzed polymerization and repolymerization.



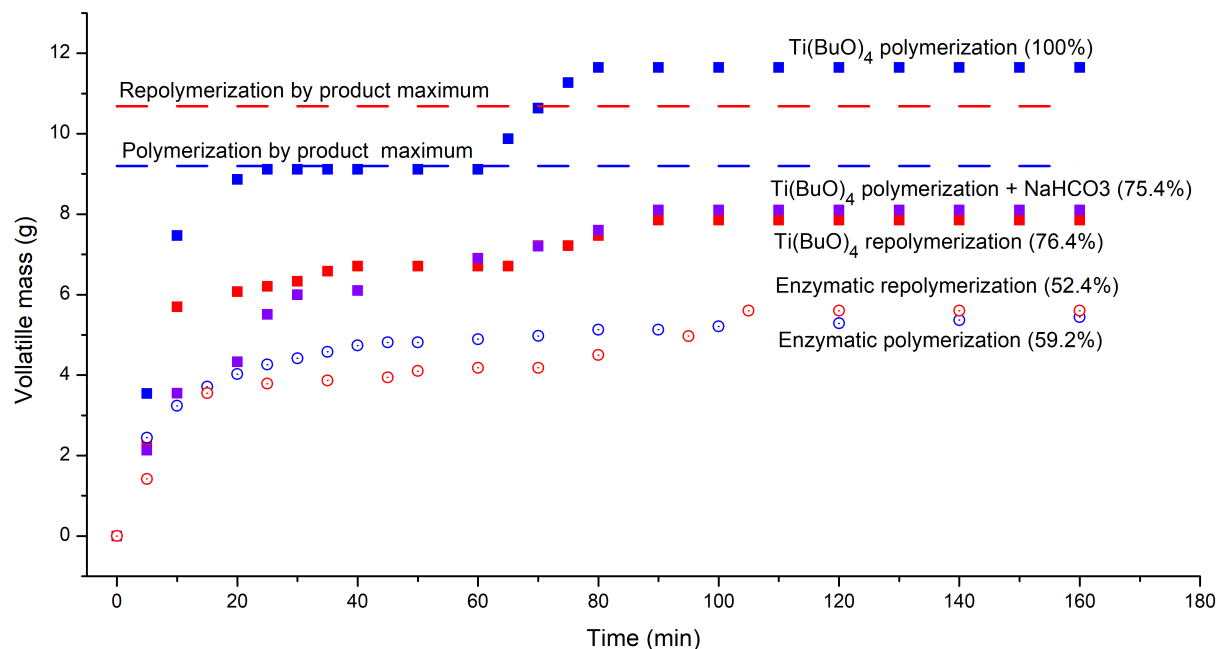
Source: The author (2026).

represents the maximum molar mass attainable under the applied bench-scale conditions (L.T. Brandão et al., 2018).

In contrast, the lower mass molar attained during the repolymerization of glycolysis products can be explained by an NaHCO_3 inhibition and higher content of oligomers at the end of glycolysis reaction. In particular, lower ethanol removal rates were observed in the first step, despite the addition of DS to adjust the molar ratio DS:BDO. The residual bicarbonate ions inhibits the $\text{Ti}(\text{O}i\text{Bu})_4$ activity during the repolymerization step (purple data on Figure 4.3.3), which is in accordance with literature studies with compounds with OH groups forming complexes (Fortunato et al., 1994), and will be further explored on the next section. The higher viscosity of the reaction medium at the end of the glycolysis step increases the mass transfer resistance to ethanol removal and, therefore, limits the repolymerization to around 76.4% of the maximum by-product mass expected for the reaction. It also should highlight the plateau observed in the removal by-product rates in the vacuum step (after 60 min), which can indicate the absence of transesterification reactions between the hydroxybutyl terminal groups in the polymer chains.

For the enzymatic system, repolymerization catalyzed by Novozym 435 likewise confirmed that glycolysis-derived oligomers are suitable substrates for lipase-catalyzed PBS synthesis. M_w decreased from 4,954 Da for polymerization from virgin monomers to 3,854 Da after repolymerization, also with a similar polydispersity of 1.55 to 1.48, respectively. Figure 4.3.2.B shows the normalized GPC distributions with overlapping and relatively narrow profiles for enzymatic polymerization and repolymerization.

Figure 4.3.3: Collected polycondensation byproduct. Square: Metal-catalyzed; Circle: Enzymatic; Blue: Virgin; Red: Repolymerization



Source: The author (2026).

In the enzymatic reaction, however, a higher response to the by-product removal was achieved on the repolymerization, showing that the depolymerization (or its catalyst), did not inhibit the reaction as much as the metal-catalyzed, reaching a conversion of 59.2% and 74.2% for virgin polymerization and repolymerization respectively, reaching the same conversion as of the metal-catalyzed repolymerization. The lower removal rates observed in the enzymatic polycondensation blank test, when compared to the metal-catalyzed blank, can be explained by higher mass transfer resistance. In particular, the lower synthesis temperature (90 °C) increases the viscosity of the reaction medium, since the reaction is conducted below the PBS melting temperature (Elias Guckert et al., 2022).

4.3.4 Experimental analytics

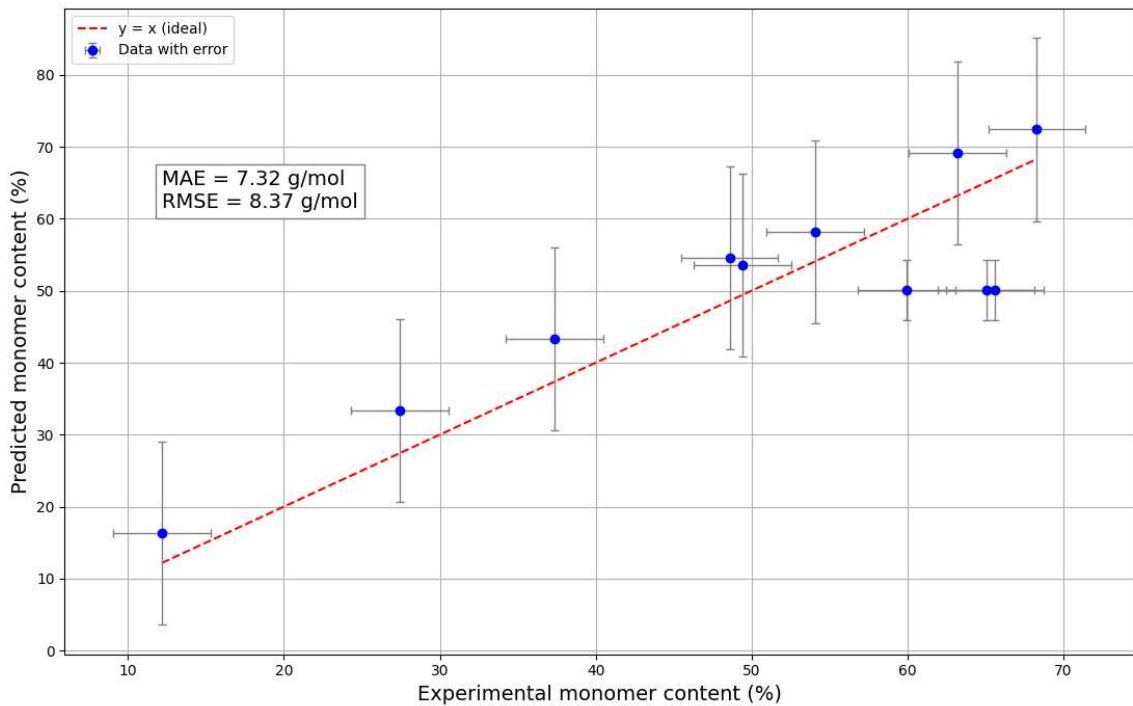
4.3.4.1 Full 2³ design of experiments

The first model designed to represent the reaction under the conditions defined on Table 4.2.1 was built using the OLS method. In this case, the DOE-based statistical model included only the main effects of the factors (temperature, 1,4-BDO and catalyst contents), and the first-order interaction terms between these factors, as seen in Equation 4.3.1 (The same equation was used on LMF and dimer content model investigation). The central point was used for curvature effect evaluation.

$$\begin{aligned} \text{Monomer}(\%) = \alpha_0 + \alpha_1 T + \alpha_2 \text{BDO} + \alpha_3 \text{Cat} + \alpha_4 (T : \text{BDO}) + \\ \alpha_5 (T : \text{Cat}) + \alpha_6 (\text{BDO} : \text{Cat}) \end{aligned} \quad (4.3.1)$$

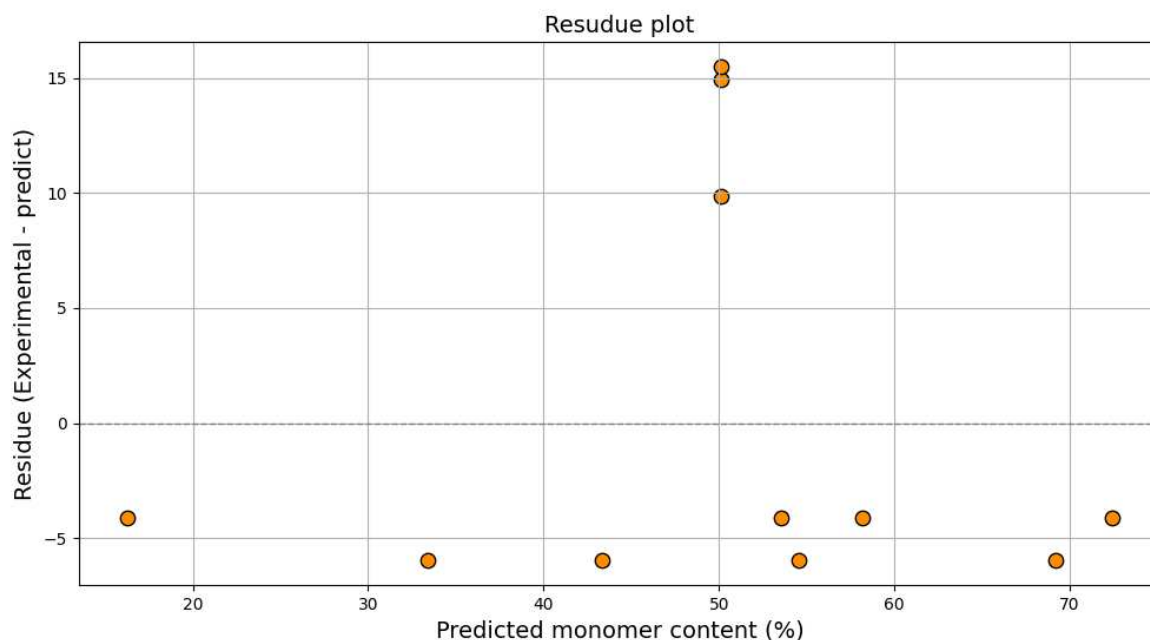
Figure 4.3.4 presents the predicted versus experimental parity plot, including the corresponding standard error bars for the evaluation of model prediction while accounting for both experimental and modelling uncertainties. In particular, the experimental and modeling uncertainties were comparable, which highlights the capability of the proposed model to describe the experimental data and their associated uncertainties. In addition, the experimental and predicted data are in close agreement and fluctuate around the identity line, which further reinforces the adequacy of the model. The residues related to the model errors are detailed on Figure 4.3.5. The results show a regular distribution, with considerable fidelity, followed by low MAE and RMSE values.

Figure 4.3.4: Pairplot graph for predicted versus experimental data with its respective standard errors for monomer content on a 2^3 full factorial model.



Source: The author (2025).

A summary of the model is presented on Table B.2.1 with the respective coefficients, standard errors and its values of normality. It shows very important data such as the values for the model coefficients and the statistical limits. Furthermore, it also demonstrates the ANOVA significance values for each factor. With a degree of confidence of 95%, the p-value for this model shows that temperature, catalyst and butanediol ratios are the most significant factors, however, the central point factor shows

Figure 4.3.5: Residue related to the model error for monomer content on a 2^3 full factorial model.

Source: The author (2025).

that a curvature effect is of significance to the model specification.

All one-way effects are considered positive effects. In particular, the monomer content increased with temperature as result of increase of glycolysis rates, as well as the mass transfer resistance reduced due to increased polymer chain segmental mobility and higher swelling of PBS beads in 1,4-BDO at temperatures above the melting point. Furthermore, the addition of the catalyst increased the reaction rates mainly at lower temperatures (as shown in Figure 4.3.7, suggesting the role of ions Na^+ and HCO_3^- in the ester bound scission (as schematically illustrated in Figure 1). Lastly, the use of higher amounts of 1,4-BDO increased the glycolysis rates across the entire range of temperature and catalyst loadings

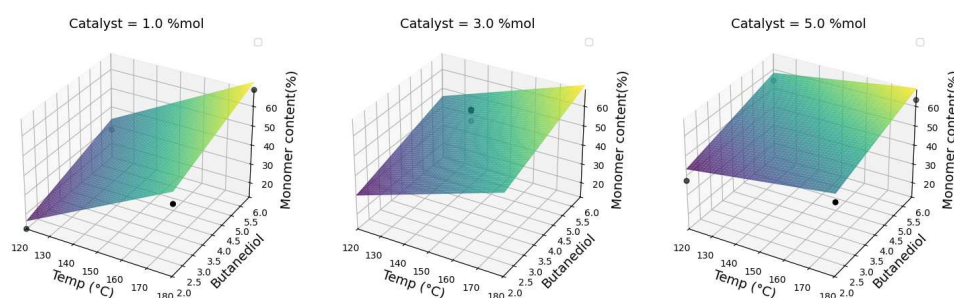
Table 4.3.2: Data summary for monomer content on a 2^3 full factorial model.

Factor	Effect	Coefficient	Std.Err.	p-value
Mean/Interc.	54.31	54.31	1.00	
Curvature (Center Point)	-18.46	-9.23	1.00	
Temperature	24.63	12.32	1.04	0.003
Butanediol	16.38	8.19	1.04	0.001
Catalyst	11.90	5.95	1.04	0.004
Temperature:Butanediol	0.37	0.19	1.04	0.011
Temperature:Catalyst	-14.02	-7.01	1.04	0.869
Butanediol:Catalyst	-1.10	-0.55	1.04	0.007

Source: The author (2025).

(as also presented in Figures 4.3.6 and 4.3.7). Particularly, higher amounts of 1,4-BDO increased the glycolysis rates by shifting the reaction equilibrium toward depolymerization and by reducing mass transfer limitations through enhanced PBS swelling and polymer chain segmental mobility. Literature data for PET glycolysis shows similar results, with an emphasis on the importance of the glycol amount, but showing the relevance of temperature and catalyst amount (Javed; Fisse; Vogt, 2023; Aguado et al., 2014).

Figure 4.3.6: Surfaces for catalyst ratios of 1%, 3% and 5% under on a 2^3 full factorial DOE model.



Source: The author (2025).

However, the interaction between temperature and butanediol content show no relevance, with a standard error value higher than its effect. Another important analysis is the negative effect of the central point, indicating a possible curvature effect, which will be further analyzed. In contrast, the interaction effect between butanediol and catalyst loadings was statistically significant. As seen in Figures 4.3.6 and 4.3.7, the addition of higher butanediol amounts had a more pronounced effect on glycolysis rates over the entire range of temperature when lower catalyst loadings were used. Similar behaviour was observed for the interaction effect between catalyst loading and temperature. At lower temperatures, higher catalyst loadings presented a more pronounced effect on glycolysis rates than at higher temperatures. These results highlight the occurrence of thermal glycolysis and, therefore, catalyst loading can be reduced by using higher amounts of glycol and higher temperatures.

Table 4.3.3 shows the main indicators describing the effectiveness of the given model. With a R^2 of a value above 0.75 it shows a regular representation of the experimental data, and could represent the reaction project. These statistical indicators show that the residuals follow an approximately normal distribution, as indicated by the Omnibus and Jarque–Bera tests with p-values above 0.05, supported by near ideal kurtosis and acceptable skewness. The low condition number confirms that multicollinearity is not a concern. However, the Durbin–Watson statistic reveals marked positive autocorrelation in the residuals, and the noticeable gap between R^2 and adjusted R^2 suggests some degree of model overfitting or imbalance in the contribution of terms. Despite these deviations, the overall set of indicators shows that the model captures the main structure of the data while also highlighting specific areas where residual

Table 4.3.3: Statistical tests for monomer content on a 2³ full factorial model.

	Value	Reference		Value	Reference
p(Omnibus):	0.222	>0,05	p(Jarque–Bera):	0.424	>0,05
Skew:	0.952	$-0.5 \leq x \leq 0.5$	Durbin–Watson:	0.487	≈ 2
Kurtosis:	2.660	$2 \leq x \leq 4$	Cond. No.	1.17	<30
R ²	0.86	> 0.85	Ajusted-R ²	0.65	> 0.85

Source: The author (2025).

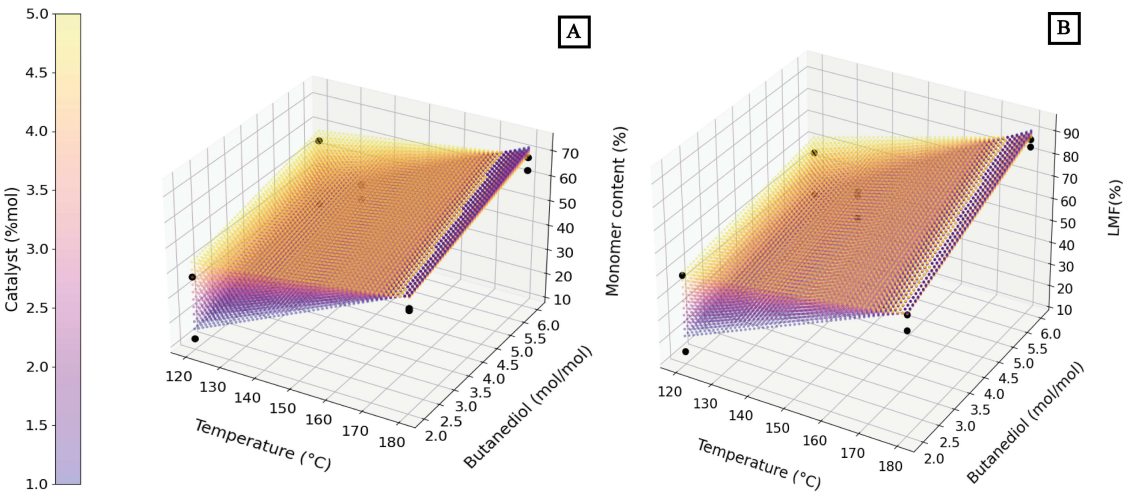
patterns and model complexity introduce imperfections that warrant attention in the interpretation.

Surfaces are shown on Figures 4.3.6 and 4.3.7.A. In those graphs, the relevance of each factor is shown as the previous analysis confirmed.

Based on this statistical behavior, such as the identified curvature effect, a lower value for Durbin–Watson, and the high difference of R², a new experimental planning was proposed to analyze the curvature effect on a rotational extension. The model was then redesigned with the addition of the runs 12 to 17, as detailed on Table 4.2.1.

With data available on Appendix B, the LMF’s statistical analysis showed similar results to the monomer content model, providing that satisfactory data can be archived through other means with adaptive analysis when the precision needed is not achievable. Furthermore, the Figure 4.3.7.B shows a very similar model behavior on the response to those factors under the same conditions to the LMF value based model.

Figure 4.3.7: 4D surface graph for a 2³ full factorial model for A) monomer content model. B) LMF model.



Source: The author (2025).

4.3.4.2 Central Composite Rotatable Design

Because the system exhibited significant curvature in the response, a Central Composite Rotatable (CCR) Design, an extension of the factorial DOE, was adopted in a rotatable configuration. In this new planning, also detailed in Table 4.2.1, the CCR design relies on the principle that each factor can be examined while all other variables are held at their center levels. Under this configuration, each factor is independently distributed at three positions, allowing the construction of the factorial and axial coordinates of the design. The CCR matrix was generated in Statistica, with orthogonality defined as the primary design criterion. The new DOE model used in the OLS method is defined on Equation 4.3.2.

$$\begin{aligned} \text{Monomer}(\%) = \alpha_0 + \alpha_1 T + \alpha_2 BDO + \alpha_3 T^2 + \alpha_4 BDO^2 + \alpha_5 Cat + \alpha_6 Cat^2 + \\ \alpha_7 (T : BDO) + \alpha_8 (T : Cat) + \alpha_9 (BDO : Cat) \end{aligned} \quad (4.3.2)$$

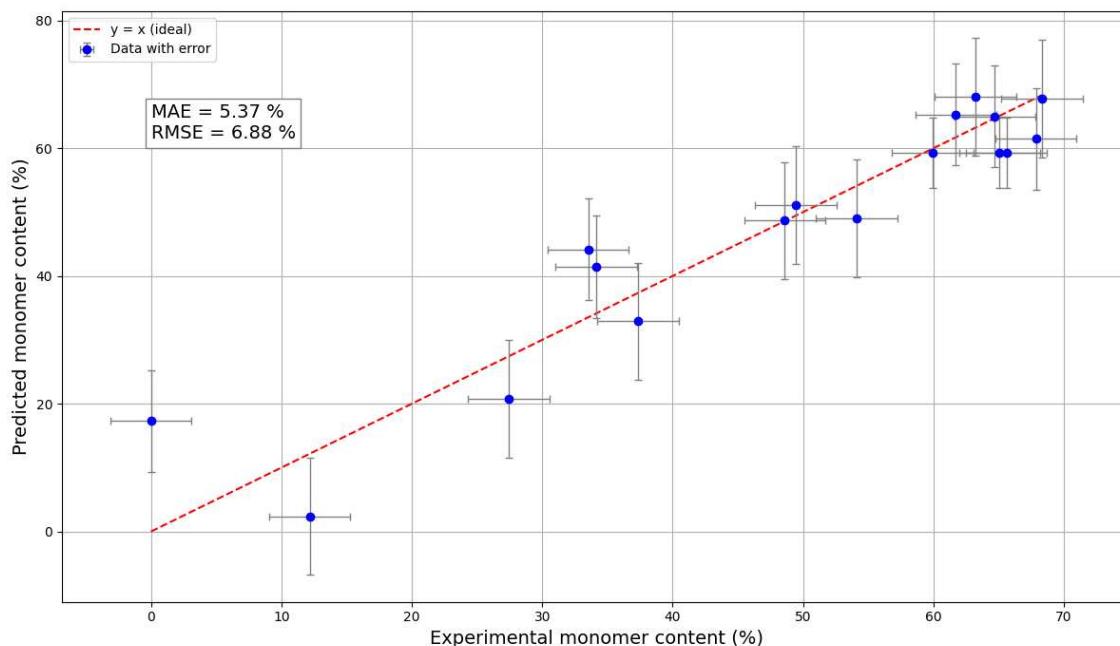
The alpha (α) value sets the distance of the axial points from the design center in a CCR and determines how the curvature information is incorporated into the quadratic model. For a rotatable CCR with k factors, α is theoretically defined in equation 4.3.3, which for $k = 3$ results in $\alpha \approx 1.682$. However, in the present study the CCR matrix was generated in Statistica under the condition of prioritizing orthogonality, and the software, therefore, adjusted the axial distance to $\alpha = 1.353$ to improve the orthogonality and numerical stability of the design.

$$\alpha = (2^k)^{1/4} \quad (4.3.3)$$

The predicted versus experimental parity plot is presented in Figure 4.3.8 , along with the corresponding standard error bars, for the evaluation of model prediction while accounting for both experimental and modelling uncertainties. In particular, one can see that both experimental and modelling uncertainties were similar, which corroborates the adequacy of the proposed design of experiments. In addition, the experimental and predicted data were close and fluctuated around the ideal identity line. The residues related to the model errors are detailed on 4.3.9. The only discrepancy in the DOE model was observed for the axial point performed at 109°C (run 12). In this condition, the glycolysis rate was very low, and no experimental monomer content was detected by GPC analysis. This result reinforces the critical role of temperature in the PBS glycolysis experiments. Even in the presence of an excess of 1,4-butanediol and with catalyst addition, it was not observed PBS depolymerization after 4h of reaction. This behavior can be explained by the fact that the axial condition at 109 °C is below the PBS melting temperature (115 °C). (Rafiqah et al., 2021) Under these conditions, the polymer remains in the solid state, resulting in limited swelling in 1,4-BDO and restricted chain segmental mobility. Consequently,

glycol diffusion into the polymer matrix is strongly hindered, and the glycolysis reaction is confined to the bead surface, leading to negligible ester bond scission and the absence of detectable monomer formation.

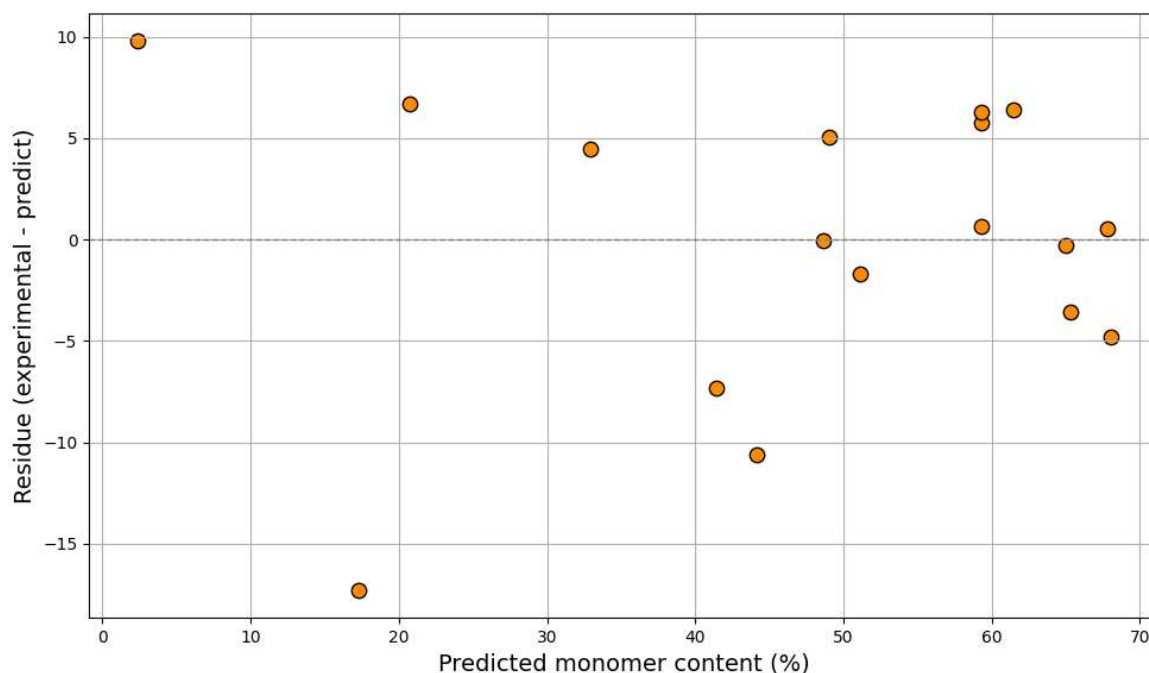
Figure 4.3.8: Pairplot graph for predicted versus experimental data with its respective standard errors for monomer content on a CCR 2^3 full factorial model.



Source: The author (2026).

The Table 4.3.4 presents the summary of the model, with the respective coefficients, standard errors and its values of normality. It shows very important data such as the values for the model coefficients and the statistical limits. It also demonstrates the ANOVA significance values for each factor. With a degree of confidence of 95%, the p-value for this model showed that temperature and catalyst loading as the significant first-order effects. However, the central point factor shows that a curvature effect is significant for the model specification. Among the quadratic effects, temperature was the only statistically significant, corroborating the expected curvature effect analyzed in the previous section, with a negative impact. This negative impact can be interpreted as a temperature range for repolymerization under high values, which causes an equilibrium effect for the depolymerization reaction. The observed maximum in monomer content is governed exclusively by temperature, as it is the only variable capable of altering the thermodynamic equilibrium constant of the reversible transesterification reaction, while catalyst loading and glycol excess mainly affect reaction kinetics.

Some of the main indicators describing the effectiveness of the model for this CCR design are presented in Table 4.3.5. With an R^2 value above 90%, the model provides an excellent representation of the experimental data and adequately captures the behavior of the reaction system. However, the

Figure 4.3.9: Residue related to the model error for monomer content on a CCR 2^3 full factorial model.

Source: The author (2026).

Table 4.3.4: Data summary for monomer content on a 2^3 full factorial model and its CCR extension.

Factor	Effect	Coefficient	Std.Err.	p-value
Mean/Interc.	59.30	59.30	6.90	
Temperature	23.91	11.95	3.89	0.02
Temperature ²	-21.77	-10.88	5.13	0.07
Butanediol	17.64	8.82	3.89	0.06
Butanediol ²	-6.47	-3.24	5.14	0.55
Catalyst	24.13	12.06	3.89	0.02
Catalyst ²	-5.18	-2.59	5.14	0.63
Temperature:Butanediol	-1.11	-0.55	4.70	0.91
Temperature:Catalyst	-14.02	-7.01	4.70	0.18
Butanediol:Catatalyst	0.37	0.19	4.70	0.97

Source: The author (2026).

adjusted R^2 shows a considerable divergence from the original R^2 , suggesting some degree of over- or under-specification in the model structure. Overall, aside from this divergence, the remaining statistical indicators strongly support the validity and robustness of the CCR model. For this CCR DOE, with the exception of the adjusted R^2 , all diagnostic tests (Table 4.3.5) show values within the excellent reference ranges for this type of model. The results indicate the absence of autocorrelation and multicollinearity, as well as no significant deviations from normality or tail behavior in the residuals.

For this CCR DOE, with the exception of the adjusted R^2 , all diagnostic tests show values within the excellent reference ranges for this type of model. The results indicate the absence of autocorrelation

Figure 4.3.10: Surfaces for catalyst ratios of 1%, 3% and 5% under CCR DOE on a 2^3 full factorial.

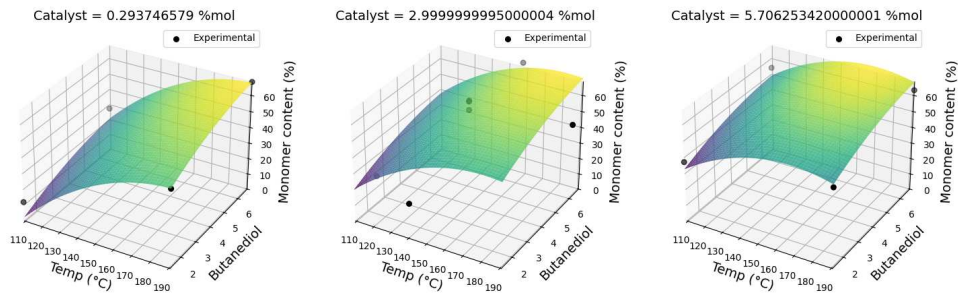


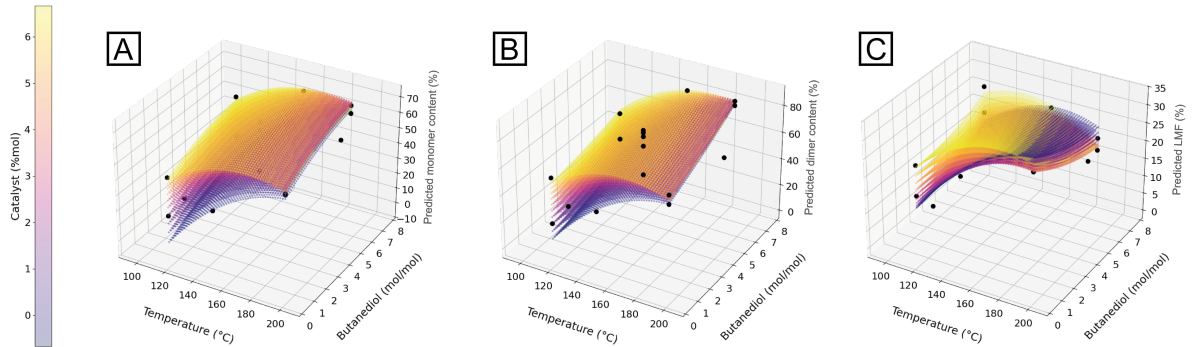
Table 4.3.5: Statistical tests for monomer content on a 2^3 full factorial model and its CCR extension.

Skew:	-0.85	$-0.5 < x < 0.5$	Durbin-Watson:	2.17	≈ 2
Kurtosis:	3.21	$2 < x < 4$	Cond. No.	4.23	< 30
R2	0.88	> 0.85	Adjusted-R2	0.73	> 0.85

Source: The author (2026).

and multicollinearity, as well as no significant deviations from normality or tail behavior in the residuals.

Figure 4.3.11: 4D Surface for a CCR DOE on a 2^3 full factorial. A) Monomer content model. B) LMF model C) Dimer content model.



Source: The author (2026).

The model surfaces are detailed on Figures 4.3.10 and 4.3.11. These results corroborated the expected behavior related to each factor, with a considerable effect of the catalyst under mild conditions, high impact of BDO and temperature. The quadratic negative effect of temperature can also be observed, providing an important global maximum that defines an excellent operating condition at 172.59 °C, BDO ratio of 6.71, and catalyst concentration of 4.69, resulting in a predicted monomer content of 72.06%.

This quadratic response factor also indicates repolymerization through the reverse mechanism, as evidenced by the dimer content model (Figure 4.3.11.C), which shows an increase in dimer content at higher temperature and BDO levels and lower catalyst level, reaffirming the direct effect of the catalyst on depolymerization. This catalyst effect is emphasized on its higher ratio, which presents a lower repolymerization effect, presented as a relative inhibition proving the sodium bicarbonate effect on the

repolymerization experimentation. It is also important to mention that the highest conversion is not necessarily the best condition. Partially depolymerized product can be preferred, if it presents good processing and purification, operating on mild conditions and better economic and environmentally.

The CCR analysis based on LMF values further corroborated the conclusions drawn from the monomer-based model. Despite reduced sensitivity to local maxima, the LMF response reproduced the quadratic temperature effect and the interaction patterns observed previously. Figure 4.3.11.B shows the CCR surface response based on LMF, which confirms the LMF relative efficiency when a monomer measurement is not possible.

4.4 Conclusion

This work provides a comprehensive analysis of an underexplored recycling method for PBS through glycolysis. Through the use of a full factorial design followed by a Central Composite Rotatable (CCR) DOE an expressive analysis was made possible, demonstrating the importance of temperature and catalyst as primary variables governing the depolymerization process, as well as revealing the critical quadratic impact of temperature. The identification of a significant quadratic temperature effect corroborates the reversible nature of transesterification and highlights the existence of optimal operating windows rather than a monotonic dependence on temperature. The CCR model achieved excellent statistical performance ($R^2 = 0.88$) and predicted an optimized condition (172.59 °C, BDO ratio 6.71, catalyst 4.69%) resulting in a monomer content of 72.06%, indicating substantial and efficient depolymerization.

Moreover, from a process-development perspective, the LMF emerges as a valuable complementary response variable, particularly for conditions where precise monomer quantification is experimentally constrained. Its ability to reproduce the main statistical trends of the system highlights its potential as a robust tool to provide analysis of depolymerization efficiency across different analytical contexts. Additionally, a few more experiments were performed to deepen understanding of this process: A simple kinetic experiment confirmed a near-equilibrium profile, and a catalyst-free run revealed that PBS inherently undergoes efficient glycolysis, with relatively good response due to its aliphatic ester structure or potential residual catalytic species in the commercial PBS sample.

The repolymerization experiments demonstrated that glycolyzed products can successfully be used under both enzymatic and metal-catalyzed conditions to recover the polymeric material. The metal-catalyzed repolymerization with $\text{Ti}(\text{BuO})_4$ resulted in $M_w = 10,835$ Da (compared to 17,788 Da from virgin monomers), while enzymatic repolymerization with Novozym 435 resulted in $M_w = 3,854$ Da (compared to 4,954 Da from virgin monomers), both with similar polydispersity indices to the virgin-based samples. These results confirm that glycolysis-derived oligomers are suitable substrates for both catalytic systems, thereby closing the material loop and reinforcing the potential of PBS glycolysis as a

viable chemical recycling route capable of producing high-quality recyclates.

Overall, the work advances the scientific basis for designing and optimizing PBS chemical recycling processes, delivering both mechanistic understanding through quadratic response modeling and statistically supported process conditions. The successful demonstration of repolymerization under relevant conditions (both metal- and enzyme-catalyzed) establishes PBS glycolysis not merely as a depolymerization technique, but as a practical component of circular polymer technologies. These insights facilitate future scale-up and contribute to establishing PBS as a truly circular bioplastic within the framework of sustainable materials management.

Chapter 5

Conclusion

This study successfully analyzed both aspects of full circular plastic production. Given that the main circular economy principles lie in sustainable production and disposal, it was possible to investigate sustainable synthesis for advanced polymerization systems, addressing the beginning of the polymer lifecycle through biobased production. Additionally, the end-of-life scenario was addressed through advanced recycling analysis.

The corresponding subjects were determined after a thorough literature analysis. For the first study, a state-of-the-art PBS copolymerization review established the current status to advance PBS polymerization systems. Additionally, an extensive analysis of chemical recycling technologies provided sufficient information to understand each advanced recycling method, its applications, and perspectives for PBS, supported by current literature, LCAs, and TEA analyses to validate a suitable chemical recycling technology for this study.

Furthermore, a detailed analysis of chemical recycling applications was conducted through statistical analysis of key process variables, providing data to identify the most important aspects of this work and future studies. Finally, a regulatory analysis, current industrial implementation mapping, and a critical perspective on these technologies were essential to discuss the industrial viability of chemical recycling processes.

The first case study employed enzymatic simultaneous ring-opening and condensation polymerization to synthesize PBS copolymers with lactones (ϵ -caprolactone and globalide) in a one-pot method (PBS-co-CL, PBS-co-GL, and PBS-co-CL-co-GL). The results showed that copolymerization with globalide (macrolactone) yielded better results, while ϵ -caprolactone (smaller ring) yielded a less stable synthesis. In addition, the products exhibited lower molar masses than conventional due to enzymatic synthesis limitations, however it was able to achieve a intermediary molar mass, with substantial increase from PBS.

Conversely, glycolysis was selected for PBS recycling analysis due to its performance and low

environmental impact in other applications, using a sustainable catalyst (sodium bicarbonate). A full factorial 2^3 DOE followed by its central composite rotatable (CCR) design was runned to analyze process performance, from the development of statistical models for output variables (monomer content, dimer content, and low molecular mass fraction). This analysis confirmed the presence of reversible reactions. In particular, the optimal condition for catalyst loading, 1,4-butanediol ratio, and temperature (172.59°C , BDO ratio of 6.71, catalyst ratio of 4.69%) achieves 72.06% monomer content. Repolymerizations succeeded under both metallic catalysis ($\text{Ti}(\text{OBu})_4$) and enzymatic catalysis (CALB N435) with a notable sodium bicarbonate inhibition effect.

Further studies on the first case should focus on improved copolymerization with higher molar masses, optimized conditions, characterization of copolymers thermal properties, and potential applications. For the second case, separation methods, new applications, life cycle assessments, and techno-economic analyses represent important areas for future research.

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Appendix A

Error equation

The error estimation builds on the main text description, where errors are assigned proportionally to measured masses sampled over time and ethanol mass loss is equally distributed.

The governing equation is:

$$Error = \frac{\sigma_{\text{ref}}}{\bar{m}_{\text{ref}}} \frac{m_i}{\bar{m}_{\text{ref}}} \quad (\text{A.0.1})$$

The experimental errors were estimated (Equation 3.2.1) for each reaction proportionally to its measured mass sampled over the time, and the mean mass loss of ethanol was distributed equally to the ethanol collected masses. σ_{ref} and $\bar{m}_{\text{ref}}$ are the standard deviation and mean mass, respectively, of the collected condensate from the PBS triplicate reaction, while m_i is the mass of the condensate collected from the reaction system.

Here, σ_{ref} represents the standard deviation of condensate masses from the PBS triplicate reference reaction, quantifying its inherent variability. $\bar{m}_{\text{ref}}$ is the corresponding mean condensate mass for PBS reaction, so their ratio yields the relative error of this stable reference.

For a given reaction, with m_i as the measured condensate mass at a specific time point, while $\bar{m}_{\text{ref}}$ denotes the reference ethanol mass at the same time point.

As a dimensionless error, it is applied through a multiplication to each point, propagating uncertainty proportionally to each sample. This approach assumes the reference variability applies broadly, adjusted by mass ratios, which is suitable for polymerization yields where condensate masses reflect reaction progress. It ensures error bars remain consistent and physically meaningful across dataset

Appendix B

LMF and Dimer glycolysis models

B.1 LMF model

Table B.1.1: Data summary for LMF on a 2³ full factorial model and its CCR extension.

Factor	Linear				CCR			
	Effect	Coefficient	Std.Err.	p-value	Effect	Coefficient	Std.Err.	p-value
Mean/Interc.	62.85	62.85	2.44	-	65.30	65.30	5.67	-
Curvature	-15.05	-7.52	2.44	0.05	-	-	-	-
Temperature	12.66	6.33	2.55	0.08	39.68	19.84	3.20	0.0004
Temperature ²		-	-	-	-25.25	-12.63	4.22	0.0201
Butanediol	20.80	10.40	2.55	0.02	21.85	10.93	3.20	0.0112
Butanediol ²		-	-	-	2.36	1.18	4.22	0.7882
Catalyst	33.73	16.86	2.55	0,01	15.269	7.63	3.20	0.0485
Catalyst ²		-	-	-	-3.01	-1.50	4.22	0.7322
Temperature:Butanediol	-1.19	-0.59	2.55	0.83	6.81	3.40345	3.86	0.4077
Temperature:Catalyst	-14.43	-7.21	2.55	0.06	-14.43	-7.21	3.86	0.1042
Butanediol:Catatalyst	6.81	3.40	2.55	0.27	-1.19	-0.60	3.86	0.8815

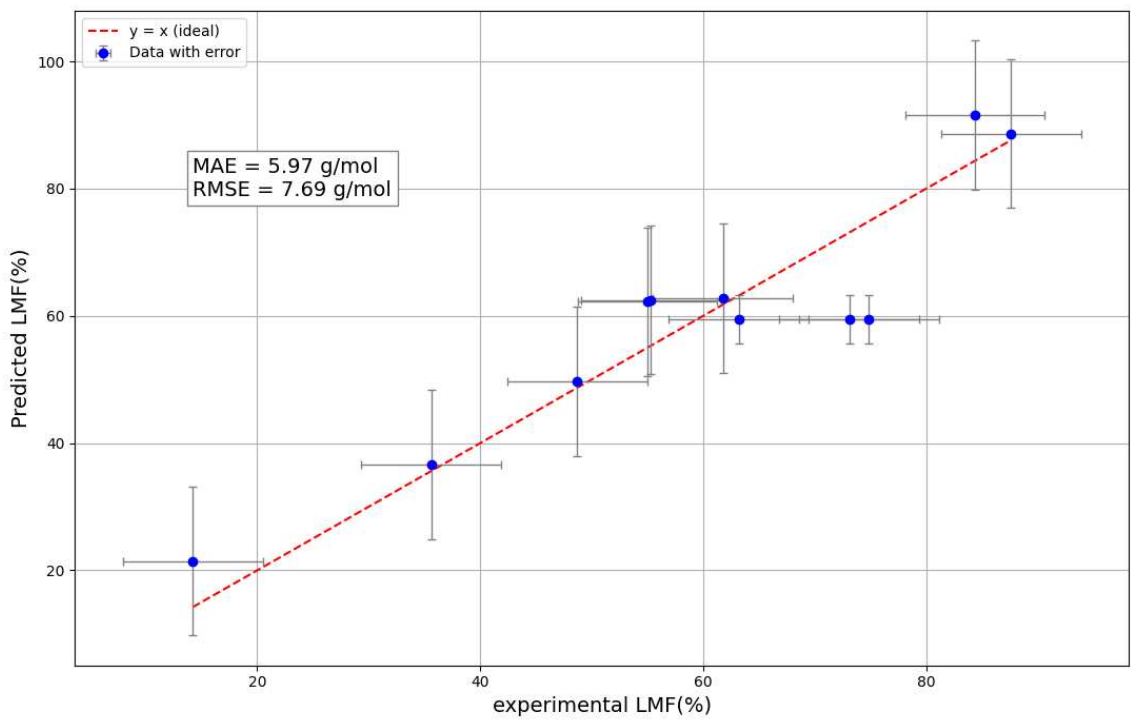
Source: The author (2026).

Table B.1.2: Statistical tests for LMF on a 2³ full factorial model and its CCR extension.

	Linear	CCR	Reference
p(Omnibus):	0.222	0.693	>0,05
Skew:	0.952	-0.402	$-0.5 \leq x \leq 0.5$
Kurtosis:	2.660	2.411	$2 \leq x \leq 4$
p(Jarque-Bera):	0.424	0.704	>0,05
Durbin-Watson:	0.487	0.703	≈ 2
Cond. No.	1.17	4.23	<30
R ²	0.859	0.908	> 0.85
Ajusted-R ²	0.648	0.790	> 0.85

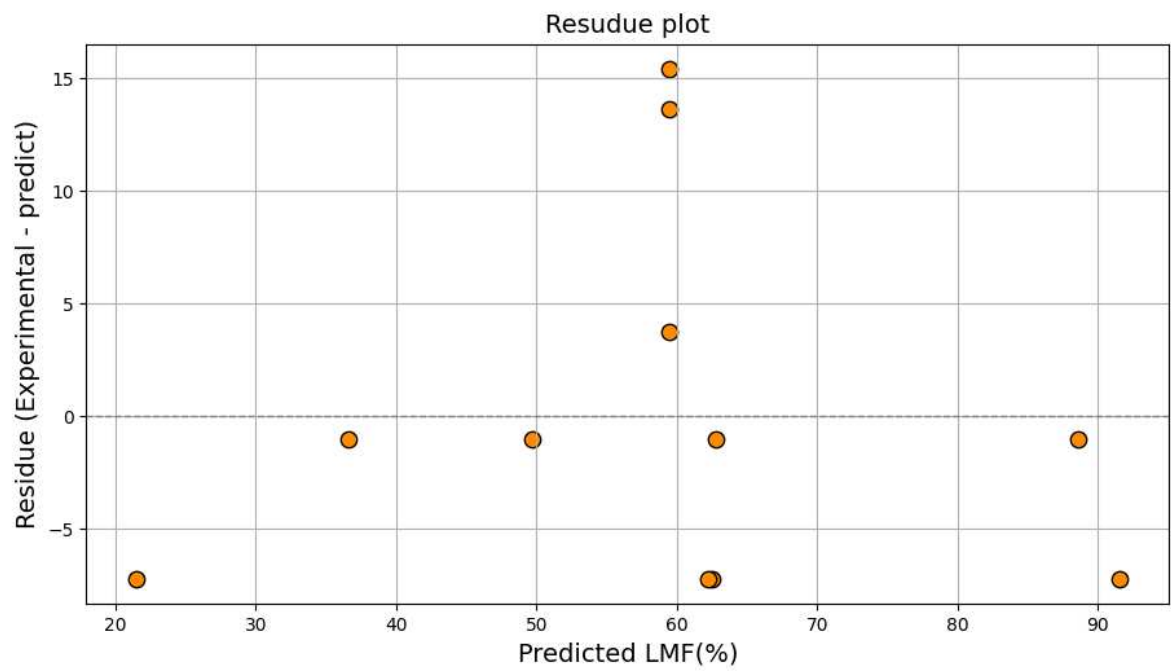
Source: The author (2026).

Figure B.1.1: Pairplot graph for predicted versus experimental data with its respective standard errors for LMF 2³ full factorial model.



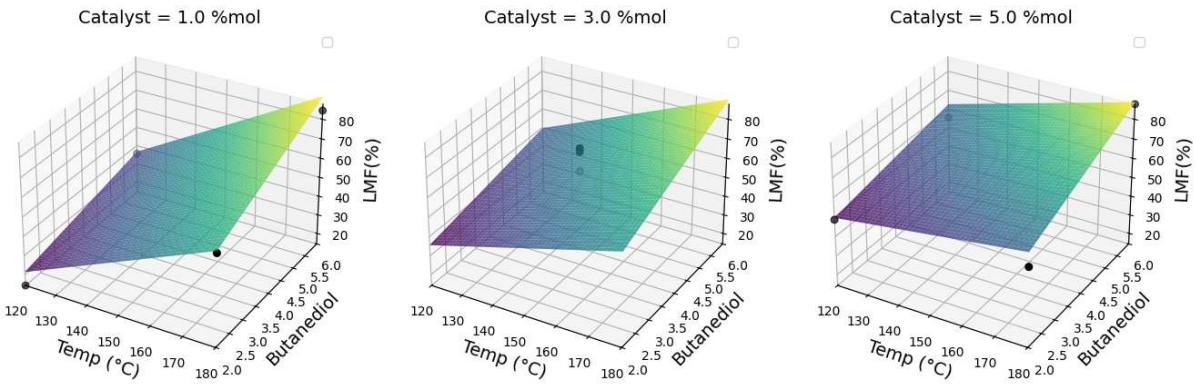
Source: The author (2026).

Figure B.1.2: Residue related to the model error for LMF content on a 2³ full factorial model.



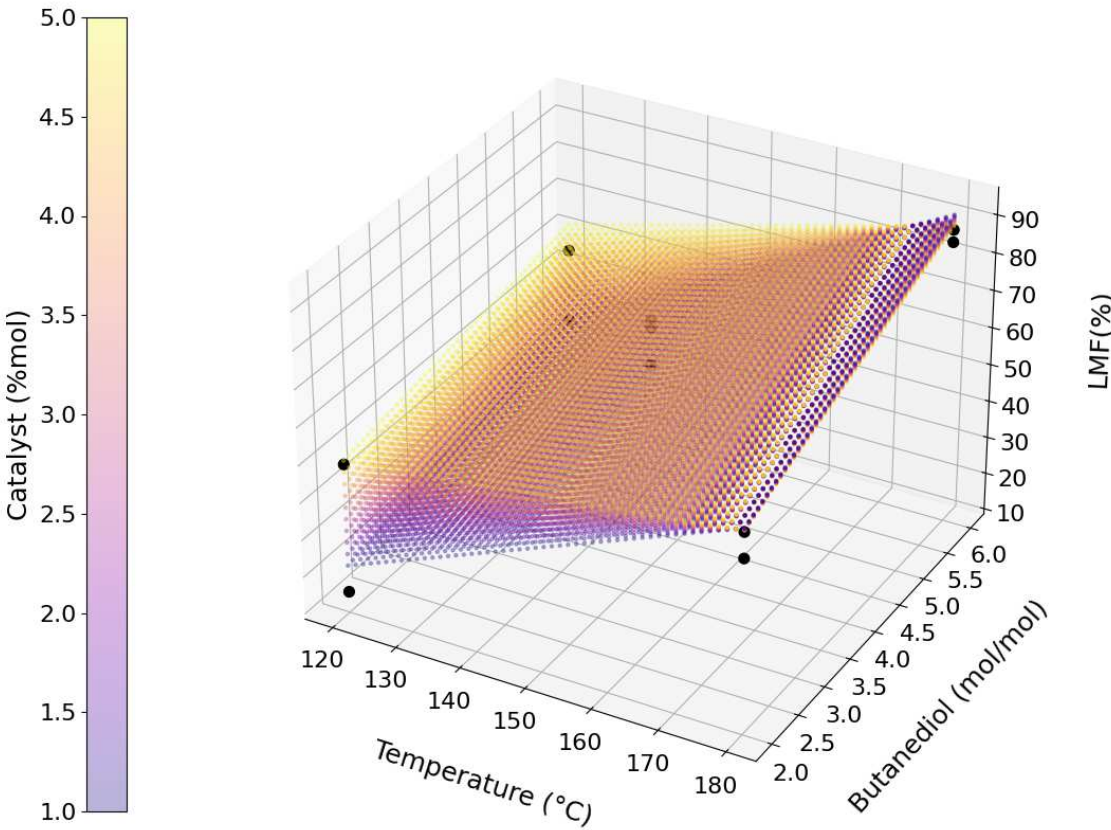
Source: The author (2026).

Figure B.1.3: 3D surface graph for each catalyst ratio analyzed on a 2^3 full factorial model for LMF output.



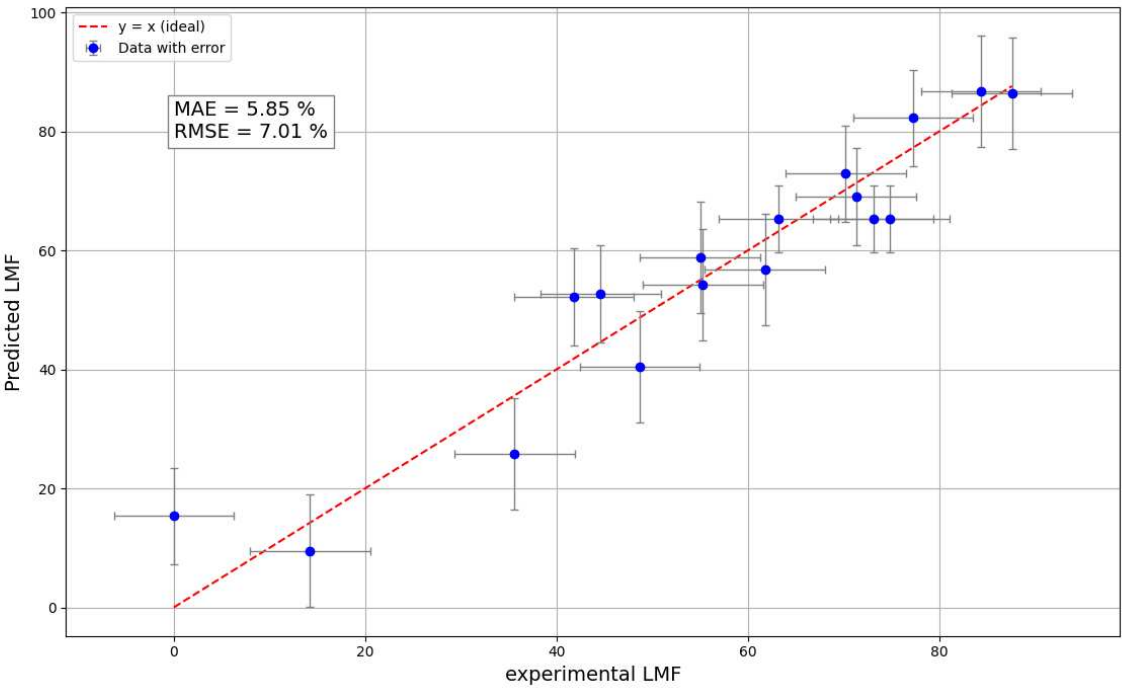
Source: The author (2026).

Figure B.1.4: 4D surface graph a 2^3 full factorial model for LMF output.



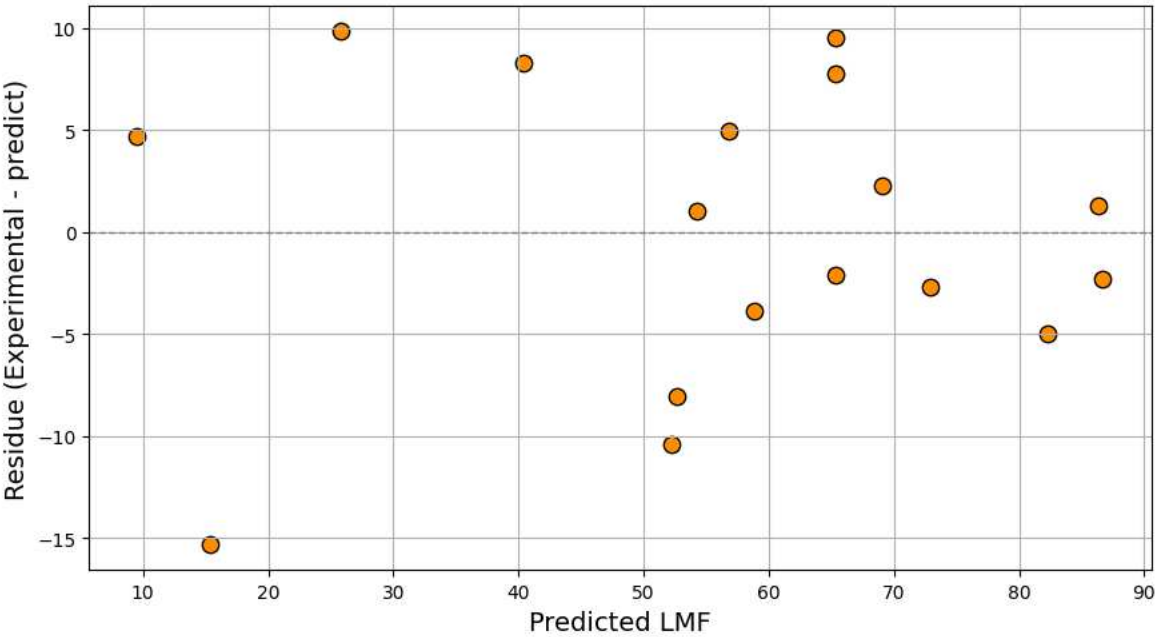
Source: The author (2026).

Figure B.1.5: Pairplot graph for predicted versus experimental data with its respective standard errors for LMF CCR 2³ full factorial model.



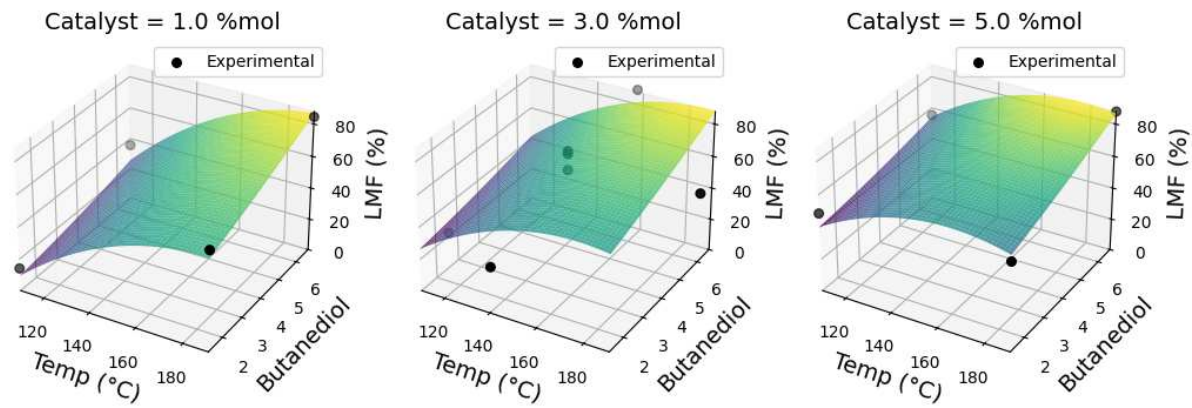
Source: The author (2026).

Figure B.1.6: Residue related to the model error for LMF content on a CCR 2³ full factorial model



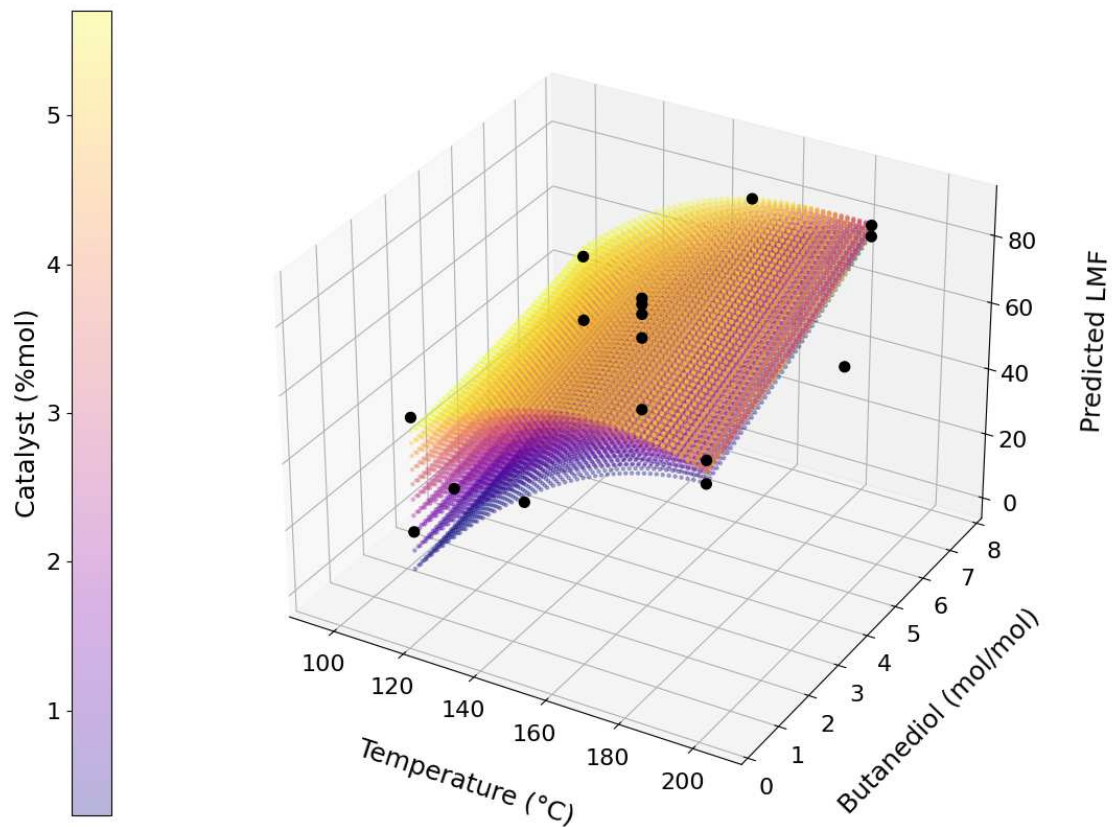
Source: The author (2026).

Figure B.1.7: 3D surface graph for each catalyst ratio analyzed on a CCR 2³ full factorial model for LMF output.



Source: The author (2026).

Figure B.1.8: 4D surface graph for a CCR 2³ full factorial model for LMF output.



Source: The author (2026).

B.2 Dimer model

Table B.2.1: Data summary for dimer on a 2^3 full factorial model and its CCR extension.

Factor	Linear				CCR			
	Effect	Coefficient	Std.Err.	p-value	Effect	Coefficient	Std.Err.	p-value
Mean/Interc.	24.35	24.35	0.23	-	24.23	24.23	2.78	-
Curvature	-2.86	-1.43	0.23	0.0086				-
Temperature	3.98	1.99	0.24	0.0038	8.09	4.04	1.57	0.0367
Temperature ²	-	-	-		-10.35	-5.18	2.07	0.0410
Butanediol	-0.49	-0.25	0.24	0.3858	-0.82	-0.41	1.57	0.8014
Butanediol ²	-	-	-		3.05	1.53	2.07	0.4854
Catalyst	3.16	1.58	0.24	0.0074	2.94	1.47	1.57	0.3809
Catalyst ²	-	-	-		2.85	1.42	2.07	0.5130
Temperature:Butanediol	-7.84	-3.92	0.24	0.0005	-1.11	-0.56	1.89	0.7768
Temperature:Catalyst	-4.79	-2.39	0.24	0.0022	-4.80	-2.40	1.89	0.2463
Butanediol:Catatalyst	-1.12	-0.56	0.24	0.1052	-7.84	-3.92	1.89	0.0774

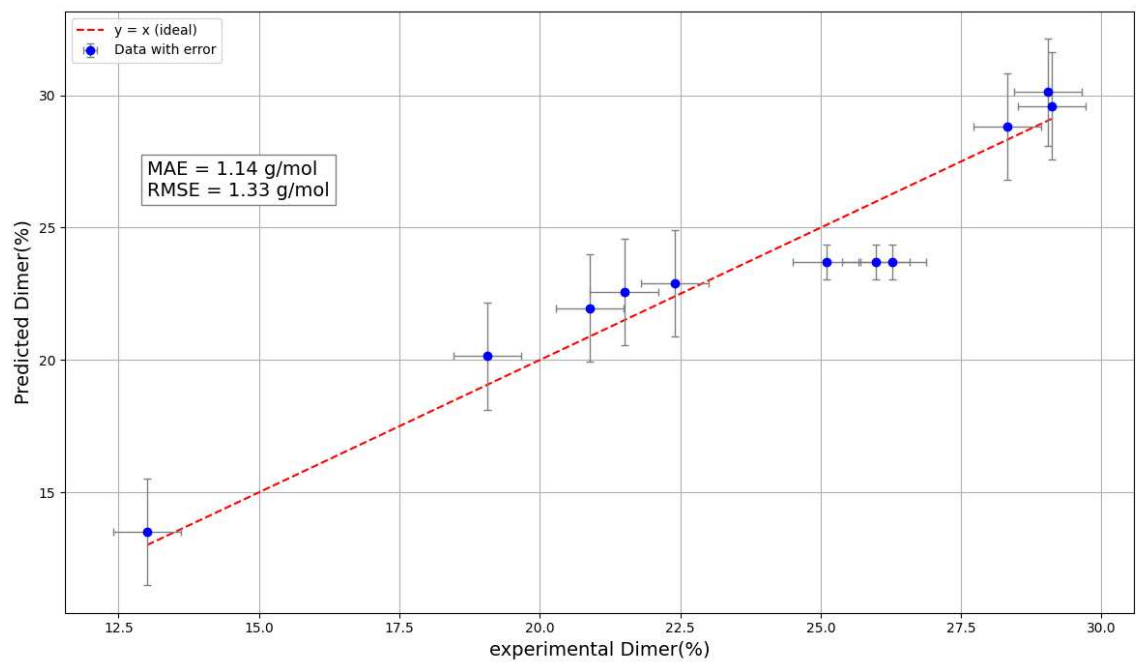
Source: The author (2026).

Table B.2.2: Statistical tests for dimer on a 2^3 full factorial model and its CCR extension.

	Linear	CCR	Reference
p(Omnibus):	0.201	0.089	>0,05
Skew:	1.018	-0.819	$-0.5 \leq x \leq 0.5$
Kurtosis:	2.349	3.854	$2 \leq x \leq 4$
p(Jarque–Bera):	0.351	0.298	>0,05
Durbin-Watson:	0.819	2.053	≈ 2
Cond. No.	1.17	4.23	<30
R ²	0.920	0.771	> 0.85
Ajusted-R ²	0.801	0.478	> 0.85

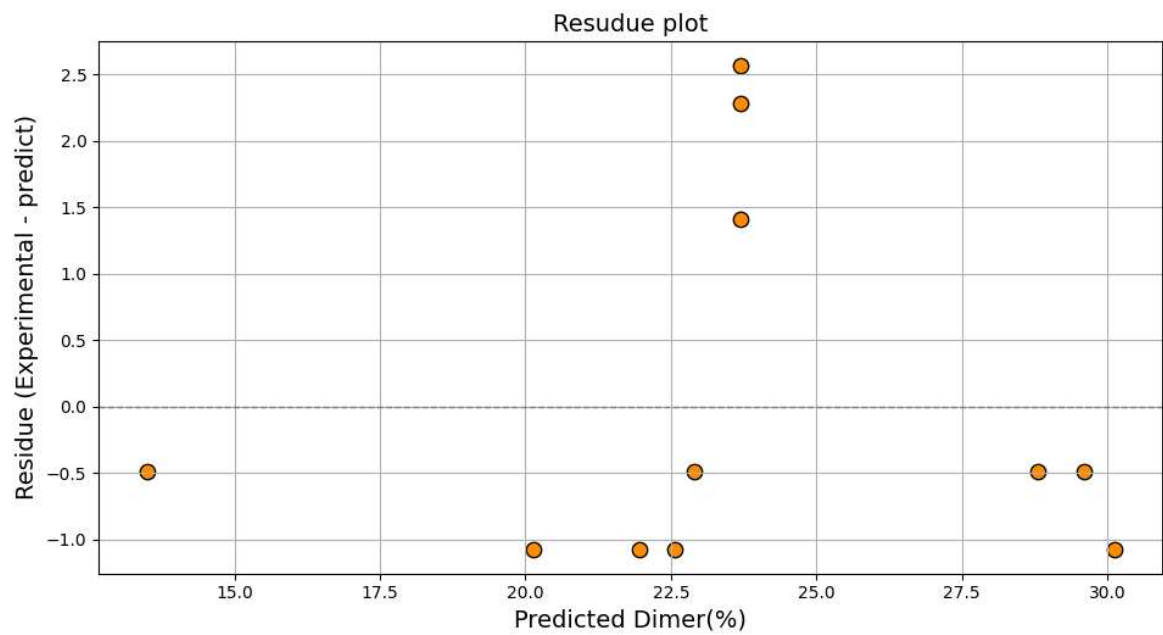
Source: The author (2026).

Figure B.2.1: Pairplot graph for predicted versus experimental data with its respective standard errors for dimer on a 2^3 full factorial model.



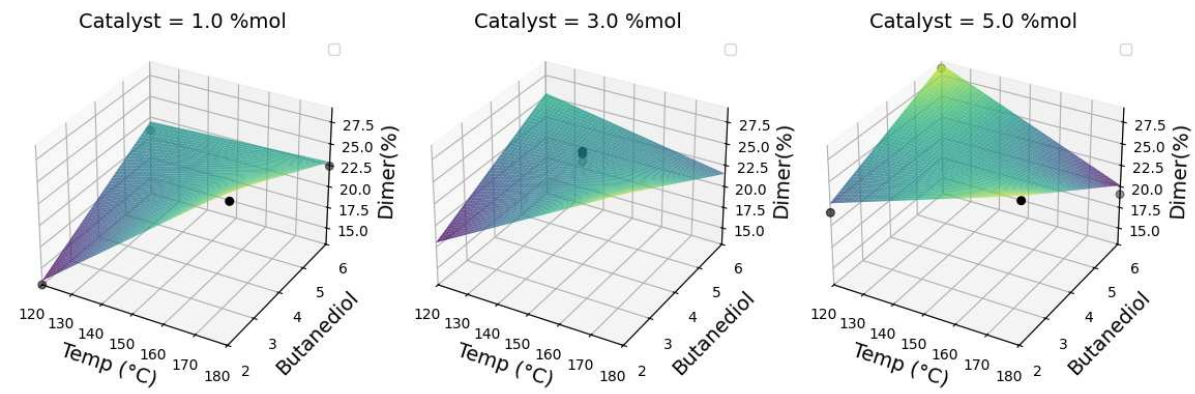
Source: The author (2026).

Figure B.2.2: Residue related to the model error for dimer content on a 2^3 full factorial model.



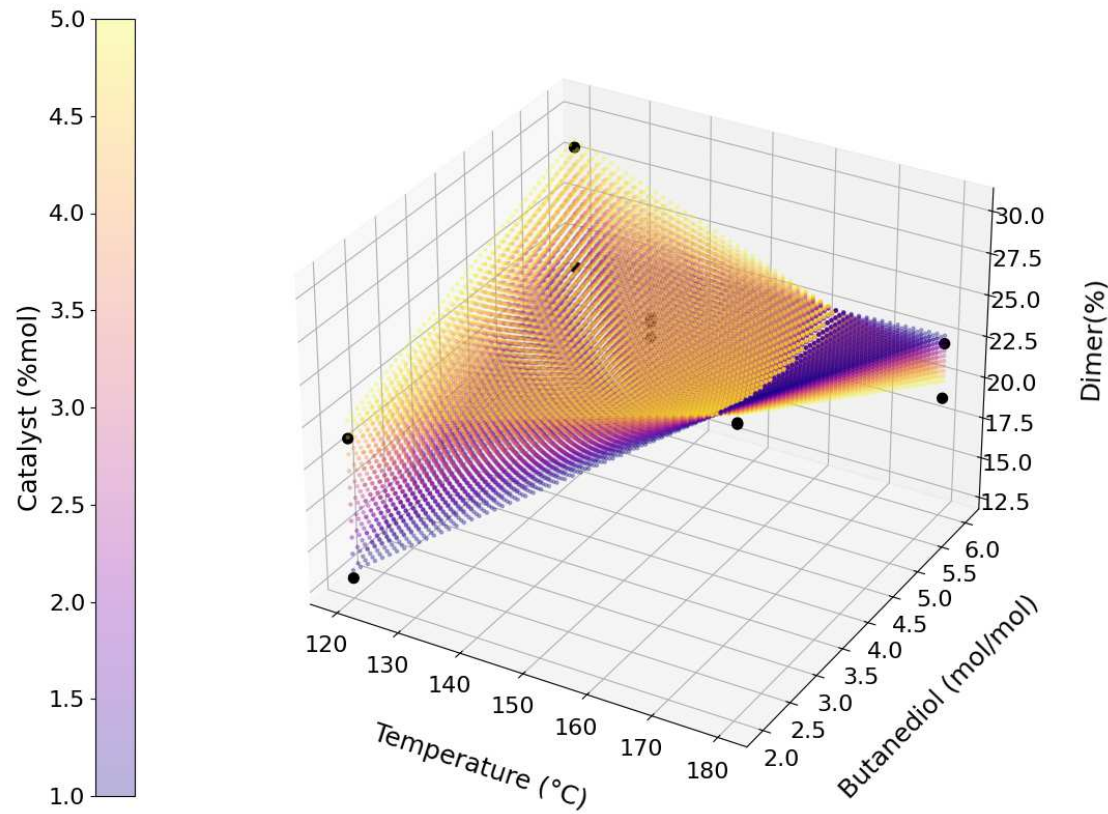
Source: The author (2026).

Figure B.2.3: 3D surface graph for each catalyst ratio analyzed on a 2^3 full factorial model for dimer output.



Source: The author (2026).

Figure B.2.4: 4D surface graph for a 2^3 full factorial model for dimer output.



Source: The author (2026).

Figure B.2.5: Pairplot graph for predicted versus experimental data with its respective standard errors for Dimer on a CCR 2³ full factorial model.

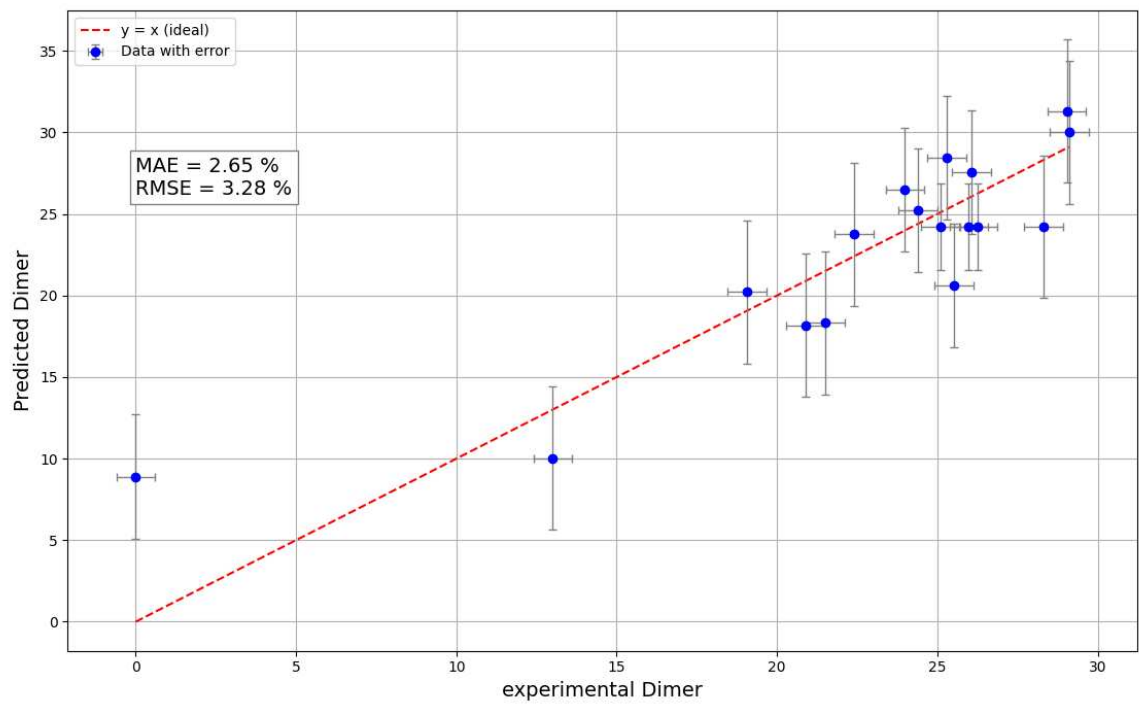
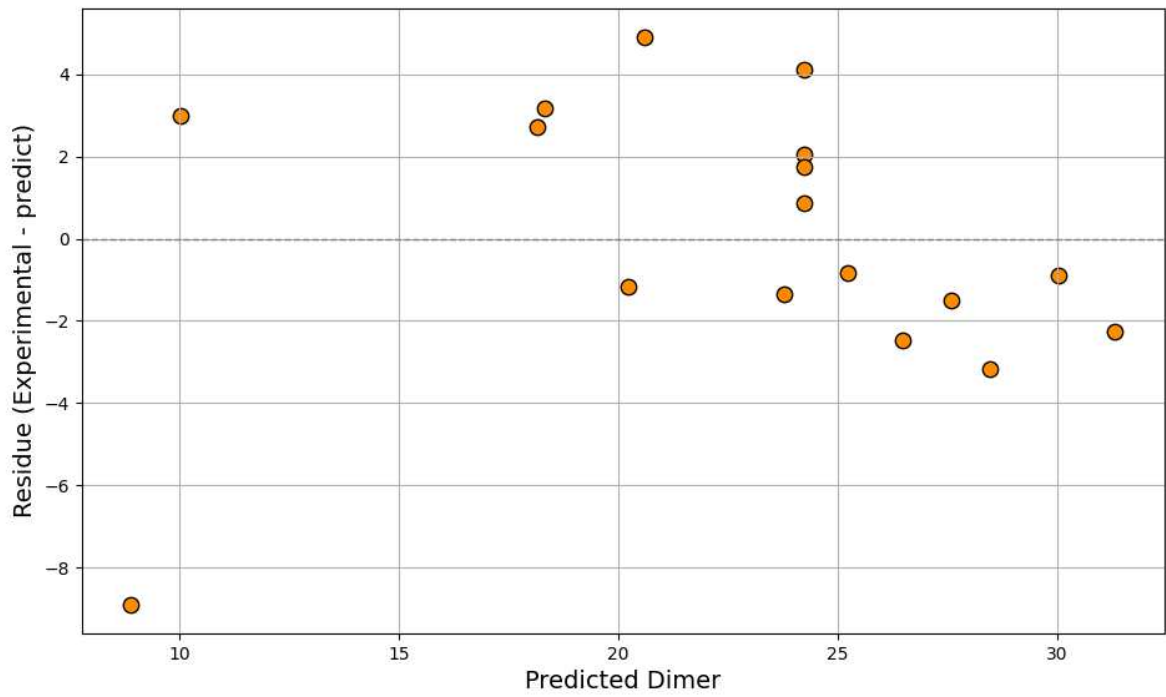
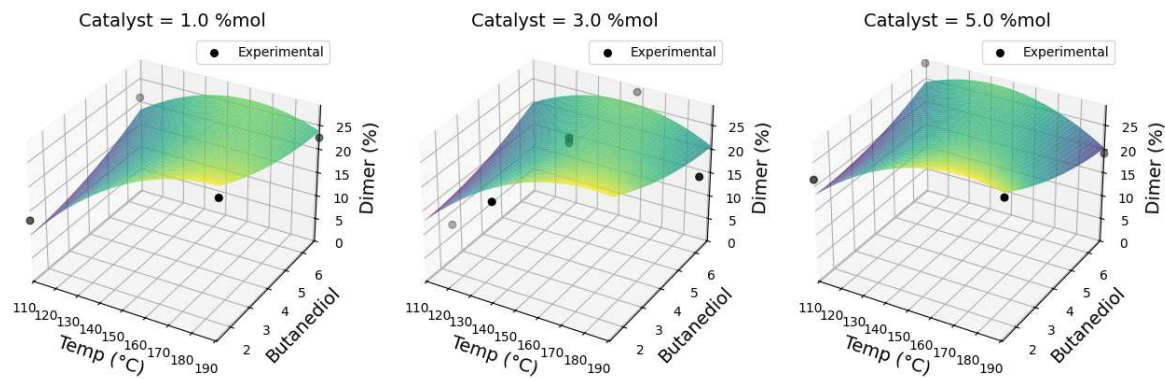


Figure B.2.6: Residue related to the model error for dimer content on a CCR 2³ full factorial model.



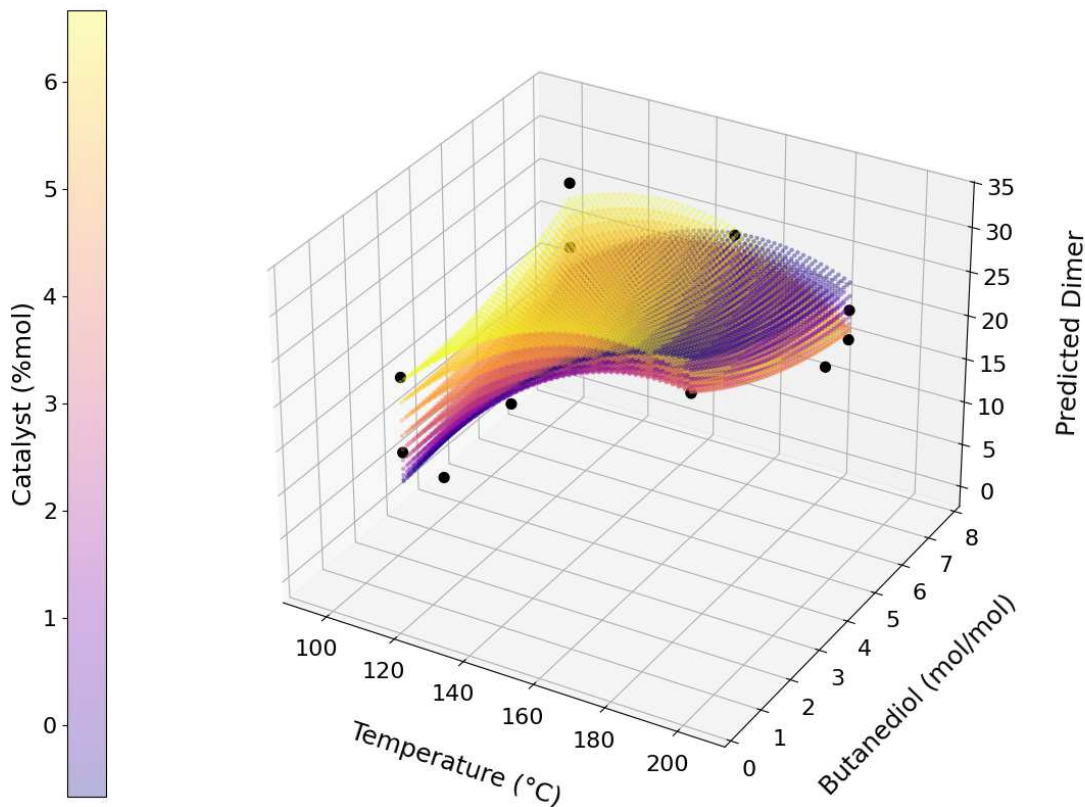
Source: The author (2026).

Figure B.2.7: 3D surface graph for each catalyst ratio analyzed on a CCR 2^3 full factorial model for dimer output.



Source: The author (2026).

Figure B.2.8: 4D surface graph for a CCR 2^3 full factorial model for dimer output.



Source: The author (2026).