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Ring Opening Polymerisation of Macrocyclic
Esters for Sustainable Packaging Applications
and Network Polymers

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Abstract

The increasing concern over climate change has led to a growing demand for sustainable materials, particularly those capable of replacing fossil-based plastics with biobased alternatives. Among these, aliphatic polyesters derived from diols and diacids have attracted attention due to their biodegradability, biocompatibility, and potential applications in packaging and biomedical fields. This thesis focuses on poly(ethylene succinate) (PES), an aliphatic polyester that is both biodegradable and potentially biobased, with the goal of developing materials for single-use packaging. Given the challenges associated with its traditional production *via* polycondensation, ring-opening polymerisation (ROP) was investigated as a promising alternative for synthesising high molecular weight PES without generating by-products. Initially, the solvent-free ROP conditions for macrocyclic esters of ethylene succinate were explored using various catalysts and different temperatures. Triphenyl bismuth (Ph_3Bi), as a catalyst with low toxicity, demonstrated excellent efficiency, enabling the synthesis of PES up to 70 $\text{kg}\cdot\text{mol}^{-1}$. The resulting PES exceeded the entanglement molecular weight, resulting in significantly improved mechanical performance, with tensile strengths up to 35 MPa and elongations at break above 275%. PES films also demonstrated outstanding oxygen barrier properties, with oxygen permeability as low as 0.008 Barrer, outperforming many conventional biodegradable packaging materials. In addition to its synthesis, this work pioneers the depolymerisation of PES back into its cyclic oligomers, a key step toward promoting circular economy strategies. Furthermore, the study explored the copolymerisation of PES with ϵ -caprolactone, finding that incorporating 15% of ϵ -caprolactone improved polymer ductility while maintaining high

oxygen barrier properties. Finally, novel unsaturated ethylene fumarate macrocycles were synthesised and used to access functional polyester networks via thiol-ene photocrosslinking. Crosslinked networks derived from both linear and cyclic oligomers were evaluated to understand the influence of topology and *cis/trans* isomer content on thermal and mechanical properties. Overall, this work combines advances in synthesis, property optimisation, and chemical recyclability to contribute to the development of circular and functional polyester materials for sustainable applications.

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List of Abbreviations

ACN	Acetonitrile
CALB	<i>Candida antarctica</i> lipase B
CB	Chlorobenzene
CDCl ₃	Deuterated chloroform
CHCl ₃	Chloroform
CL	ϵ -caprolactone
Cyc(ES) _n	Cyclo oligo ethylene succinate
Cyc(EF) _n	Cyclo oligo ethylene fumarate
$\bar{D}_M$	Dispersity
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCB	Dichlorobenzene
DCM	Dichloromethane
DMAP	2-Dimethylaminopyridine
DMF	<i>N,N</i> -Dimethylformamide
DMTA	Dynamic mechanical thermal analysis
DOX	2,2-dibutyl-1,3,2-dioxastannolane
DP	Degree of polymerisation
DPP	Diphenyl phosphate
DSC	Differential scanning calorimetry
E	Young's modulus
E'	Storage modulus
E''	Loss modulus
ED-ROP	Entropy-driven ring-opening polymerisation
ES	Ethylene succinate
FTIR	Fourier transform infrared
G'	Storage modulus

G''	Loss modulus
G_N	Entanglement modulus
GVL	γ -valerolactone
G_x	Crossover modulus
h	Hour
HDPE	High-density polyethylene
HPLC	High-pressure liquid chromatography
IM	Imidazole
LDPE	Low-density polyethylene
$Lin(EF)_n$	Linear oligo ethylene fumarate
MALDI-ToF	Matrix-assisted laser desorption/ionisation time-of-flight
M_c	Critical molecular weight
M_e	Entanglement molecular weight
min	Minute
mg	Milligram
mL	Milliliter
mmol	Millimole
M_n	Number average molecular weight
mol	Mole
MPa	Megapascals
MS	Mass spectroscopy
MSA	Methanesulfonic acid
M_w	Mass average molecular weight
NEt ₃	Triethylamine
NMR	Nuclear magnetic resonance
PBAT	Poly(butylene adipate terephthalate)
PBF	Poly(butylene furanoate)
PBS	Poly(butylene succinate)
PCL	Poly(caprolactone)

PEF	Poly(ethylene furanoate)
PES	Poly(ethylene succinate)
PET	Poly(ethylene terephthalate)
PGA	Poly(glycolic acid)
PHB	Poly(hydroxybutyrate)
Ph ₃ Bi	Triphenyl bismuth
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PO ₂	Oxygen permeability
PP	Polypropylene
PS	Polystyrene
PVL	Poly(valerolactone)
ROP	Ring-opening polymerisation
SEC	Size exclusion chromatography
Sn(Oct) ₂	Tin (II) 2-ethylhexanoate
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
T_c	Ceiling temperature
T_{cc}	Cold crystallisation temperature
T_f	Floor temperature
$T_{d,5\%}$	Temperature at 5% weight loss
TFA	Trifluoromethanesulfonic acid
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melting temperature
$T_{max\%}$	Temperature at maximum rate of decomposition
TMPMP	Tris(3-mercapto propionate)
T_{rc}	Melt recrystallisation temperature

TTS	Time-temperature superposition
U_T	Ultimate toughness
UV	Ultraviolet
VL	δ -valerolactone
WVTR	Water vapour transmission rate
X_c	Percentage crystallinity
δ	Chemical shift
ΔH_c	Enthalpy of crystallisation
ΔH_m	Enthalpy of melting
ΔH_m°	Enthalpy of melting for 100% crystalline polymer
σ_B	Ultimate tensile strength
σ_Y	Yield strength
ϵ_B	Elongation at break

Declaration of Authorship

This thesis is submitted to the University of Birmingham in support of my application for the Doctor of Philosophy degree. This thesis has been composed by myself, and no material contained here has been submitted for any previous application for any other degree or at any other institution.

The work presented, including experiments, characterisation, data collection and analysis, was carried out by myself between November 2021 and October 2024, except in the case outlined below:

Chapter 3 - Sien De Neve (visiting Master's student at the University of Basque Country) collected kinetic and characterisation data for several copolymerisations. Dr. Ainara Sangroniz Agudo (University of Basque Country) performed some of the O₂ and water permeability tests.

Chapter 1: Introduction

1.1 Sustainability for Plastic Packaging

Plastics have become indispensable in countless applications thanks to their versatility. From packaging and consumer goods to healthcare and construction, these materials offer advantages in durability, lightweight properties, and cost-effective production. As a result, global plastic consumption has soared, with Europe alone consuming 49.1 million tonnes in 2021.¹ Packaging, accounting for 40.5% of this figure, is a primary driver of plastic demand and presents the highest waste generation as a consequence of its short lifecycle.² The most used plastics in packaging, such as poly(ethylene terephthalate) (PET), high-density poly(ethylene) (HDPE), low-density poly(ethylene) (LDPE), and poly(propylene) (PP), excel in performance owing to their strong covalent bonds and high crystallinity, showing poor or no environmental degradation.³ This persistence leads to plastic accumulation in landfills, oceans, and ecosystems, posing a significant threat to wildlife and human health. The breakdown of plastic waste into microplastics further aggravates the issue, contaminating water sources, soil, and the food chain.⁴ Besides, those plastics are produced from non-renewable fossil fuels, so they contribute to resource depletion and greenhouse gas emissions and create sustainability problems.

Recognising the urgent need to address plastic problems, researchers and industries are exploring different solutions. Mechanical recycling became one of the most common strategies for reducing plastic waste in plastic packaging with high turnover rates of collected post-consumer waste; however, the challenge in plastic waste separation associated with the decreased quality of the recycled material limits its application.⁵ Therefore, there is a growing emphasis on developing plastics from renewable sources and designing materials with inherent degradability. Additionally,

end-of-life management is gaining traction, aiming to create a circular plastic economy where waste becomes a valuable resource rather than a burden.⁶

1.2 Polyesters

1.2.1 Biodegradable Polymers

Biodegradable polymers offer a promising solution to traditional plastics for short-term food packaging owing to their potential to be composted together with food waste, thereby reducing environmental impact.⁷ The degradation can occur enzymatically by the action of fungi, bacteria and algae, or by thermal or photodegradation hydrolysis, typically within an acceptable time after usage, often up to six months for compostable polymers.⁸ Aliphatic polyesters have emerged as a leading candidate within this category with their hydrolysable ester linkages, demonstrating utility in packaging, lithium-ion batteries, and biomedical applications.⁹⁻¹¹ Some of their increasing prevalence is also driven by the readily available bio-based precursors, such as succinic acid and fumaric acid, approved by the US Department of Energy as alternatives to petroleum-based substitutes, and renewable diols such as 1,2-ethanediol and 1,2-propanediol.^{12, 13}

The biodegradability of polyesters is mostly through hydrolysis, and the rate of this process can be influenced by structural factors such as molecular weight, crystallinity, and hydrophilicity.¹⁴ Higher molecular weights generally slow down hydrolysis by reducing chain mobility and limiting enzyme accessibility, while increased hydrophobicity decreases polymer–water interactions and water permeability, reducing the availability of water molecules necessary for hydrolysis. Similarly, higher crystallinity restricts water diffusion due to tightly packed and highly ordered regions,

where strong intermolecular interactions and steric effects inhibit plasticisation and enzymatic attack.

While polyesters such as poly(lactic acid) (PLA), poly(butylene adipate terephthalate) (PBAT), and poly(butylene succinate) (PBS) have been commercialised, they often have limitations of slow degradation under environmental conditions (Figure 1.1).¹⁵⁻¹⁹ On the other hand, poly(ethylene succinate) (PES) biodegradability has been extensively studied in the literature, as a wide range of microorganisms can break it down such as including thermophilic species, mesophilic bacteria, and fungi relatively shorter time frames.^{20, 21} It can be degraded by the enzyme poly(hydroxy butyrate) (PHB) depolymerase, as well as hydrolysed by lipase or serine proteases.^{22, 23} Furthermore, PES degradation rates are faster than those of the commercial aliphatic polyesters, emerging as a promising candidate for sustainable plastics.²⁴⁻³¹

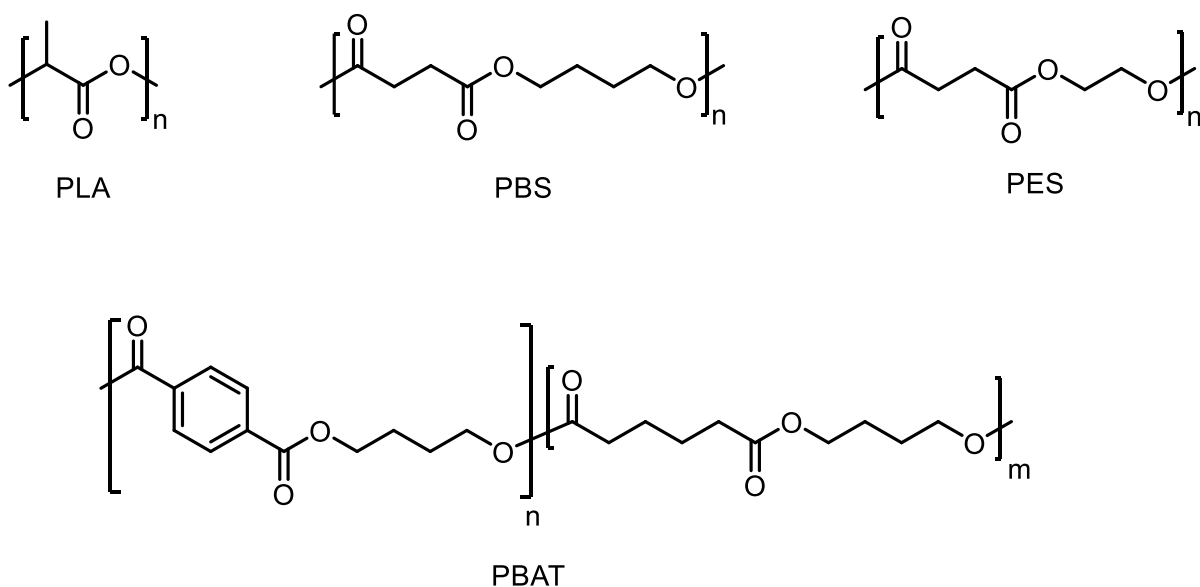


Figure 1.1 Chemical structures of PLA, PBS, PES, and PBAT.

1.2.2 Production Methods

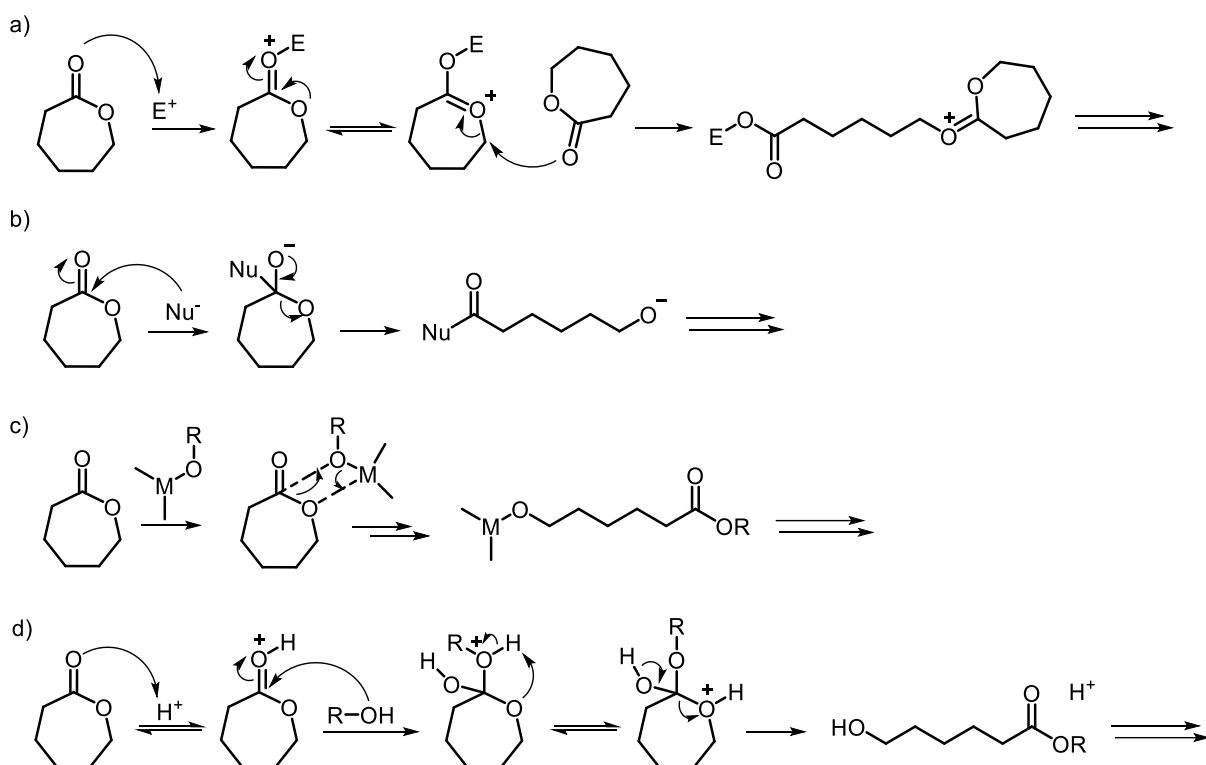
The traditional way of producing diol/diacid-type aliphatic polyester involves polycondensation, a process where monomers are directly linked while by-products such as water or alcohol are also formed. This reaction follows a step-growth polymerisation mechanism, in which polymer chains grow through the successive reaction of functional groups on oligomers or monomers rather than adding monomer units to a single growing chain. In the step-growth mechanism, high conversion is necessary to reach high molecular weight polymers, which can only be achieved if those byproducts are removed. The challenge lies in removing these by-products from the reaction mixture as the reaction becomes highly viscous.³² Therefore, high temperatures and low vacuum are necessary to remove the by-products and achieve acceptable molecular weights. This process often takes long reaction times, and to reach high molecular weights under these conditions leads to highly dispersed polymers. Moreover, these conditions lead to significant energy consumption and the volatilisation of a substantial amount of starting materials and their oligomers.³³ In addition, side reactions such as etherification can form dialkylene glycol ether units within the polymer chains, disrupting the polymer structure and reducing crystallinity.³⁴ Chain growth polymerisation provides control over both the polymer structure and rate of polymerisation. A prominent example is ring-opening polymerisation (ROP), which efficiently produces polyesters without byproducts under mild reaction conditions.³⁵

1.3 Ring Opening Polymerisation

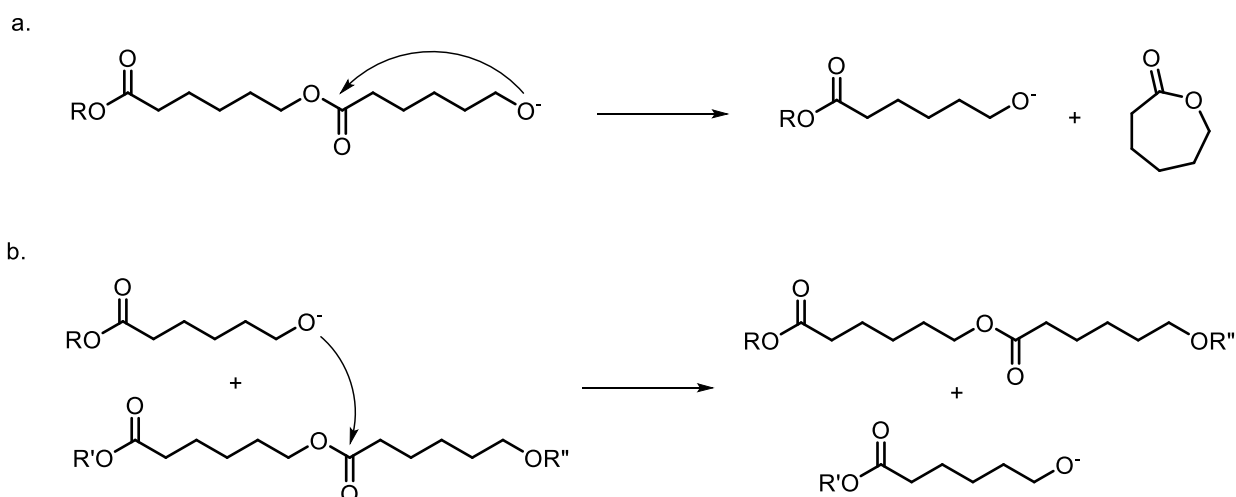
1.3.1 General Mechanism

ROP is a chain-growth polymerisation technique where the reactive end of a polymer chain reacts with a cyclic monomer, opening the cyclic monomer's ring system, to form a longer polymer chain. Most of the monomers are heterocycles containing ether, acetal, ester, and amide bonds and exhibit high polarity, facilitating ring opening through heterolysis. Therefore, ROP can be initiated by numerous nucleophiles and electrophiles and propagate with various mechanisms, including cationic, anionic, coordination insertion and activated monomer pathways (Scheme 1.1).³⁶

ROP of cyclic esters is prone to side reactions through transesterification, which can occur either within a single polymer chain (intramolecular) or between different polymer chains (intermolecular) (Scheme 1.2).³⁷ Intramolecular transesterification, also referred to as backbiting, involves a nucleophilic addition-elimination between the active chain end and the ester group of the same polymer chain, resulting in the formation of cyclic species. Intermolecular transesterification follows the same mechanism, but it involves the active chain end of one polymer reacting with the ester group of another polymer chain, leading to the segmental exchange of macromolecules. Both reactions disrupt the polymer backbone and cause shortening or extending of polymer chains, resulting in broad molecular weight distributions, which limits the synthesis of the controlled polymer and consequently affects the final polymer's thermomechanical properties. The rate and extent of these reactions highly depend on the catalyst-initiator systems, temperature, and reaction time.



Scheme 1.1 Different ROP mechanisms for ϵ -Caprolactone, a) Cationic, b) Anionic, c) Coordination-insertion, d) activated monomer, adapted from Cama *et al.*³⁶



Scheme 1.2 Transesterification reactions demonstrated on PCL a. Intramolecular, b. Intermolecular.

1.3.2 Thermodynamics of ROP

As in any chemical reaction, the thermodynamic feasibility of ROP is governed by the change in Gibbs free energy of polymerisation (ΔG_p) (Eq. 1.1). A negative ΔG_p

indicates a thermodynamically favoured process, while a positive ΔG_p a disfavoured one.

$$\Delta G_p = \Delta H_p - T\Delta S_p \quad \text{Eq. 1.1}$$

where ΔH_p and ΔS_p correspond to enthalpy and entropy change of polymerisation, respectively, and T is the absolute temperature. ΔG_p can be further defined as the sum of the standard Gibbs free energy of polymerisation (ΔG_p^θ) and a term related to the instantaneous monomer concentration ($\ln[M]$) when following Flory's principles (Eq 1.2).

$$\Delta G_p = \Delta G_p^\theta - RT\ln[M] = \Delta H_p^\theta - T(\Delta S_p^\theta + R\ln[M]) \quad \text{Eq. 1.2}$$

where R is the gas constant, ΔH_p^θ and ΔS_p^θ are the standard polymerisation enthalpy and entropy change, respectively.

The reversible nature of the propagation step in the ROP leads to a distinct equilibrium between the cyclic monomer and the linear polymer. This equilibrium is characterised by a specific concentration of unreacted monomers at the reaction's end, known as the equilibrium monomer concentration ($[M]_{eq}$), which is lower than the initial monomer concentration ($[M]_0$) as polymerisation proceeds.³⁸ The critical temperature, ceiling temperature (T_c) and floor temperature (T_f), mark the point where polymerisation reaches equilibrium, where ΔG_p is zero, and there is no net monomer conversion. Dainton and Irvin linked this thermodynamic equilibrium to the $[M]_0$, asserting that attainable molecular weight of the polymer at equilibrium is strongly influenced by the relationship $[M]_0$ and $[M]_{eq}$, and these concentrations can be determined by ΔH_p^θ and ΔS_p^θ along with temperature, T_c or T_f (Equations 1.3 and 1.4).³⁹

$$T_c = \frac{\Delta H_p^\theta}{\Delta S_p^\theta + R \ln[M]_0} \text{ (when } \Delta H_p^\theta < 0 \text{ and } \Delta S_p^\theta < 0 \text{)} \quad \text{Eq. 1.3}$$

$$T_f = \frac{\Delta H_p^\theta}{\Delta S_p^\theta + R \ln[M]_0} \text{ (when } \Delta H_p^\theta > 0 \text{ and } \Delta S_p^\theta > 0 \text{)} \quad \text{Eq. 1.4}$$

When both the ΔH_p^θ and ΔS_p^θ are negative, increasing the polymerisation temperature raises $[M]_{eq}$. Eventually, at or above the ceiling temperature, where $[M]_{eq}$ equals $[M]_0$, the system no longer favours the formation of high molecular weight polymer. Conversely, when both ΔH_p^θ and ΔS_p^θ are positive, $[M]_{eq}$ decreases as temperature rises, meaning the reaction favours the polymer formation more strongly as the temperature rises. In this case, a floor temperature exists below which polymerisation is thermodynamically unfavourable.

1.3.2.1 Effect of Ring Size

The polymerisation behaviour of cyclic esters is significantly influenced by ring size and substitution pattern, as these factors determine the magnitude and sign of ΔH_p and ΔS_p .³⁸ A primary driving force for the polymerisation of small cyclic compounds is ring strain, arising from deviations in bond angles and unfavourable interactions between H-atoms, or substituents.⁴⁰ In systems where monomer-polymer-solvent interactions are minimal, polymerisation enthalpy can be used as a measure of ring strain. In the ROP of small cycles (typically atom number in the ring ≤ 7), polymerisation is accompanied by decreased entropy (negative ΔS_p) due to restricted molecular movement. Consequently, polymerisation is thermodynamically favoured only when the energy released from reducing ring strain ($\Delta H_p < 0$) outweighs the entropy loss ($T\Delta S_p$ in Eq 1). As a result, monomers with higher ring strain exhibit lower $[M]_{eq}$. When the magnitude of $T\Delta S_p$ outweighs the ΔH_p , the temperature is T_c .

The magnitude and the sign of ΔH_p and ΔS_p change as the ring size of cyclic esters enlarges (Figure 1.2). While the exact definition of a macrocycle can vary, compounds with rings containing 14 or more atoms typically exhibit minimal ring strain and are considered macrocycles.⁴¹ Without consequential ring strain, the ring-opening reactions of these compounds are associated with insignificant enthalpy changes. This type of polymerisation only occurs if it is entropically favourable, termed entropy-driven ROP (ED-ROP). As macrocycles have a limited number of conformations, conformational flexibility increases significantly upon ring opening, favouring entropy gain. Consequently, ED-ROP of macrocycles can achieve high monomer conversion when the process is thermodynamically feasible, and the mechanism is accessible.⁴²

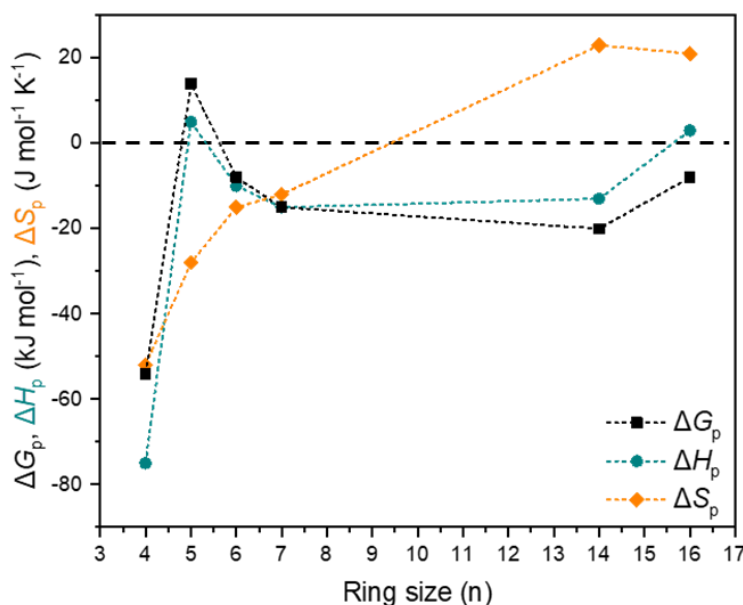


Figure 2.2 Gibbs free energy, enthalpy and entropy for ROP of cyclic esters according to the ring size (n = number of carbon atoms per ring), adapted from Duda and Kowalski.³⁸

1.3.2.2 Entropy-Driven ROP (ED-ROP)

Although ROP is a chain-growth process, the underlying theory of ED-ROP is derived from the step-growth process, which inherently generates cyclic oligomers due

to the random and probabilistic nature of the reaction combined with the entropic factors that favour intramolecular cyclisation. Macrocycles are formed *via* intramolecular reactions, which are either end-to-end closure or backbiting, depending on reaction conditions and the characteristics of the initiator or catalyst (Scheme 1.2).⁴³ Jakobson and Stockmeyer's theory on intramolecular reactions within polycondensations elucidated the equilibrium between macrocycles and linear polymers in concentrated solutions.⁴⁴ This equilibrium defines a critical monomer concentration at a given temperature, with high concentrations favouring linear polymers and low concentrations promoting cyclic formation (Figure 1.3).

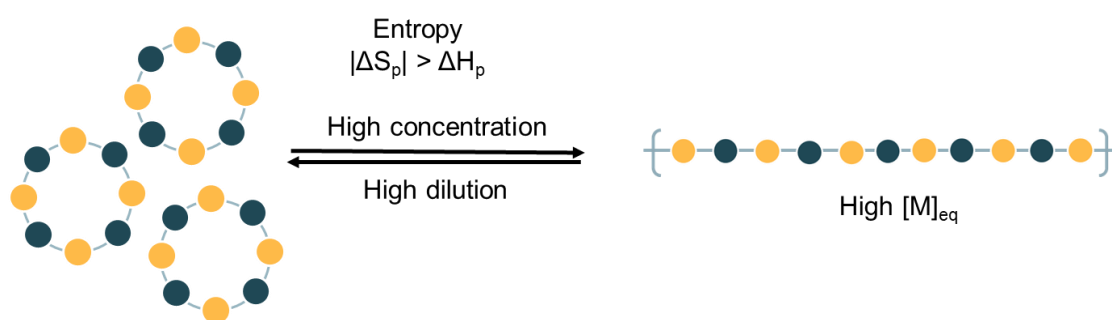


Figure 1.3 Ring-chain equilibria.

Macrocycles experience little to no strain in their molecular structure because the atoms within the ring can arrange themselves in a way that closely resembles their preferred bonding distances and angles. In this case, the enthalpy changes are insignificant in the polymerisation process, and the changes in entropy become the primary driving force. Two key contributors are the entropy of mixing and the increase in conformational entropy upon ring opening.^{45, 46} The former refers to the natural tendency of systems to move towards a state of maximum disorder with a preference for a mixture of monomers, oligomers, and polymers.⁴³ Additionally, as the macrocycle is opened, the resulting molecule gains rotational and torsional freedom, leading to an increase in the number of possible arrangements.⁴¹ Together, these entropic forces

facilitate high monomer conversion during ED-ROP. As a consequence of the nature of the polymerisation process, the resulting polymer exhibits a characteristic most probable distribution of molar masses ($\bar{D} = M_w/M_n \approx 2$).⁴¹

However, in dilute conditions, concentration-dependent translational entropy enhances for both macrocycles and linear polymers. Owing to their mobility, the increase is more advanced in individual cyclic molecules, shifting the equilibrium towards cyclic formation.⁴³ Consequently, neat polymerisation conditions are favoured for ED-ROP to increase the conversion of macrocycles to linear polymers. Under neat polymerisation conditions, macrocycles can account for less than 2% of the final product.⁴² In most cases, there is a solubility difference between the macrocycles and their corresponding polymer, which can be used to isolate the polymer from the macrocycles by polymer precipitation.

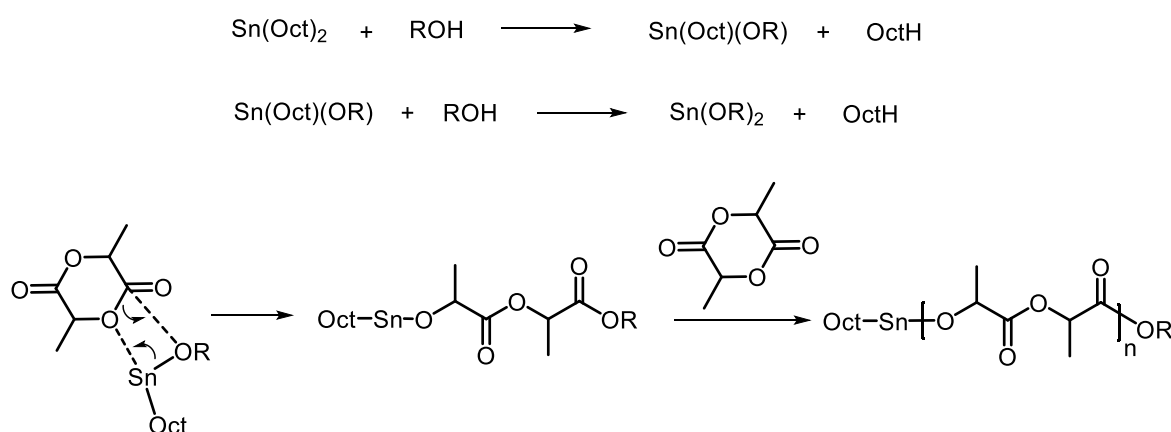
1.3.3 Catalysts for ROP

The polymerisation kinetics of a cyclic monomer are directly influenced by the choice of catalyst. Selecting the right catalyst is essential to ensure the polymerisation proceeds efficiently within a reasonable time while maintaining precise control over molecular weight, polymer dispersity, and chain structure. Catalysts used in this process are generally categorised into metal-based and organic catalysts, each offering distinct advantages and disadvantages.

1.3.3.1 Metal-based Catalysts

Aliphatic polyesters are conveniently synthesised through metal-catalysed ROP owing to their high reactivity and versatility of the metal-ligand systems. Among the most popular catalysts for both academic and industrial applications are tin(II) and

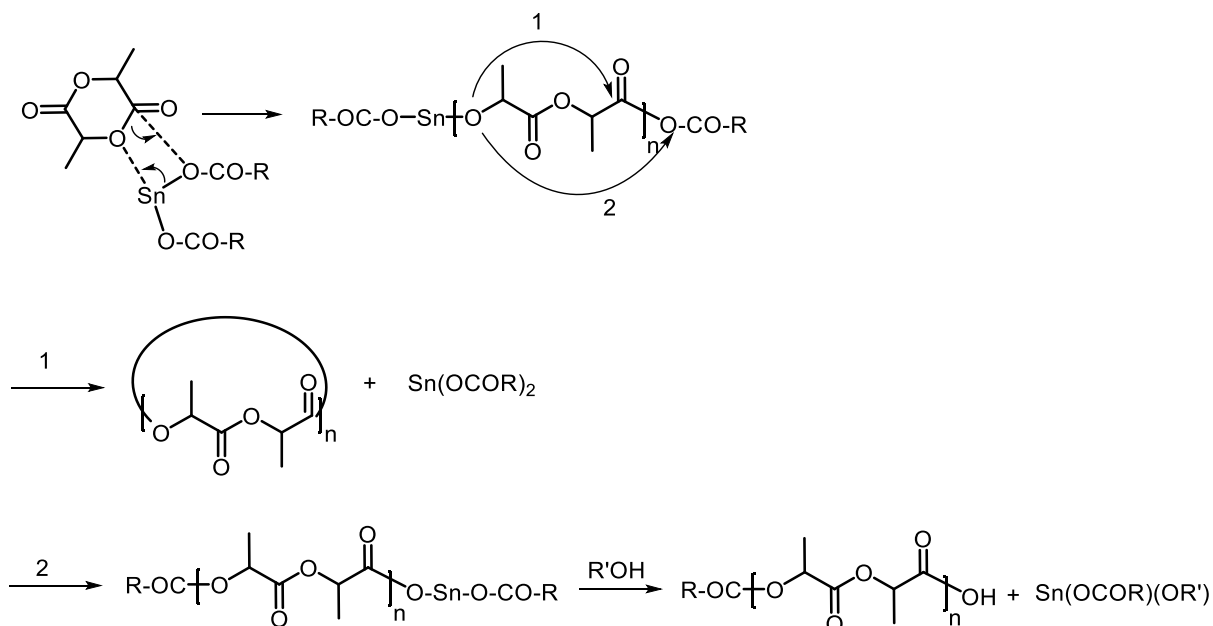
tin(IV) alkoxides or carboxylates. Tin (II) 2-ethylhexanoate, also called stannous octoate ($\text{Sn}(\text{Oct})_2$), is particularly prevalent in the commercial production of polylactides from cyclic dimers. While several coordination-insertion mechanisms have been proposed for $\text{Sn}(\text{Oct})_2$, it is commonly understood that the $\text{Sn}(\text{Oct})_2$ first converts to tin(II) monoalkoxide [$\text{Sn}(\text{Oct})(\text{OR})$] or dialkoxide [$\text{Sn}(\text{OR})_2$], which serve as the true initiators in ROP, as they are more nucleophilic than the Sn-carboxylate group (Scheme 1.3).^{47, 48} The presence of the tin alkoxide intermediate has been directly observed using matrix-assisted laser desorption/ionisation time-of-flight mass spectroscopy (MALDI-ToF MS) during the polymerisation of lactide (LA) and ϵ -caprolactone (ϵ -CL).⁴⁹ Therefore, introducing a protic reagent, such as an alcohol, often accelerates the reaction.⁴⁸ Excessive amounts of protic reagent can also lead to chain transfer reactions, limiting molecular weight and increasing dispersity; thus, the amount and type of protic reagent should be chosen carefully. Without protic additives, impurities within the monomer or $\text{Sn}(\text{Oct})_2$, such as water and octanoic acid, may serve as co-initiators.⁴⁷



Scheme 1.3 Mechanism of the alcohol-initiated and $\text{Sn}(\text{Oct})_2$ catalysed ROP of lactide, adapted from Kricheldorf and Weidner.⁵⁰

Recently, another mechanism has been suggested for $\text{Sn}(\text{Oct})_2$ catalysed ROP, particularly polymerisation at temperatures around or above 160 °C. At high

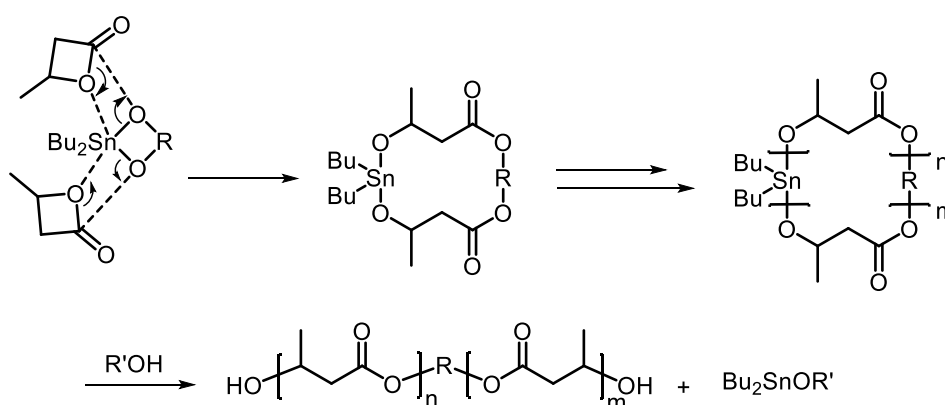
temperatures, neat $\text{Sn}(\text{Oct})_2$ becomes highly reactive and rapidly polymerises lactide without alcohol, making nearly all PLLA cyclic when the lactide to catalyst ratio exceeds 1000:1.⁵¹ Kricheldorf and Weinder suggested that the ROP-POC (ring-opening polymerisation with concurrent polycondensation cyclisation) mechanism, in which two end groups of a polymer chain react with one another to form a cyclic polymer, is responsible for the formation of cyclic polymers, especially when the concentration of active species is low (Scheme 1.4).⁵² Additionally, cyclic species form through the back-biting reaction, which increases at temperatures above 130 °C and with prolonged reaction times. This process is inevitable when preparing high-molecular-weight PLLA at elevated temperatures, which is why commercial PLLA typically contains 1–3% cyclic content, representing the predominant species in mass spectra in the mass range below 6000 $\text{g}\cdot\text{mol}^{-1}$.⁵¹



Scheme 1.4 ROP-POC mechanism of $\text{Sn}(\text{Oct})_2$ catalysed lactide polymerisation, adapted from Kricheldorf and Weidner.⁵¹

Other catalysts developed for ROP of lactide are predominantly based on metal alkoxide complexes, such as $\text{Al}(\text{OiPr})_3$, $\text{Sn}(\text{OBu})_2$, and Bu_3SnOMe . These systems

offer the advantage of the alkoxide group serving as both the catalyst ligand and the initiator, which can start the polymerisation process without the need for co-initiators. This dual functionality can minimise side reactions and enhance control over molecular weight distribution. Cyclic dibutyl tin(IV) alkoxide species also exemplify this class of catalysts, following a ring-expansion polymerisation (REP) mechanism (Scheme 1.5).⁵³⁻⁵⁶ The catalyst, acting as an initiator, becomes covalently attached to the polymer chain, obtaining cyclic polyesters. As the Sn–O–CH bonds are unstable and prone to hydrolysis and alcoholysis at room temperature, the linear polymers can be isolated at the end of the reaction when exposed to air or precipitated in methanol.⁵⁷



Scheme 1.5 REP of β -Butyrolactone reported by Kricheldorf and Lee.⁵⁸

Tin compounds are the most used initiators and catalysts for ROP of cyclic esters, owing to their excellent performance and ease of synthesis. However, concerns about their toxicity to living organisms have prompted researchers to explore less harmful alternatives. Bismuth salts and complexes have emerged as promising options because of their very low toxicity. Bismuth salts like acetate, subcarbonate, subcitrate, and subsalicylate have long been used as internal and external medications, particularly for treating gastrointestinal conditions.⁵⁹ In fact, the toxicity of various heavy metals on kidney tubules was assessed, and bismuth salts (Bi^{3+}) were found to be less toxic than zinc (Zn^{2+}), a metal essential to human nutrition.⁶⁰ Therefore, significant

efforts have since been focused on developing bismuth-based compounds as less toxic and efficient catalysts for the ROP of cyclic ester monomers. Tin compounds and their bismuth analogues share many similarities, particularly in their reactivity in transesterification. Following the studies made with tin complexes, it is expected that initiators and catalysts containing bismuth-alkoxide groups would demonstrate the highest reactivity.⁵⁹ However, simple bismuth alkoxides, $\text{Bi}(\text{OR})_3$, are challenging to synthesise and exhibit low thermal stability compared to tin alkoxides.^{61, 62} As an alternative triphenyl bismuth (Ph_3Bi), commercially available, have been reported as a catalyst and found highly effective ROP catalyst in δ -valerolactone, ϵ -caprolactone and lactide.^{19, 63, 64} It was suggested that Ph_3Bi converts to bismuth monoalkoxide or dialkoxide groups that initiate the polymerisation, a mechanism similar to $\text{Sn}(\text{Oct})_2$ catalysed ROP.⁶³

1.3.3.2 Organic Catalysts

While significant progress has been achieved with organometallic catalysts for ROP, the resulting polymers are often contaminated with metal impurities, which can negatively affect the performance of biodegradable polymers, or polymers in biomedical and microelectronic applications. In this context, organocatalysts have gained attraction in the past 20 years as they provide the advantage of acting as a catalyst without the residual metal contaminants. The first organocatalyst reported in polymerisation was 4-dimethylaminopyridine (DMAP) to produce PLA with excellent molecular weight control and narrow dispersity.⁶⁵ Following this study, the field of organocatalysis rapidly expanded, offering highly reactive and selective catalysts as promising alternatives to traditional organometallic catalysts, including N-heterocyclic carbenes such as 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),⁶⁶ bicyclic

guanidine bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),⁶⁷ thiourea/amines,⁶⁸ phosphines,⁶⁹ and phosphazenes. Additionally, Brønsted acids, such as methanesulfonic acid (MSA), trifluoromethanesulfonic acid (TFA),⁷⁰ and diphenyl phosphate (DPP),⁷¹ were also identified as effective catalysts for the ROP of cyclic esters.

Although many organocatalysts have been optimised to suit various reaction conditions, solvents, and monomers, their reliance on low temperatures and solvent-based systems limits their industrial applicability. An emerging strategy to enhance the thermal stability of organocatalysts is the use of hydrogen bond donor-acceptor complexes.⁷²⁻⁷⁶ Recent studies have investigated several ionic organocatalysts created by combining bases such as imidazole (IM), TBD, DMAP, and DBU with acids including MSA, TFA, and benzoic acid (BA) (Figure 1.4). Notably, some of these catalysts have demonstrated stability and efficiency at significantly elevated temperatures (≥ 150 °C). For example, Jehanno *et al.* reported that a 1:1 mixture of TBD and MSA forms a highly stable protic ionic complex capable of catalysing the glycolysis of PET, also effective in the self-condensation of BHET at 250 °C, resulting in new PET with a molecular weight of $12 \text{ kg}\cdot\text{mol}^{-1}$.⁷³ Building on this concept, Anderre *et al.* examined a combination of MSA and DMAP, achieving the production of stereoregular PLLA with a molecular weight of $40 \text{ kg}\cdot\text{mol}^{-1}$ under bulk conditions at temperatures as high as 180 °C.⁷⁵

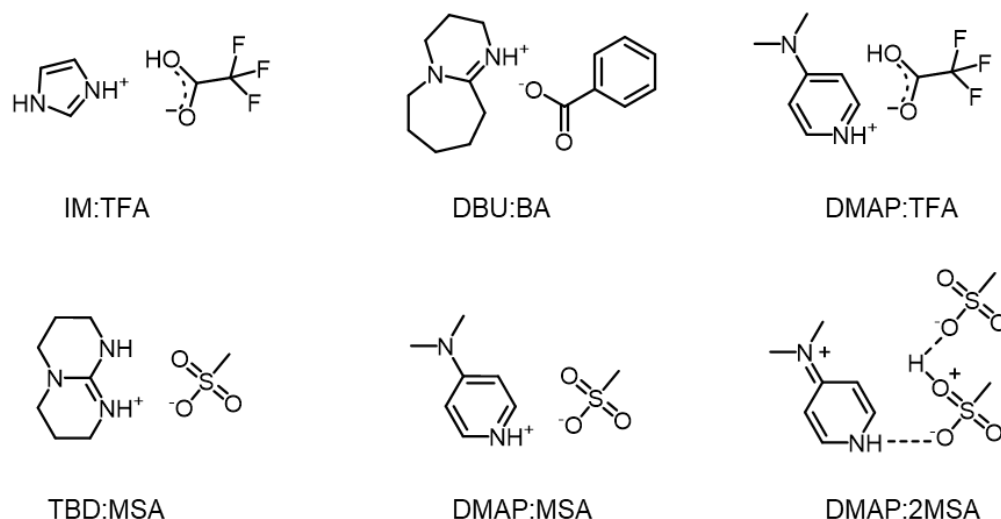


Figure 1.4 Chemical structures of some acid-base ionic organocatalysts.

1.4 Closed-loop Recycling

1.4.1 Circular Approach for Sustainable Plastics

Biodegradable polymers offer a solution to the persistent problem of non-degradable plastic waste, particularly for single-use items that are difficult to collect and recycle. While biodegradable polymers have seen significant commercial success, their degradation into CO₂ and H₂O yields no recoverable material or energy, making them economically inefficient.⁷⁷ To address this, the development of closed-loop recyclable polymers is essential.

At the end of their lifecycle, chemically recyclable materials that can be depolymerised back into their original monomers can then be polymerised to create new polymers with the same quality as virgin materials. This ideal "monomer-polymer-monomer" cycle represents a truly circular approach (Figure 1.5).⁷⁸ Aliphatic polyesters produced through the ROP of lactones show promise in this area. ROP's success in chemically recyclable polymers is attributed to the lower energy required for polymerising heterocyclic monomers and lower T_c value than vinyl polymers.⁷⁹ In

theory, the concept of depolymerisation is thermodynamically possible for every polymer however, balancing depolymerisability and thermal stability is a key challenge. Polymers with low T_c may prematurely degrade during use, while those with high T_c are energy-intensive and prone to degradation during depolymerisation.⁸⁰ Therefore, polymers derived from heterocyclic monomers have great potential in chemical recycling due to their moderate T_c values (>250).⁸¹

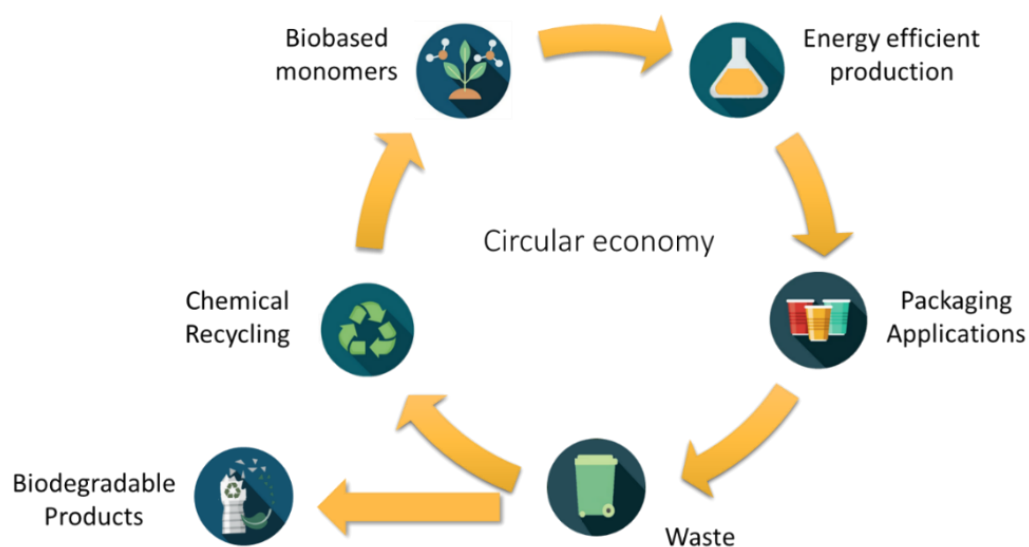


Figure 1.5 Ideal circular economy model for plastics.

1.4.2 Monomer-Polymer-Solvent Interactions

The critical temperature, T_c , is well-established to be concentration-dependent, decreasing at lower monomer concentrations. Consequently, thermodynamic equilibrium can be shifted towards depolymerisation by reducing monomer concentration or increasing temperature. Apart from concentration, experimental evidence indicates that the surrounding conditions of cyclic monomers and the corresponding polymer (type of solvent or its absence) influence the monomer-polymer equilibrium; thereby influencing T_c . For example, Odelius *et al.* employed Hildebrand solubility parameters (δ_s) to demonstrate that solvents with a stronger affinity for the

monomer can promote T_c depression and PLA depolymerisation under milder conditions, highlighting the potential for monomer selectivity.⁸² Olsén *et al.* further contributed to this, proposing that lower polarity solvents increase ring strain in 2-allyloxymethyl-2-ethyl-trimethylene carbonate monomer, favouring polymerisation, while higher polarity solvents reduce ring strain, promoting depolymerisation.⁸³ Solvent polarity also influences polymerisation entropy; higher polarity solvents create a more ordered solvent network, reducing the entropy increase during polymerisation, whereas lower polarity solvents exhibit less ordered structures, leading to a larger entropy gain.⁸³ While solvents with higher interactions with monomers than the polymer can influence the equilibrium in the depolymerisation direction, they can also be useful during purification processes, taking advantage of the solubility difference between macrocycles and their polymers. Li *et al.* have established a chemical recycling method of poly(ethylene adipate), PEA, in a solvent that dissolves the polymers only at high temperatures.⁸⁴ By doing so, they easily isolated the cyclic ethylene adipate oligomers by precipitating the remaining polymer from the depolymerisation solution after cooling to room temperature (Figure 1.6).

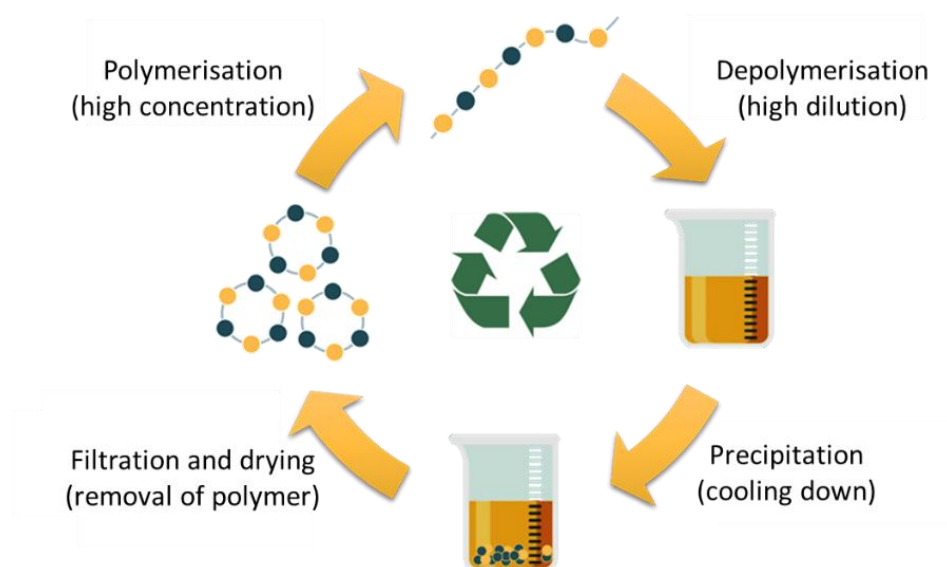


Figure 1.6 Depolymerisation-polymerisation cycles with monomer isolation.

1.4.3 Catalysts for Chemical Recycling

Thermodynamic conditions favouring depolymerisation ($T > T_c$) are necessary but insufficient for spontaneous depolymerisation of terminated chains. Once polymerisation is halted by catalyst removal or deactivation, the polymer becomes kinetically trapped and stabilised by the energy barrier. To initiate the depolymerisation of these chains, sufficient energy to surpass this energy barrier is required along with necessary thermodynamic conditions.⁸⁵ Effective catalysts can significantly lower the energy barrier, accelerating depolymerisation, thereby improving monomer recovery efficiency and reducing energy consumption.⁸⁰

Tin octanoate, di-n-butyltin oxide, and di-n-butyltin alkoxides such as di-n-butyltin methoxide, di-n-butyltin butoxide, and cyclic stannoxane are commonly employed due to their ability to facilitate transesterification reactions inherent to cyclo-depolymerisation of polyesters and give high yields of macrocycles.^{82, 84, 86-89} Metal halides, such as stannous chloride, zinc chloride, ferric chloride, magnesium chloride or manganese chloride, could also promote depolymerisation and cyclisation; however, it has been shown previously that the depolymerisation yields do not exceed 5-20%.^{88, 90, 91} Enzymatic depolymerisation of polyesters into cyclic oligomers is also achievable using lipase enzymes such as *Candida antarctica* lipase B. This enzyme successfully catalysed the depolymerisation of poly(hexamethylene terephthalate) and poly(hexamethylene furanoate) (PHMF),⁹² poly(butylene adipate) (PBA) and PBS,⁹³ PCL,^{94, 95} PHB,⁹⁶ and PES⁹⁷ into their corresponding cyclic oligomers.

1.5 Synthesis of Macrocyclic Esters for ROP

Although ROP is a promising method for polyester production, the limited availability of cyclic esters remains a major challenge. Commercially and naturally sourced lactones such as ϵ -caprolactone, lactides, and ω -pentadecalactone, represent a small subset of available options. Various synthetic routes have been explored in the literature to obtain cyclic esters from diacids and diols, primarily involving either exploiting ring-chain equilibria or employing direct chemical cyclisation methods.

1.5.1 Ring-Chain Recycling

As detailed in Section 1.4, the ring-chain equilibrium can be manipulated to favour cycle formation. Two primary methods have been employed for this purpose. The first involves establishing an equilibrium between linear and cyclic species followed by the continuous removal of cyclic products through high vacuum distillation. While this approach presents a potential for scale-up, its applicability is limited to a few volatile cyclic monomers. Alternatively, a highly diluted reaction environment (<3 wt%) can be created to promote cycle formation. This method, commonly utilised at the laboratory scale, faces challenges in scaling up due to the requirement for substantial solvent volumes and extended reaction times.⁹⁸

Despite these limitations, cyclo-depolymerisation has proven to be a versatile technique for synthesising a range of macrocycles. Inspired by the pioneering work of Carothers *et al.*, which demonstrated the production of macrocycles from aliphatic diols and diacids using metal halide catalysts,⁹⁰ subsequent research has expanded the scope of this method to encompass various diol-diacid-based cyclic oligoesters, including ethylene furanoate,⁹⁹ ethylene adipate,⁸⁴ and dimethyl furandicarboxylate.⁵⁴

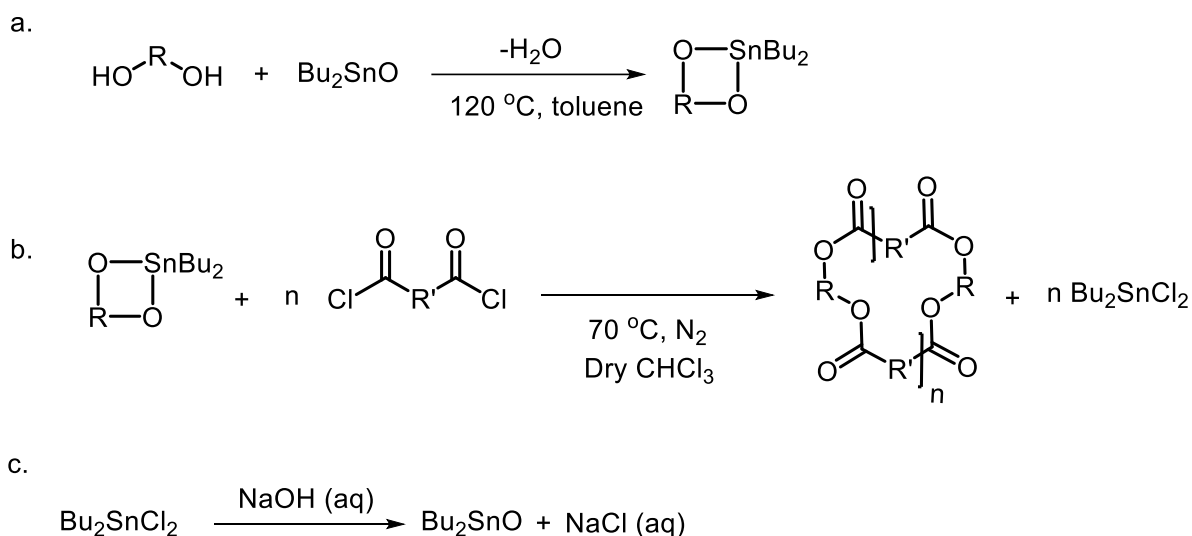
1.5.2 Pseudo-high dilution condensation

The high dilution depolymerisation technique favours cyclic formation by reducing the probability of two monomers reacting to form back the linear chain. Brunelle *et al.* refined this technique by slow addition and simultaneous mixing of diacid and diol at low concentrations typically below 0.2 M, eliminating the need for larger solvent volumes, characteristic of traditional high-dilution methods.⁵³ This approach requires the presence of unhindered tertiary amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO), which facilitates rapid and complete reactions, and using anhydrous solvents. When the rate of addition of the starting reactants is slower than the rate of the condensation reaction, the reaction occurs under high dilution conditions. This method suits macrocycles that, once formed, are stable under the reaction conditions and it has been successfully applied to synthesise various macrocyclic esters, including butylene succinate,¹⁰⁰ ethylene succinate,⁹⁷ 2,5-furandicarboxylate,¹⁰¹ and ethylene adipate.¹⁰²

1.5.3 Tin Mediated Esterification

In the 80s, Shanzer and colleagues published a series of studies on cyclic dibutyl tin(IV) alkoxides as a template for synthesising cyclic tetra-esters through reaction with diacyl dichlorides (Scheme 1.6).¹⁰³⁻¹⁰⁶ The procedure starts by converting diols into cyclic dibutyltin(IV) alkoxide compounds using Bu_2SnO . The nucleophilic reactivity of diols is enhanced to form macrocyclic esters by condensation with dihalides. Initially proposed as a route to regioselective cyclic tetra-esters, subsequent studies revealed that the method produced an oligomeric distribution of products governed by thermodynamic equilibrium rather than selectivity.¹⁰⁷⁻¹⁰⁹ Nevertheless, cyclic dibutyltin(IV) alkoxides have proven to be a highly efficient transesterification catalyst

for forming macrocyclic oligo-esters from diacyl dichlorides. It functions as both a reagent and catalyst, driving the reaction to equilibrium while consumed. Importantly, the cyclo-oligomerisation proceeds under mild conditions and the tin-containing byproduct (Bu_2SnCl_2) can be readily removed from the reaction mixture through recrystallisation from hexane and can be converted back to Bu_2SnO by base hydrolysis, preventing the continuous consumption of the reagent.¹¹⁰



Scheme 1.6 Synthesis of macrocyclic esters through tin-mediated esterification. a. Diol conversion to cyclic dibutyl tin(IV) alkoxide template; b. Macrocycle formation *via* condensation of cyclic dibutyl tin(IV) with diacyl dichloride; c. Base hydrolysis of Bu_2SnO .

1.6 Packaging Polymers

1.6.1 Barrier Properties and Requirements

In recent years, the packaging industry has increasingly adopted plastic materials as alternatives to traditional materials like aluminium and glass. This shift is driven by the lower production costs and reduced carbon footprint associated with plastics compared to those of traditional materials.^{111, 112} However, while plastics offer advantages like lightweight and durability, they may not be as impermeable to gases

as glass or aluminium. Depending on the product, packaging may need to protect against light, water, CO₂, O₂, aromas or other elements. To address this, the industry has focused on developing new technologies to ensure the suitability of plastic packaging for products that require specific barrier properties to maintain their shelf life which represents the time a product remains of acceptable quality. High water vapour and oxygen permeability can especially compromise the chemical and physical integrity of packaged food and promote microbial growth. However, the classification of barrier grades based on permeability performance is not standardised, as the effectiveness of a barrier material depends on the specific application. For instance, poly(glycolic acid) (PGA) may provide an effective barrier against water vapour for cheese packaging but might not be suitable for instant coffee, which requires a different level of barrier protection. (Figure 1.7).¹¹³

Generally, as the degree of crystallinity increases, barrier properties improve because permanent diffusion primarily occurs in the amorphous regions.¹¹⁴ Consequently, most biodegradable polyesters perform poorly for water and oxygen barrier properties, except for PGA and some PHAs, which demonstrate medium to low oxygen and water permeability due to their high crystallinity.¹¹⁵ The weak barrier performance of polyesters is not solely attributed to low crystallinity but also influenced by other factors, including polymer hydrophilicity, chain mobility and free volume, as well as the chemical nature and size of the permeant.¹¹⁶ For example, polar permeants tend to diffuse more easily through polar polymers; in the case of polyesters, the polar ester linkages increase water affinity, leading to plasticisation of the polymer matrix, expansion of free volume, and enhanced permeability. This greater chain mobility not only facilitates water diffusion but can also promote the transport of other small molecules, such as oxygen. Therefore, the barrier properties of commonly studied

biodegradable polymers need significant improvement to meet the high standards required for food packaging, demanding strong gas and water vapour resistance.

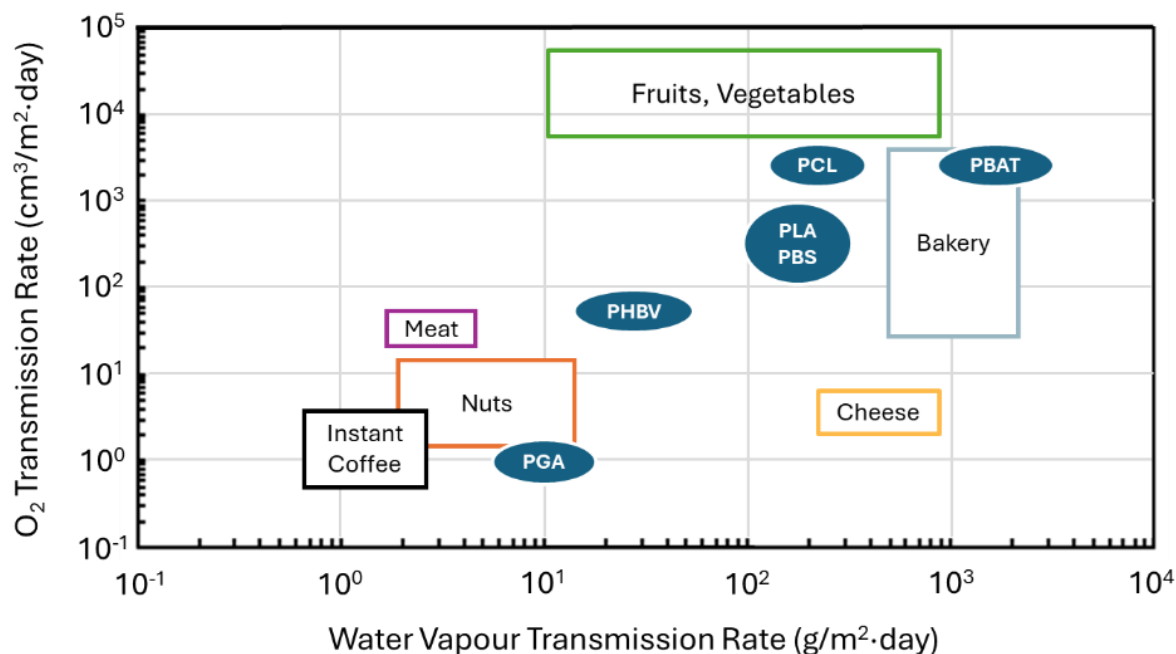


Figure 1.7 Barrier requirements for selected food packaging, adapted from Wang *et al.*¹¹⁷ combined with oxygen/moisture permeability data of biodegradable polymers: poly (glycolic acid) (PGA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), PLA, PBS, PCL, PBAT.¹¹⁵

1.6.2 Measurement of Barrier Properties

The gas barrier properties of a polymer refer to its ability to resist gas penetration and the challenges associated with gas passage. Gas and vapour permeation through a polymer occurs following several steps: first, the permeant is absorbed into the polymer matrix; next, it undergoes solubility and diffusion from areas of high concentration to low concentration across the matrix; finally, the permeant desorbs from the opposite surface (Figure 1.8).¹¹⁸ These barrier properties are typically assessed using metrics such as transmission rate, permeation, or permeability, which describe the underlying mechanisms of gas transport. The transmission rate indicates the volume or weight of a permeant that passes through a film per unit area over time,

under equilibrium conditions. Permeance, on the other hand, is the transmission rate divided by the partial pressure difference of the permeant across the film. Permeability is particularly useful for comparing different polymers, as it is calculated by multiplication of the permeance and the film thickness, making it independent of thickness. However, it is important to note that permeability measurements can vary when taken at different thicknesses, even after normalising for thickness.

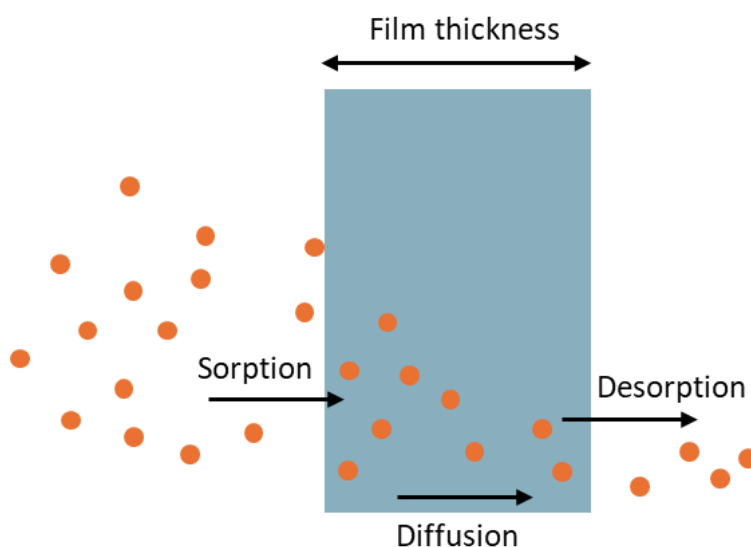


Figure 1.8 Permeation of small molecules through polymer matrix.

A material does not have a uniform permeability for all gases or vapours. The transmission rate varies depending on the specific gas, and in some cases, even on different isotopes of the same vapour.¹¹⁹ A material may allow water vapour to pass through easily while resisting the flow of others like oxygen, carbon dioxide, or hydrocarbons. Additionally, factors such as the pressure difference across the material and the temperature significantly influence gas transmission. Therefore, vapour permeability is typically reported for specific materials at defined temperatures, material thicknesses, and vapour partial pressures.

Permeability is independent of thickness and allows for the comparison of barrier properties across different materials under similar testing conditions (e.g., temperature, relative humidity, and pressure). The vapour permeability of a material is mathematically described by the Eq 1.5:

$$\frac{dM_{gas}}{dt} = P \frac{A \Delta p}{l} \quad \text{Eq. 1.5}$$

where P is the permeability, dM_{gas} is the amount of gas passing through the barrier, dt is the time it takes for gas to pass through the barrier, A is the surface area of the barrier, l is the film thickness, and Δp is the partial pressure difference across the barrier.

The transmission rate or permeability of a gas or vapour through a polymer can be measured using various methods. O_2 permeation (PO_2) is typically measured according to ASTM D3985 standards, typically using an analyser from MOCON, which uses a coulometric sensor to quantify the amount of oxygen passing through the film.¹²⁰ Water vapour transmission rates (WVTR) are generally measured following ASTM E96 using a gravimetric desiccant method where the change in weight of a small container partially filled with water and a polymer film sealing is measured.¹²¹ However, other methods to measure PO_2 and WVTR may produce data varying in magnitude and units. Regardless of the units used, they should accurately reflect key factors like the area the gas passes through, the time to reach equilibrium, pressure difference, and material thickness (Table 1.1). Since permeability and transmission rates are affected by environmental conditions, it is essential to report the characterisation temperature and relative humidity alongside these values.

Table 1.1 Most common units for barrier parameters.

Barrier Property	Equation	Unit
Water Vapour Transmission Rate	$\frac{\text{weight passes through}}{\text{area} \cdot \text{time}}$	$\text{g/m}^2 \cdot \text{day}$
Water Vapour Permeability	$\frac{\text{WVTR} \cdot \text{thickness}}{\text{saturated pressure} \cdot \Delta \text{RH}\%}$	$\text{g} \cdot \text{mm/m}^2 \cdot \text{day} \cdot \text{Pa}$
Oxygen Transmission Rate	$\frac{\text{Volume passed through}}{\text{area} \cdot \text{time}}$	$\text{cm}^3/\text{m}^2 \cdot \text{day}$
Oxygen Permeability	$\frac{\text{OTR} \cdot \text{thickness}}{\text{O}_2 \text{ partial pressure difference}}$	$\text{cm}^3 \cdot \text{mm/m}^2 \cdot \text{day} \cdot \text{atm}$

1.6.3 Mass Transfer in Polymeric Films

The permeation of gases or vapours through polymeric materials is determined by the polymer matrix's ability to absorb and diffuse the penetrant, a process known as the "solubilisation-diffusion" mechanism. The exchange of penetrants between the polymer packaging and its external environment is influenced by both thermodynamic and kinetic factors. To clarify the impact of these factors and better understand changes in barrier properties, gas and vapour permeation through films is typically discussed in terms of solubilisation and diffusion separately. Thus, permeability (P) is primarily related to diffusion (D) and solubility (S), as shown in Eq. 1.6.

$$P = D \cdot S \quad \text{Eq. 1.6}$$

The diffusion coefficient (D) describes the movement of low molecular weight penetrants through polymer chains, typically derived from Fick's first law of diffusion, which relates the flux (F) to the concentration gradient, assuming the diffusion occurs only in the direction between the two surfaces of the polymer film.¹²² It assumes that the rate of mass transfer is proportional to the concentration gradient, which is considered to be linear over the distance travelled (Eq 1.7).

$$F = -D \frac{dc}{dx} \quad \text{Eq. 1.7}$$

where c is concentration, x is the direction of diffusion, and dc/dx is the concentration gradient along the flow direction. In steady-state conditions, in which the system reaches equilibrium and the permeant concentrations on both sides of the film, c_1 and c_2 , are constant, Eq. 1.7 can be integrated over the entire thickness of the film (l) (Eq. 1.8)

$$F = D \frac{c_1 - c_2}{l} \quad \text{Eq. 1.8}$$

When the concentrations on both sides of the film are constant, F can also be described as the amount of permeant (Q) passing through a surface of unit area (A) per unit of time (t) (Eq 1.9).

$$F = \frac{Q}{At} \quad \text{Eq. 1.9}$$

By replacing F with Q/At in Eq 1.8:

$$Q = D \frac{(c_1 - c_2)At}{L} \quad \text{Eq. 1.10}$$

For gases, it is more practical to measure the equilibrium pressure (p) in relation to the polymer, rather than the actual concentration within the polymer. At low concentrations and assuming no interaction between the permeant and the polymer, Henry's law applies,¹²² allowing c to be expressed as:

$$c = S \cdot p \quad \text{Eq. 1.11}$$

where S is the solubility coefficient, characterises the dissolution of a penetrant in a polymer. Applying 1.10 to 1.8:

$$Q = DS \frac{(p_1 - p_2)At}{L} \quad \text{Eq. 1.12}$$

Which can be arranged with Eq. 1.6 as:

$$P = DS = \frac{QL}{(p_1 - p_2)At} = \frac{QL}{At\Delta p} \quad \text{Eq. 1.13}$$

Δp is the pressure gradient of the permeant on both sides of the polymeric film. It can be seen from this equation that gas purity, environmental humidity, and temperature will influence the pressure gradient. Therefore, humidity and temperature must be labelled when the permeability or transmission rate is reported.

1.7 Project Aims and Objectives

This thesis aims to expand the understanding and practical applicability of PES, a biodegradable polyester, by exploring ROP routes for its synthesis and end-of-life recycling. Traditional methods such as polycondensation typically yield low molecular weight PES with broad dispersity and require high energy inputs, limiting its performance and scalability. Although recent studies have demonstrated the potential of ROP using macrocyclic esters for other aliphatic polyesters, a comprehensive investigation of this approach for PES remains underexplored.

The primary objective of Chapter 2 is to establish an efficient synthetic pathway for PES via ROP of ethylene succinate macrocycles. This includes the use of low-toxicity metal catalysts, solvent-free conditions, and short reaction times, developments that contrast with prior literature that relied on tin-based catalysts and

less sustainable methods. Moreover, the work pioneers the chemical recycling of PES by demonstrating its depolymerisation back to macrocycles under thermodynamically controlled conditions, enabling a closed-loop lifecycle.

Chapter 3 aims to tailor the properties of PES through copolymerisation with commercial lactones such as ϵ -caprolactone and δ -valerolactone. While copolymerisation is a known strategy to improve polymer flexibility and processability, its impact on PES barrier performance has not been systematically studied. This thesis addresses that gap by correlating copolymer composition with mechanical properties and gas permeability, comparing the results with conventional and biodegradable alternatives.

In Chapter 4, the scope of macrocyclic monomers is expanded through the synthesis of novel ethylene fumarate macrocycles. Linear and cyclic ethylene fumarate oligomers were used as resins for thiol-ene crosslinking to understand the network properties based on their topology and *cis/trans* isomerism. This work introduces topologically distinct oligomers as resins for thiol-ene photocuring, enabling a fundamental comparison of how molecular architecture governs thermomechanical and swelling properties of the resulting networks.

Together, the chapters build a coherent narrative from polymer design to synthesis, property optimisation, and circularity. The research aims not only to extend the synthetic methods for biodegradable polyesters but also to provide a platform for designing recyclable materials with tailored performance for sustainable packaging applications.

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Chapter 2: Synthesising High Molecular Weight Poly(ethylene succinate) and Its Chemical Recycling through Ring-Chain Equilibria

2.1 Introduction

Biodegradable polymers are potential alternatives for short-term food packaging as they can be composted with food waste, reducing environmental impact.¹ While biodegradable polyesters such as poly(lactic acid) (PLA), poly(caprolactone) (PCL), polybutylene adipate terephthalate (PBAT), and poly(butylene succinate) (PBS) have gained interest as an alternative to traditional plastics, they often have limitations associated with their degradation rate under environmental conditions, and/or their barrier properties.²⁻⁶ In contrast, poly(ethylene succinate) (PES), a flexible semicrystalline polymer with melting temperature (T_m) around 100 °C and glass transition temperature (T_g) around -10 °C, represents promising sustainable food packaging material due to its exceptional biodegradability. Many microorganisms readily break down PES faster than other aliphatic polyesters like PBS and PLLA.⁷⁻¹⁶

Typically, PES is produced by polycondensation, which requires high vacuum conditions and elevated temperatures to remove condensation byproducts and achieve desired molecular weights and polymer properties. As the reaction progresses and viscosity increases, removal of byproducts becomes more challenging, extending the reaction time. The prolonged exposure to high temperatures (≥ 230 °C) not only drives up production cost and energy consumption but also leads to thermal degradation of PES, resulting in low molecular weights, poor mechanical properties and decolouration of the final product.¹⁷ All of these production challenges hinder PES commercialisation.

Ring-opening polymerisation (ROP) is preferred for polymerising strained lactones and amides, offering milder reaction conditions and shorter reaction times compared to polycondensation. These advantages enable the synthesis of polyesters

with controllable molar mass, narrow molecular weight distribution ($1 \leq \bar{D}_M \leq 1.5$) and well-defined end groups. However, when applied to macrocyclic esters that are unstrained, ROP becomes an entropically driven process (ED-ROP), which complicates the achievement of controllable molecular weights, narrow molecular weight distributions and desired end group fidelity due to the equilibration process.¹⁸ Despite these challenges, ED-ROP can still be advantageous over polycondensation as it can achieve high yields and high molecular weight polymers with a less energy-intensive polymerisation. For instance, polycondensation polymers such as PBS, poly(ethylene adipate) (PEA), poly(ethylene furanoate) (PEF), and poly(butylene furanoate) (PBF) have been obtained through ED-ROP from their macrocyclic oligomers.¹⁹⁻²⁴

These macrocycles are not naturally existing molecules; thus, a precursor step is required to produce cyclic oligomers of condensation polymers. Existing methods of synthesising cyclic esters from dicarboxylic acids and diols, such as high dilution condensation and cyclo-depolymerisation, can be resource-intensive and complex, involving large amounts of solvent or vacuum distillation and laborious purification steps. For example, Morales-Huerta *et al.* presented an important first example of the ROP of ethylene succinate macrocycles with an enzymatic approach *via Candida antarctica* lipase B (CALB), which is considered a green catalyst.²⁰ They synthesised the macrocycles through high dilution condensation, reacting ethylene glycol, dimethyl succinate, and 100 wt% CALB relative to the total monomer concentration. Although this method provided a successful route to macrocycle formation, it required a highly diluted mixture (0.02 M) and a reaction time of 48 h, followed by a 24 h enzymatic polymerisation. The resulting polymer's weight average molecular weight (M_w) was measured as $65 \text{ kg}\cdot\text{mol}^{-1}$ with a dispersity ($(\bar{D}_M = M_w/M_n)$) of 1.7 by size exclusion

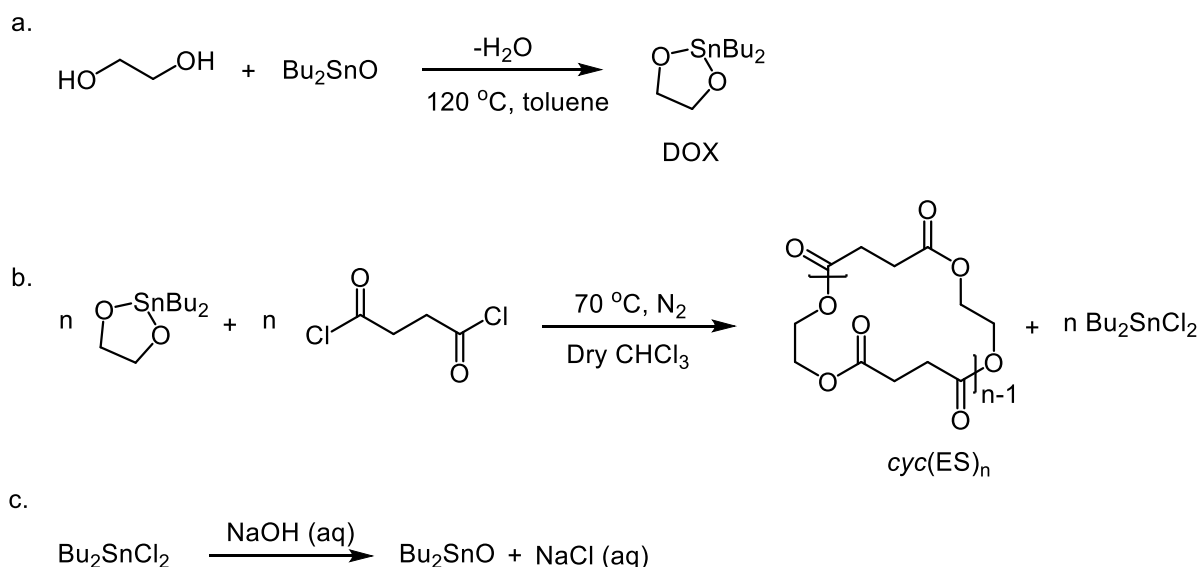
chromatography (SEC) relative to poly(methyl methacrylate) (PMMA) standards; however, the mechanical properties of the resulting polymer were not investigated. Therefore, this chapter aimed to develop a more efficient and practical process to obtain PES in high molecular weights that can exceed the critical molecular weight (M_c) and investigate the mechanical properties of the final product. Polymers typically exhibit enhanced properties such as tensile strength and elongation at their critical molecular weight, typically 2 times the polymer's entanglement molecular weight ($M_c \approx 2M_e$).²⁵ The M_c of PES was determined by analysing the time and temperature data collected during oscillatory shear rheology tests on the melted material.

In order to obtain ethylene succinate macrocycles $\text{cyc}(\text{ES})_n$ in high yields, tin-mediated esterification was chosen as an efficient method that does not require high solvent usage or vacuum distillation.²⁶ Then, the ED-ROP of $\text{cyc}(\text{ES})_n$ was investigated in terms of temperature and catalyst, resulting in PES surpassing the M_c . Moreover, by tuning the ring-chain equilibria between $\text{cyc}(\text{ES})_n$ and PES, a closed-loop chemical recycling pathway from PES to $\text{cyc}(\text{ES})_n$ was also established, offering a fully circular process and a potential replacement for the non-sustainable plastics currently employed in the market.

2.1 Result and Discussion

2.2.1 Cyc(ES)_n synthesis

The cyc(ES)_n was obtained by tin-mediated esterification.²⁷ It involves the reaction of dibutyltin(IV) oxide (Bu₂SnO) with ethylene glycol to obtain 2,2-dibutyl-1,3,2-dioxastannolane (DOX) through azeotropic distillation in toluene. The following reaction is a condensation of DOX with succinyl chloride (Scheme 2.1). Dibutyltin(IV) dichloride (Bu₂SnCl₂) was formed at the end of the reaction and isolated by recrystallisation from hexane. Cyc(ES)_n was further purified by silica gel plug in 80% yield. Although not explored in this study, isolated Bu₂SnCl₂ can be converted to Bu₂SnO to recover reagents for monomer synthesis (Scheme 2.1c).²⁸



Scheme 2.1 Synthesis of cyc(ES)_n through tin-mediated esterification.

High-performance liquid chromatography-mass spectrometry (HPLC-MS) was used to determine the ring size distribution in the cyc(ES)_n, which showed that it was dominated by dimeric rings, followed by trimers and progressively smaller quantities of larger rings and monomeric rings (Figure 2.1). Decreasing the concentration of the

reaction media or increasing the succinyl chloride (SC) to DOX ratio slightly shifted the distribution towards smaller oligomers.

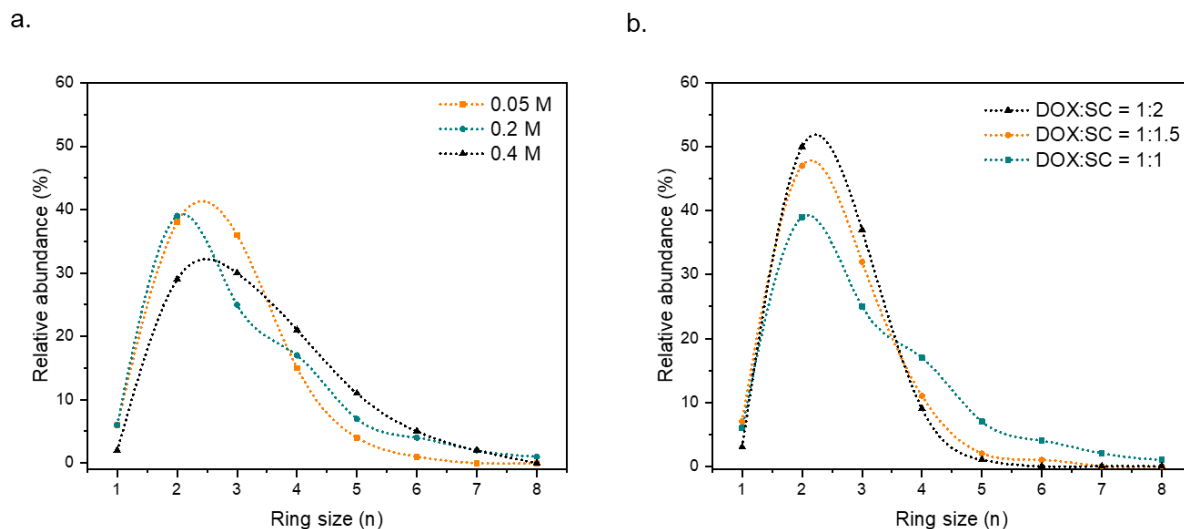


Figure 2.1 Ring size distribution obtained from chromatographic separation in HPLC-MS a. Reactions were conducted at different concentrations in chloroform with 1:1 SC to DOX ratio, b. Reactions were conducted at 0.2 M concentration in chloroform with different SC to DOX ratios.

2.2.2 Polymerisation of $\text{cyc}(\text{ES})_n$

ROP of $\text{cyc}(\text{ES})_n$ is an entropy-driven process (ED-ROP), where the increase in conformational freedom upon the ring opening of unstrained macrocycles ($\Delta H \approx 0$) favours the reaction. This reaction benefits from high monomer concentrations that limit the translational entropy by restricting individual molecule mobility. Moreover, elevated temperatures decrease the Gibbs free energy of polymerisation by the $-T\Delta S$ term. Therefore, a temperature screen was first conducted in solvent-free conditions to optimise the entropy gain. Polymerisations were carried out using commercially available tin octanoate ($\text{Sn}(\text{Oct})_2$, 0.2 mol%) catalyst at 125, 150 and 175 °C, temperatures above the polymer's melting point ($T_m \approx 100$ °C) but below the degradation temperature of macrocycles ($T_{d,5\%} = 200$ °C, measured by thermal gravimetric analysis, TGA). As expected, the conversion rate and the number average

molecular weight (M_n) increased with temperature, reaching $65.2 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 1.58$) at 175°C after 5 h and $30 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 2.54$) at 150°C after 10 h (Figure 2.2). A decrease in M_n was observed after prolonged reaction times, which indicates the attainment of ring-chain equilibrium.

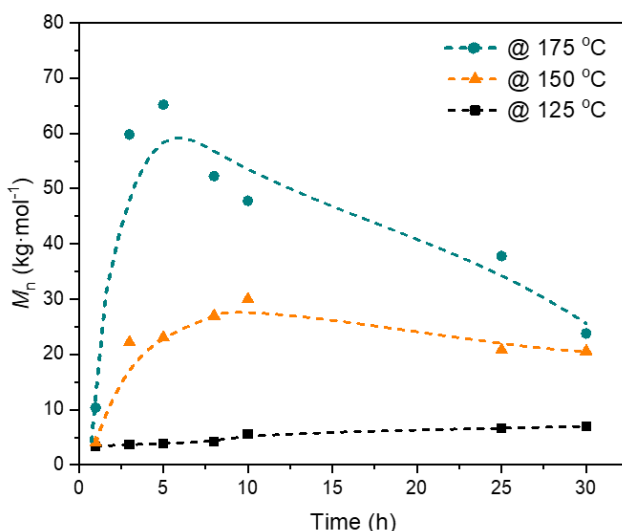


Figure 2.2 Effect of temperature and time on M_n evolution in ROP of $\text{cyc}(\text{ES})_n$ carried out in the presence of $\text{Sn}(\text{Oct})_2$ (0.2 mol%) in the melt.

Subsequently, ROP at 175°C was investigated with various catalysts, including an ionic complex of 4-(dimethylamino)pyridine (DMAP) with two equivalents of methanesulfonic acid (MSA), triphenyl bismuth (Ph_3Bi) and DOX (Figure 2.3). DMAP-MSA (1 mol%), chosen as a thermally stable organocatalyst,²⁹ was combined with benzyl alcohol as an initiator ($[\text{M}]_0:[\text{I}]_0 = 100$). However, it fell short of the targeted M_n ($28 \text{ kg}\cdot\text{mol}^{-1}$), achieving $5.2 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 1.86$). Metal-base catalysts DOX and Ph_3Bi were used in the same ratio as $\text{Sn}(\text{Oct})_2$ (0.2 mol%) without an additional initiator. DOX catalyst was readily available from the first step of $\text{cyc}(\text{ES})_n$ synthesis (Scheme 2.1a), obtained polymers with a maximum M_n of $34.8 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 1.59$). Bismuth compounds are recognised for their lower toxicity than other metal-based catalysts,³⁰ and Ph_3Bi , achieving an M_n of $66.5 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 1.32$) within 1 h, demonstrating superior ROP efficiency compared to $\text{Sn}(\text{Oct})_2$. The SEC analysis of the unpurified

polymer showed traces of $\text{cyc}(\text{ES})_n$, with the peak areas reflecting the relative concentrations of components in the product mixture. At equilibrium, the system was found to consist of approximately 95% polymer, consistent with the expected ring-chain equilibrium characteristic of the ED-ROP process.

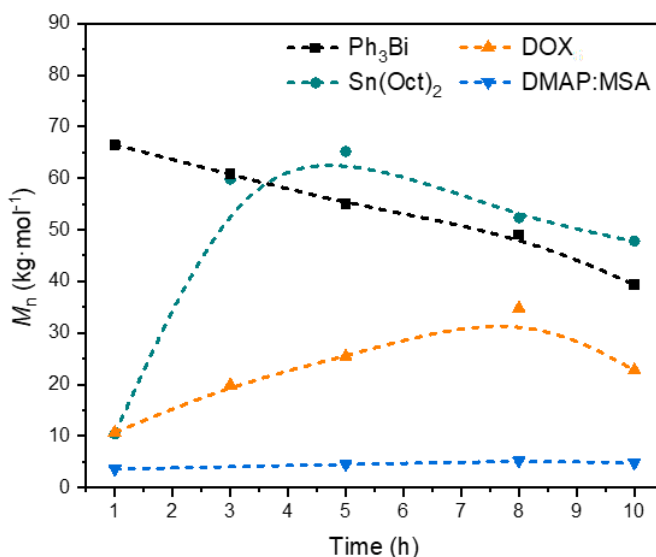


Figure 2.3 Evolution of M_n of PES in ROP of $\text{cyc}(\text{ES})_n$ at 175 °C using Ph_3Bi , $\text{Sn}(\text{Oct})_2$, DOX and DMAP:MSA as a catalyst carried out in the melt.

2.2.3 Thermomechanical Properties of PES

High molecular weight polyesters are crucial for manufacturing materials with desirable processing characteristics and mechanical performance. Higher molecular weights beyond a critical value (M_c) generally enhance tensile strength and elongation. PES production through polycondensation is usually reported as 15-25 $\text{kg}\cdot\text{mol}^{-1}$ measured by SEC relative to polystyrene (PS) standards.^{17, 31, 32} To investigate the effect of molecular weight, PES was scaled up to 3 g, obtaining PES with 70 $\text{kg}\cdot\text{mol}^{-1}$ and 27 $\text{kg}\cdot\text{mol}^{-1}$ respectively, as determined by SEC (relative to PS standards). Their absolute molecular weight measurements using an SEC system equipped with multi-angle light scattering detection (SEC-MALS) revealed that the M_n were 42.7 $\text{kg}\cdot\text{mol}^{-1}$ ($\mathcal{D}_M = 1.5$) and 24.6 $\text{kg}\cdot\text{mol}^{-1}$ ($\mathcal{D}_M = 1.6$), respectively.

TGA, as expected, revealed a correlation between molecular weight and thermal stability in PES. As M_n increased from 24.6 kg·mol⁻¹ to 42.7 kg·mol⁻¹, the temperature at which 5% degradation occurred ($T_{d,5\%}$) rose from 311 °C to 317 °C, and the temperature corresponding to the maximum rate of decomposition ($T_{max\%}$) increased from 380 °C to 400 °C (Figure 2.4).

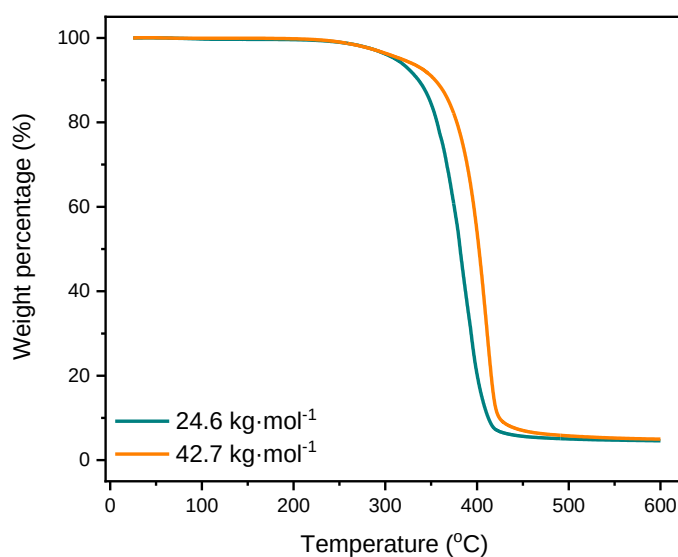


Figure 2.4 TGA thermograms of PES 24.6 kg·mol⁻¹ and 42.7 kg·mol⁻¹ at a heating rate of 10°C/min.

PES is a semicrystalline polymer exhibiting T_m of 97-102 °C and T_g of -11 °C at a heating rate of 10 °C/min after cooling from the melt state at a cooling rate of 10 °C/min (Figure 2.5a). PES typically shows slow crystallisation behaviour, and cold crystallisation from the amorphous phase is expected when the cooling rate is faster than 5 °C/min in differential scanning calorimetry (DSC) analysis. Cold crystallisation behaviour was found to be the same for both polymers ($T_{cc} = 38$ °C, $\Delta H_{cc} = 20$ J/g). Another crystallisation exotherm was observed just before the melting endotherm, which was reported before as the recrystallisation of the melt of the crystallites with low thermal stability.³³ This was at a lower temperature with a smaller endotherm for PES 42.7 kg·mol⁻¹ ($T_{rc} = 76$ °C, $\Delta H_{rc} = 3.7$ J/g) than for PES 24.6 kg·mol⁻¹.

¹ ($T_{rc} = 82\text{ }^{\circ}\text{C}$, $\Delta H_{rc} = 9.6\text{ J/g}$). The molecular weight affects PES's crystallisation behaviour since the chain entanglements hinder the molecular reorganisation from entangled states to crystalline structures. This effect can be seen as the melting endotherm of PES becomes smaller with increasing molecular weight. The final degree of crystallinity (X_c) was found to be 22% for lower M_n PES and 15% for higher M_n PES, calculated using the ratio of $\Delta H_m/\Delta H_m^0$, where ΔH_m is the heat of fusion determined from the sample's heating scan exotherm peak minus the endotherm peaks during heating, while ΔH_m^0 , the heat of fusion for pure crystalline PES (180 J/g).⁸ Dynamic mechanical thermal analysis (DMTA) reveals that the storage (E') and loss (E'') moduli of lower M_n PES exhibit higher moduli than higher M_n PES in both the glassy and rubbery regions (Figure 2.5b). This contradicts the general expectation of an increasing moduli with higher molecular weight. The lower crystallinity and broader molecular weight distribution of higher M_n PES likely contribute to this discrepancy. The glass-transition temperature (T_g), determined from the peak value of E'' , varies slightly based on their molecular weight: 1°C for lower and 3°C for higher M_n PES.

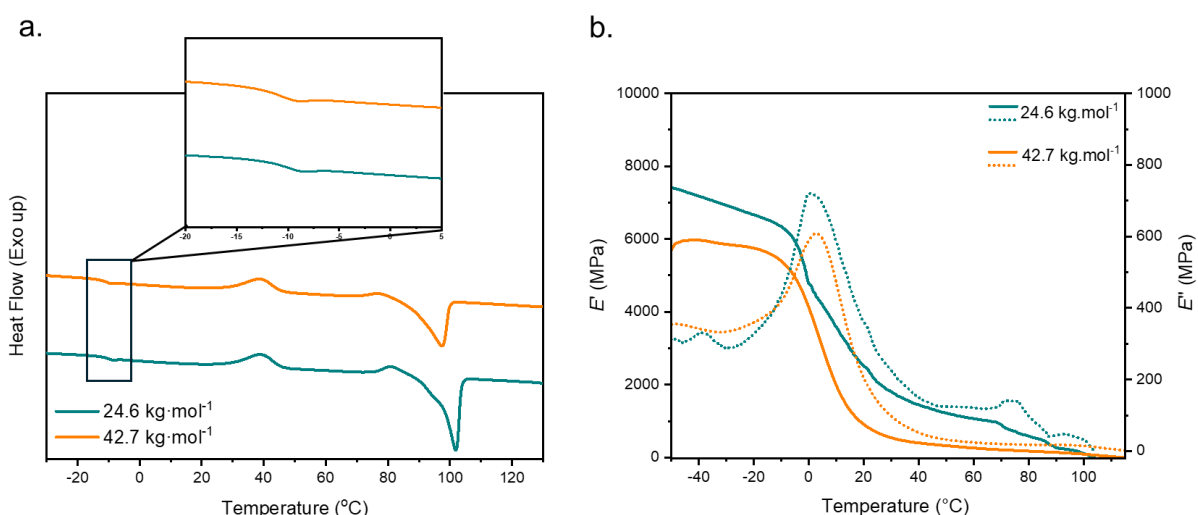


Figure 2.5 Thermomechanical properties of PES of 24.6 and 42.7 kg·mol⁻¹ a. DSC thermogram at a heating rate of 10 °C/min, b. E' and E'' against the temperature of PES films of 24.6 and 42.7 kg·mol⁻¹ analysed in bending mode in DMTA.

Tensile tests were conducted on dog-bone-shaped specimens to compare ultimate tensile strength (σ_B), elongation at break (ϵ_B), Young's modulus (E) and ultimate toughness (U_T) of two PES in different molecular weights. The PES with M_n of $24.6 \text{ kg}\cdot\text{mol}^{-1}$ displayed a tensile strength of $13.1\pm0.6 \text{ MPa}$ and modulus of $845\pm59 \text{ MPa}$. However, its low molecular weight makes it a brittle material with a low ϵ_B of $3.8\pm0.5 \%$ (Figure 2.6). PES with M_n of $42.7 \text{ kg}\cdot\text{mol}^{-1}$ resulted in a softer ($E = 548\pm82 \text{ MPa}$) and much more flexible ($\epsilon_B = 279\pm46 \%$) but also a much stronger material ($\sigma_B = 36.6\pm11 \text{ MPa}$). Consequently, it could be described as a tough material with a toughness (U_T) of $79\pm28 \text{ MJ}\cdot\text{m}^{-3}$. It exhibited a strain-hardening phenomenon after the yield point ($\sigma_Y = 20\pm3 \text{ MPa}$) during a non-uniform necking accompanied by periodical stress fluctuation. The instability of necking has been observed in several thermoplastic polymers, such as amorphous poly(ethylene terephthalate) (aPET), high-density poly(ethylene) (HDPE), syndiotactic poly(propylene) (sPP), and PBS.³⁴⁻

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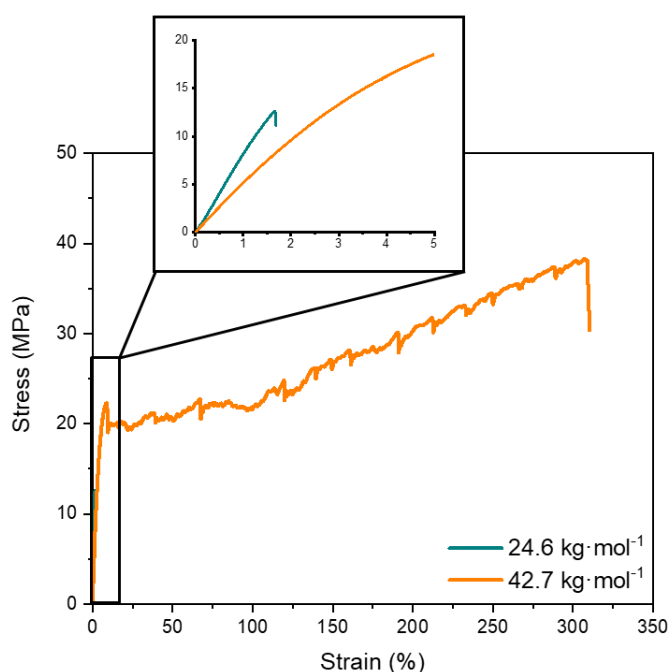


Figure 2.6 Exemplary stress vs strain curves of PES 24.6 and $42.7 \text{ kg}\cdot\text{mol}^{-1}$ (1 mm/min , ambient temperature).

Oscillatory shear rheology was used to determine the molecular weight between entanglements (M_e) and critical molecular weight (M_c), considering the difference in thermomechanical performance upon a change in the M_n of PES from $24.6 \text{ kg}\cdot\text{mol}^{-1}$ to $42.7 \text{ kg}\cdot\text{mol}^{-1}$. Individual frequency sweeps (2.0% strain, 0.1–100 Hz) were run on PES of $42.7 \text{ kg}\cdot\text{mol}^{-1}$ to record the dynamic storage (G') and loss (G'') moduli over a range of temperatures (from 80 to 140 °C with 20 °C increments) within the confines of the linear viscoelastic region. The data was merged into the corresponding time-temperature superposition (TTS) using the principles of Williams-Landel-Ferry theory and referenced to 120 °C to obtain a broader frequency curve between 10^{-1} – 10^5 rad/s (Figure 2.7).³⁸

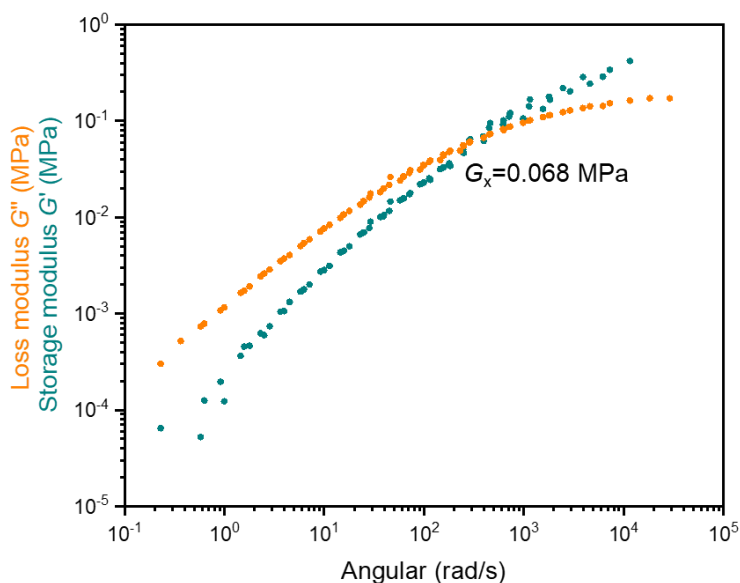


Figure 2.7 Overlay plots of time-temperature superposition curve by rheometer frequency sweeps performed on PES $42.7 \text{ kg}\cdot\text{mol}^{-1}$.

The expanded frequency curve shows the rubbery transition ($G' > G''$) from the viscous flow region ($G' < G''$); however, it does not reveal the plateau region at higher frequencies due to the limited processing window of PES. Therefore, the plateau modulus (G_N^0) was estimated as 0.295 MPa by Nobine-Cocchini's approximation (Eq

2.1) for high dispersity semi-crystalline polymers, where the crossover modulus and the plateau modulus correlated with M_w , M_n and M_z .^{39, 40}

$$\log\left(\frac{G_x}{G_N^0}\right) = \frac{-0.524 + 0.341 \log\left(\frac{M_w}{M_n}\right) - 1.843 \log\left(\frac{M_z}{M_w}\right)}{1 - 0.559 \log\left(\frac{M_w}{M_z}\right) + 0.841 \log\left(\frac{M_z}{M_w}\right)} \quad \text{Eq. 2.1}$$

where G_x is the crossover modulus ($G_x = G' = G''$). Estimated G_N^0 was then used to calculate the M_e according to Eq. 2.2.⁴¹

$$M_e = \frac{\rho RT}{G_N^0} \quad \text{Eq. 2.2}$$

where R is the gas constant ($8.314 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T is the reference temperature in Kelvin (393.15 K), and ρ is the melt density of PES, estimated as 1.24 g/cm^3 from pressure-volume-temperature (PVT) data at 393.15 K atmospheric pressure. M_e was estimated with the given formulations as $13.7 \text{ kg} \cdot \text{mol}^{-1}$, and M_c , typically estimated to be twice M_e , as $27.4 \text{ kg} \cdot \text{mol}^{-1}$, from the Likhtman-McLeish theory.⁴¹

Although these results are tentative due to the approximations in the calculation of G_N^0 , the estimated M_c accurately predicts the tensile behaviour of PES materials. While PES $24.6 \text{ kg} \cdot \text{mol}^{-1}$ is below the estimated M_c and exhibits brittle behaviour, PES $42.7 \text{ kg} \cdot \text{mol}^{-1}$, exceeding the estimated M_c , demonstrates remarkable stiffness, ductility, and toughness. These results support the effectiveness of the ED-ROP technique in producing industrially applicable materials.

2.2.4 Depolymerisation of PES

ED-ROPs take advantage of the dynamic equilibrium between the macrocyclic oligomers and the corresponding polymer in the presence of a catalyst. The position

of this equilibrium is very sensitive to the concentration, shifting towards the polymer at high concentrations and towards the macrocycles at high dilutions. Therefore, cyclo-depolymerisation can be achieved at high dilution. Additionally, a solvent system that selectively dissolves macrocycles at ambient temperatures while retaining the polymer until heated could facilitate a simple separation process through cooling and precipitation at the end of the depolymerisation reaction. To explore this potential, first, a comparative solubility study was conducted, including toluene, xylene, acetonitrile (ACN), *N,N*-dimethylformamide (DMF), chlorobenzene (CL), dichlorobenzene (DCB) and γ -valerolactone (GVL) (Table 2.1). Among these solvents, ACN, DMF, DCB and GVL exhibited the desired solubility difference. However, depolymerisation in DMF showed impurities in each trial, which was speculated to be due to the side reactions involving solvent degradation products at high temperatures, such as dimethylamine and formic acid. Depolymerisation in ACN did not yield any *cyc*(ES), likely due to the low boiling point of the solvent not achieving the ceiling temperature (T_c).

Table 2.1 Solubility of *cyc*(ES)_n and PES in different solvents.

Solvent	<i>cyc</i> (ES) _n	PES (at RT)	PES (at bp of the solvent) ^a
Toluene	-	-	-
Xylene	-	-	-
ACN	+	-	+
CB	+	-	-
DCB	+	-	+
DMF	+	-	+
GVL	+	-	+

^a Observed at the boiling point of the solvent; for toluene at 110 °C, xylene at 139 °C, ACN at 82 °C, CB at 132 °C, DCB at 180 °C, DMF at 153 °C, GVL at 205 °C.

The depolymerisation of PES into cyc(ES)_n was successfully achieved in DCB using Bn₂SnO (3 wt%) as a catalyst at 180 °C. The purification protocol proved effective, as demonstrated by the high purity of ¹H NMR and MALDI-ToF spectra of the resulting macrocycles (Figure 2.8).

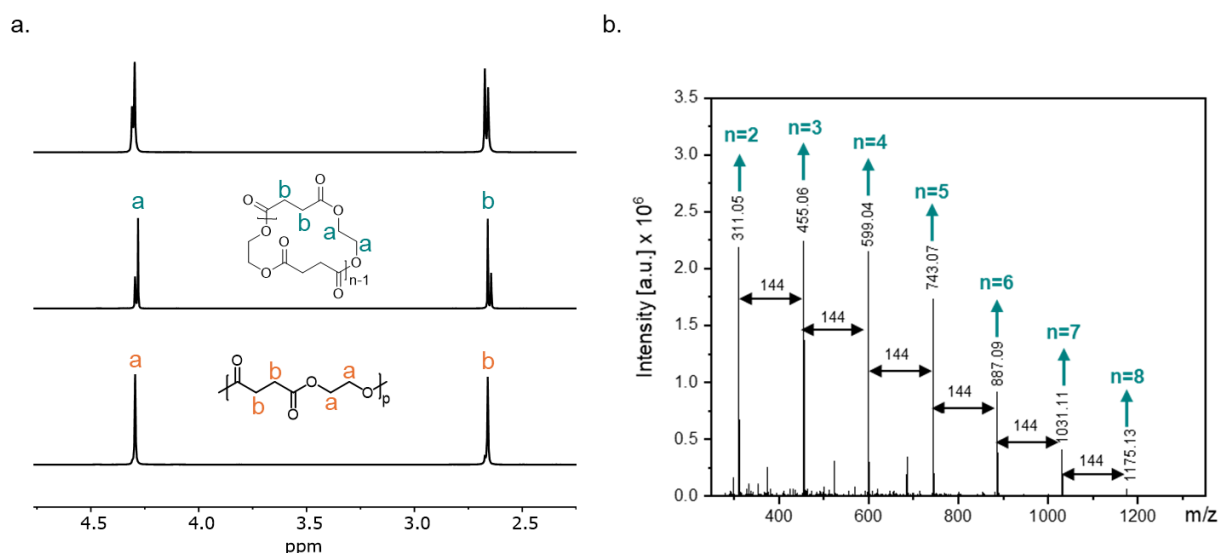


Figure 2.8 a. Stacked ¹H NMR spectra (400 MHz, 298 K, CDCl₃) of depolymerised sample in DCB after purification (top), cyc(ES)_n macrocycles for reference (middle) and PES (bottom); b. MALDI-ToF spectrum of the depolymerised sample in DCB after purification.

Two depolymerisations in DCB were conducted with initial PES concentrations of 25 g/L and 10 g/L, as in previously reported polyester cyclo-depolymerisation conditions.^{42, 43} As expected, higher yields were obtained at lower PES concentrations (Figure 2.9a). However, larger solvent volumes and increased energy consumption for solvent removal reduce the overall efficiency of the process. The rate of increase in yield decreased as the system approached equilibrium, with final yields around 75% and 40% for 10 g/L and 25 g/L concentrations, respectively. HPLC-MS analysis confirmed that the ring size distribution slightly shifted towards larger oligomers at higher PES concentrations (Figure 2.9b).

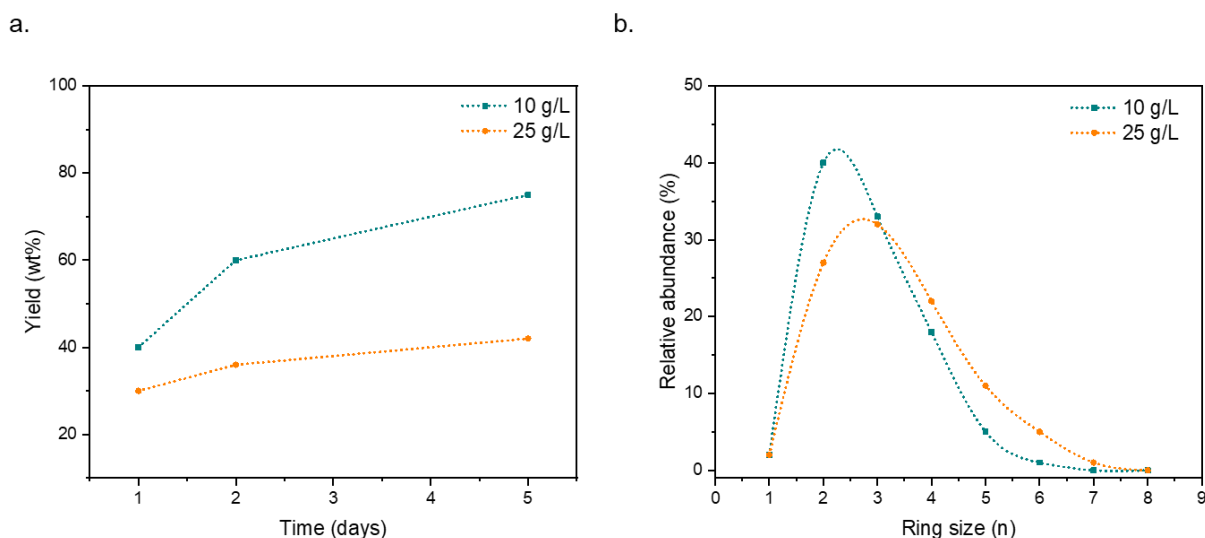


Figure 2.9 a. Depolymerisation yield vs time plot at different reaction concentrations; b. Ring size distribution graph of depolymerisation fractions at different concentrations.

GVL was also explored as a greener alternative to DCB as a depolymerisation solvent. Unlike the toxic and hazardous nature of DCB, GVL is considered a safe and environmentally friendly solvent derived from renewable sources like cellulose or hemicellulose.⁴⁴ First, PES was depolymerised in GVL at 200 °C and a concentration of 25 g/L using the same catalyst (Bu_2SnO , 3wt%), yielding macrocycles with a ring size distribution similar to those obtained in DCB (Figures 2.10a and 2.10b). However, the reaction mixture's darkening and the broadening of peaks in the ^1H NMR spectrum suggested potential product decomposition at this temperature (Figure 2.10c). To prevent the decomposition of $\text{cyc}(\text{ES})_n$, depolymerisation in GVL was attempted at lower temperatures (180 °C and 160 °C), but it was not successful. Unfortunately, these temperatures proved insufficient to promote the recycling of PES, possibly due to being below T_c of the polymerisation-depolymerisation equilibrium in GVL.

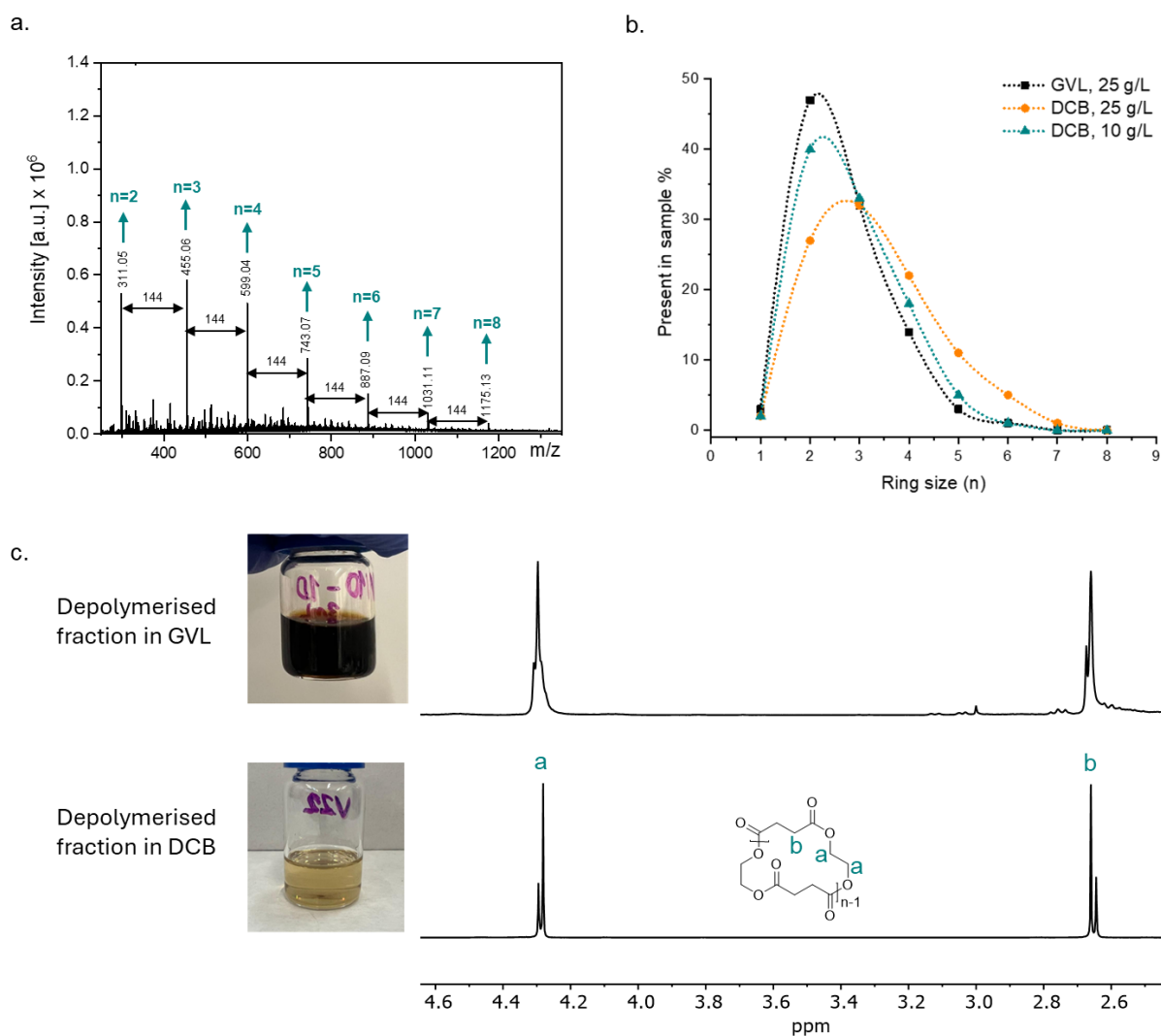


Figure 2.10 a. MALDI-ToF spectrum of the depolymerised sample in GVL after purification; b. Ring size distribution of depolymerisation fractions in different solvents and concentrations; c. Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of sample depolymerised in DCB at 180 °C for reference (bottom) and in GVL at 200 °C with visuals of reaction mixtures.

2.3 Conclusion

In this chapter, the synthesis and polymerisation of poly(ethylene succinate) (PES) from ethylene succinate macrocycles were explored as an alternative to traditional condensation methods. Introducing triphenyl bismuth (Ph_3Bi) as a catalyst enhanced the efficiency of ED-ROP, leading to faster reaction rates and higher molecular weights than the traditional $\text{Sn}(\text{Oct})_2$ catalyst in solvent-free conditions. Through optimisation of reaction conditions, PES exceeding the critical molecular weight (M_c) were synthesised, achieving enhanced mechanical properties critical for industrial applications.

Additionally, the research explored the depolymerisation of PES, an essential step in achieving a closed-loop recycling system. The depolymerisation study demonstrated the importance of solvent selection. While DCB, providing differential solubility to macrocycles and polymers, facilitated the separation and purification steps, side reactions were observed when depolymerisation was conducted in DMF and in GVL. While further work is needed to investigate greener solvents, optimise yield and reduce energy consumption, the progress made in this chapter lays a solid foundation for future advancements in PES recycling. This recyclability, coupled with the ability to tune PES properties through controlled polymerisation, supports the potential of PES in advancing circular economies and reducing reliance on non-sustainable packaging materials. Together, these findings highlight the practical applications and benefits of ED-ROP for the scalable production of high-performance biodegradable PES.

2.5 Appendix

2.5.1 Proton (^1H) NMR Spectra

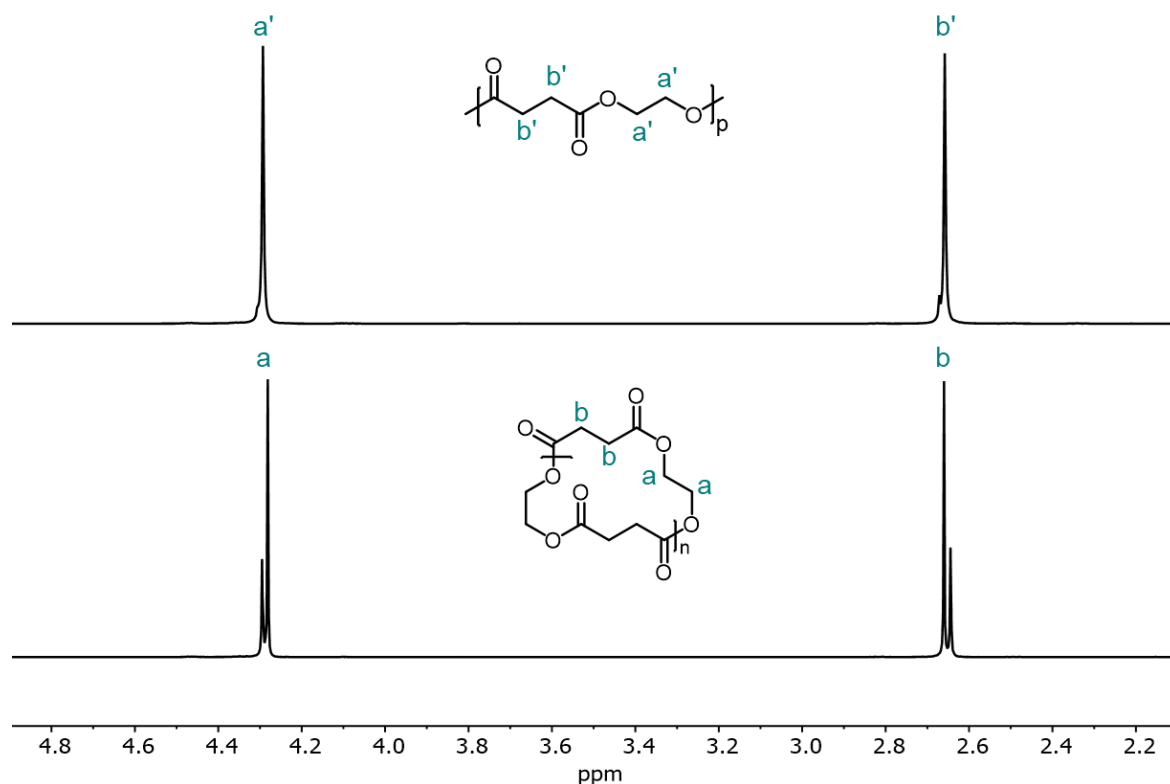


Figure A2.1 Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of cyc(ES) $_n$ (bottom) and PES (top).

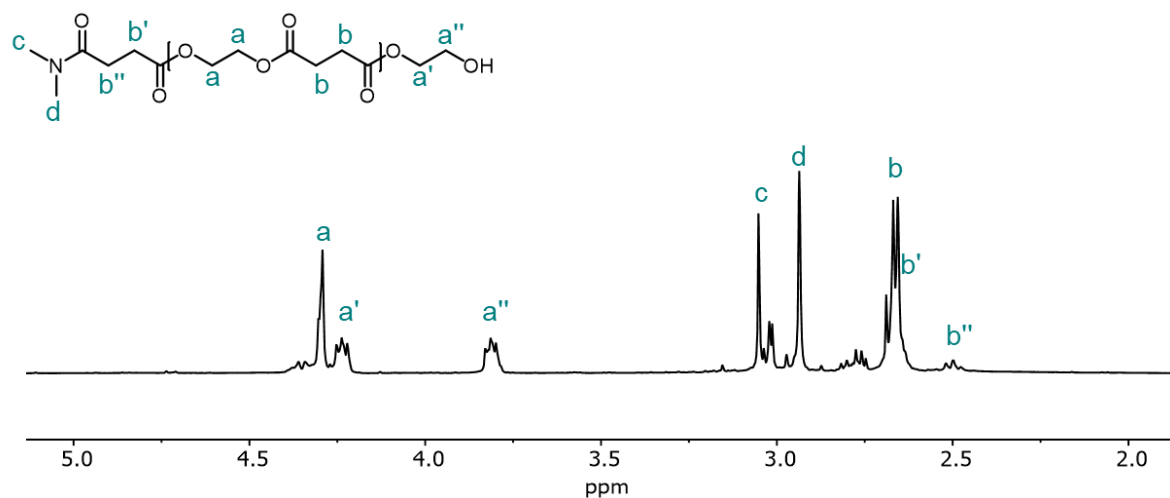


Figure A2.2 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of product depolymerised in DMF.

2.5.2 Carbon (^{13}C) NMR Spectra

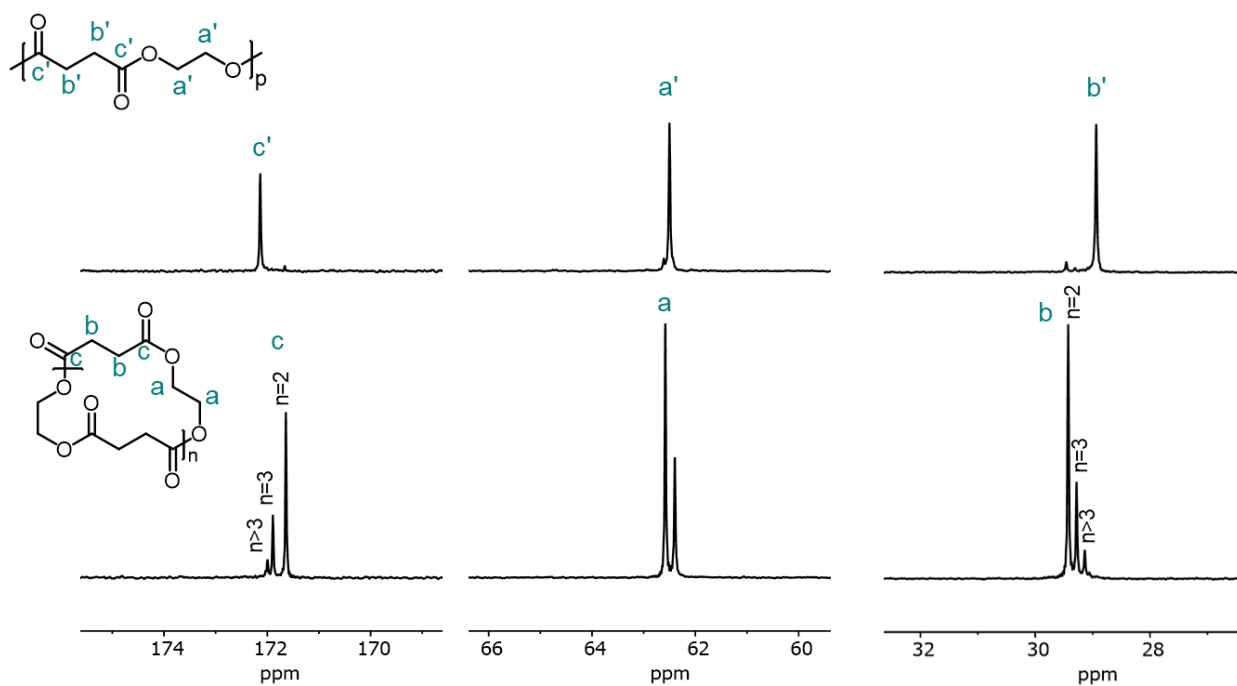
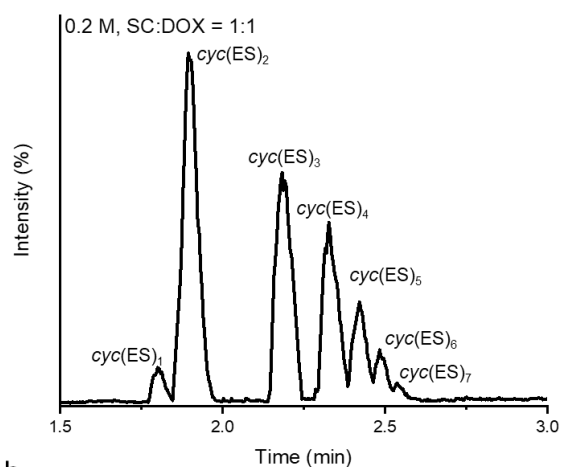


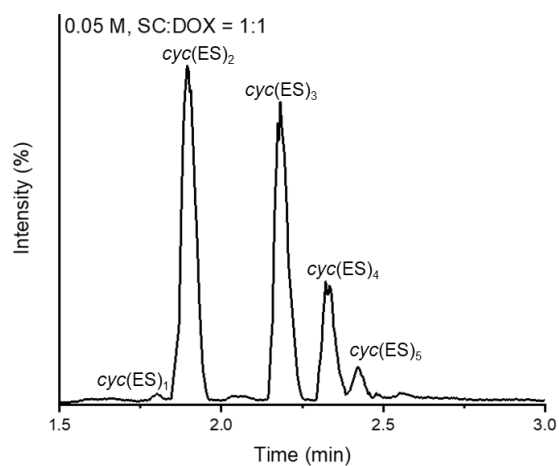
Figure A2.3 Stacked ^{13}C NMR spectra (101 MHz, 298 K, CDCl_3) of $\text{cyc}(\text{ES})_n$ (bottom) and PES (top).

2.5.3 HPLC Chromatograms

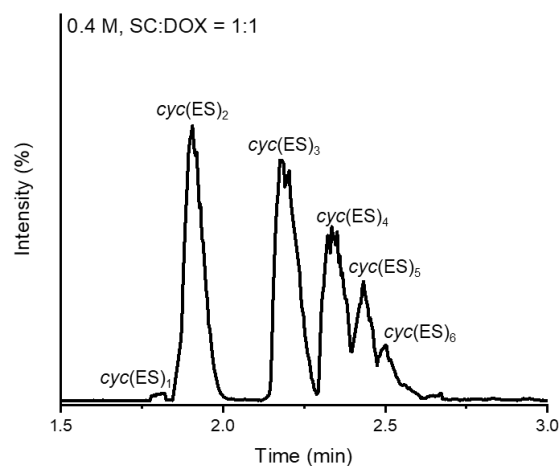
a.



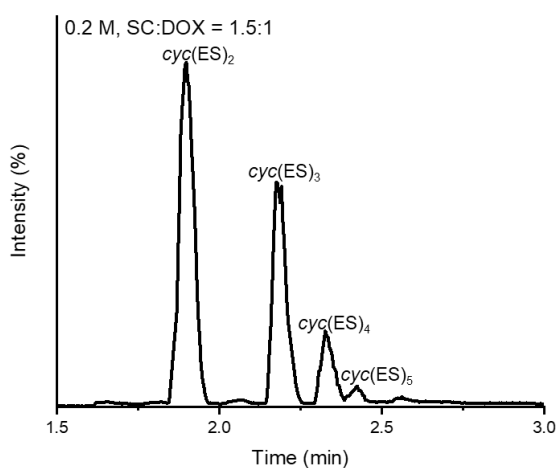
b.



c.



d.



e.

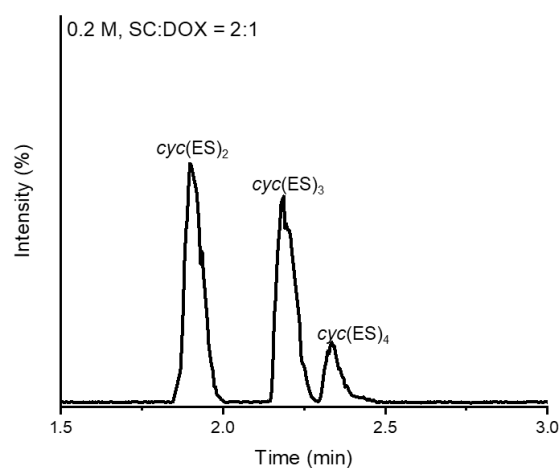


Figure A2.4 HPLC chromatograms of $cyc(ES)_n$ synthesised in different conditions: a. Reaction of SC to DOX 1:1 in 0.2 M; b. Reaction of SC to DOX 1:1 in 0.05 M; c. Reaction of SC to DOX 1:1 in 0.4 M; d. Reaction of SC to DOX 1.5:1 in 0.2 M; e. Reaction of SC to DOX 2:1 in 0.2 M.

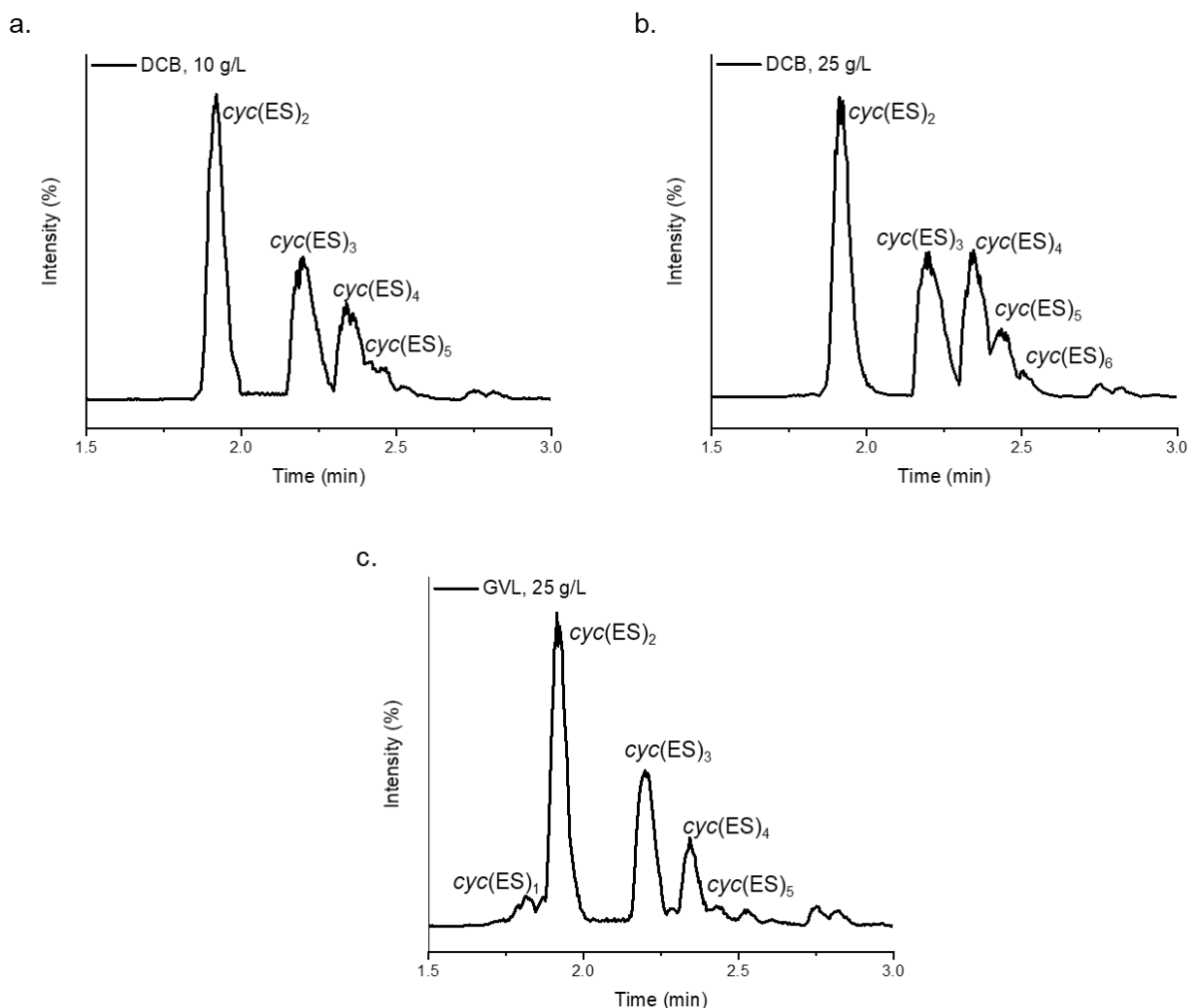


Figure A2.5 HPLC chromatograms of $\text{cyc}(\text{ES})_n$ obtained by depolymerisation of PES
a. in DCB at 10 g/L concentration; b. in DCB at 25 g/L concentration; c. in GVL at 25 g/L concentration.

2.5.4 SEC Data of PES

Table A2.1 SEC^a results of $\text{Sn}(\text{Oct})_2$ (0.2 mol%) catalysed ROP at 125 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	3.4	4.9	1.45
2	3	3.7	6.1	1.60
3	5	3.9	6.3	1.63
4	8	4.2	6.5	1.57
5	10	5.6	16.8	2.96
6	25	6.7	14.9	2.23

^a In CHCl_3 (0.5% NEt_3) eluent, calibrated against polystyrene standards.

Table A2.2 SEC^a results of Sn(Oct)₂ (0.2 mol%) catalysed ROP at 150 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	4	6.4	1.59
2	3	22.2	53	2.48
3	5	23.1	45	1.94
4	8	27	68.7	2.54
5	10	30	76.5	2.54
6	25	20.8	43.3	2.08
7	30	20.6	40.7	1.96

^a In CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.**Table A2.3** SEC^a results of Sn(Oct)₂ (0.2 mol%) catalysed ROP at 175 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	10.4	17.8	1.70
2	3	59.8	89.2	1.49
3	5	65.2	103.4	1.58
4	8	52.3	93.8	1.79
5	10	47.8	83.8	1.75
6	25	37.8	59.7	1.57
7	30	23.8	40.4	1.69

^a In CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.**Table A2.4** SEC^a results of Ph₂Bi (0.2 mol%) catalysed ROP at 175 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	66.5	88.3	1.32
2	3	60.8	95	1.56
3	5	51.6	94.1	1.82
4	8	49.0	61.6	1.25
5	10	39.4	70.3	1.78

^a In CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.

Table A2.5 SEC^a results of DOX (0.2 mol%) catalysed ROP at 175 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	10.7	26.2	2.43
2	3	19.9	33.3	1.67
3	5	25.5	41.9	1.64
4	8	34.8	55.5	1.59
5	10	22.8	43.8	1.91

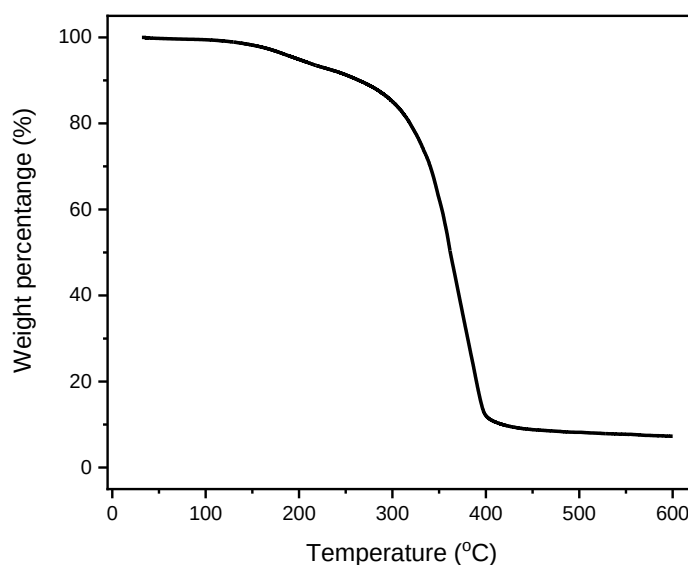
^a In CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.

Table A2.6 SEC^a results of DMAP:MSA ([M]₀: [C]: [I]=100:1:1) catalysed, Benzyl alcohol initiated ROP at 175 °C in melt.

Entry	Time (h)	M_n (kg·mol ⁻¹)	M_w (kg·mol ⁻¹)	$\bar{D}_M$
1	1	3.6	6.2	1.72
2	5	4.5	7.9	1.75
3	8	5.2	9.8	1.86
4	10	4.8	8.5	1.74

^a In CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.

2.5.5 Thermomechanical Properties

**Figure A2.6** TGA thermogram of cyc(ES)_n at a heating rate of 10 °C/min.

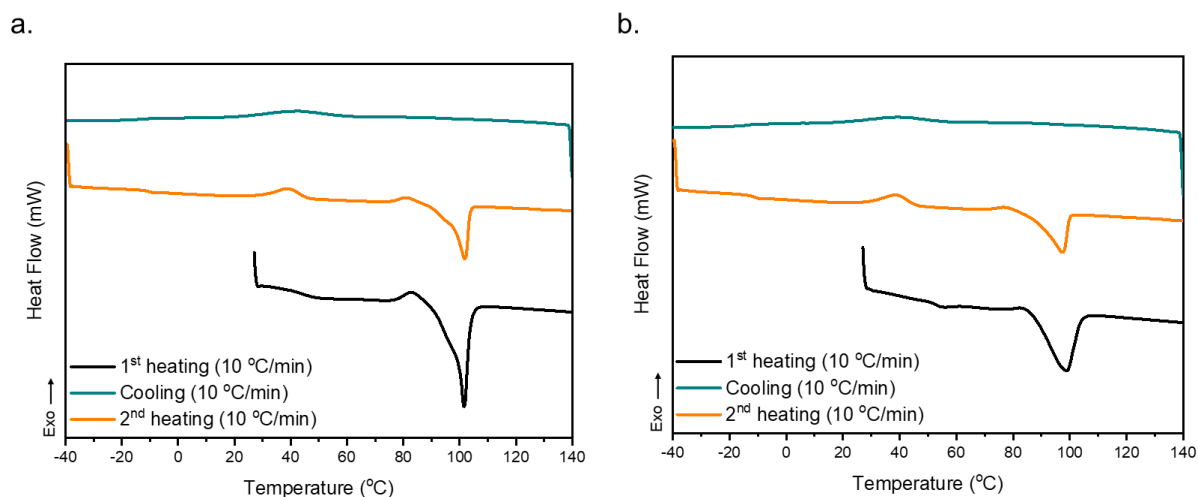


Figure A2.7 DSC thermograms of a. PES 14 kg·mol⁻¹; b. PES 38 kg·mol⁻¹.

Table A2.7 Tensile test results of PES of 14 kg·mol⁻¹.

Entry	E (MPa)	σ_B (MPa)	ϵ_B (%)	U_T (MJ/m ³)
1	889	13.6	3.22	1.318
2	854	13.4	3.95	1.236
3	782	12.4	4.26	1.136

Table A2.8 Tensile test results of PES of 38 kg·mol⁻¹.

Entry	E (MPa)	σ_Y (MPa)	σ_B (MPa)	ϵ_B (%)	U_T (MJ/m ³)
1	525	22	30.4	310	84.6
2	480	22.5	49.2	302	104.4
3	640	16	29.2	226	48.7

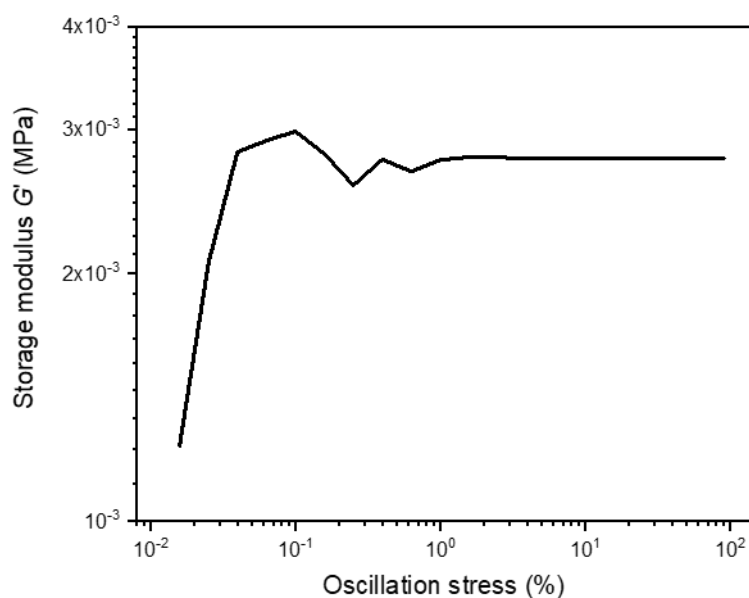


Figure A2.8 Strain sweep of PES at 120 °C and 1 Hz frequency.

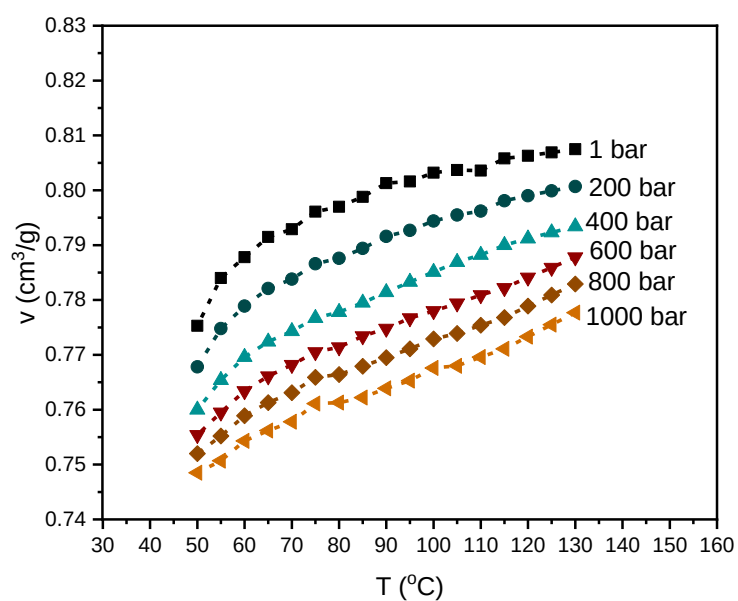


Figure A2.9 The specific volume as a function of temperature at various pressures. Melt density at atmospheric pressure was obtained from extrapolation using the Tait equation (equipment software), 1.24 g/cm³ at reference temperature (120°C).

2.6 References

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Chapter 3: Investigation of Mechanical and Barrier Properties of Poly(ethylene succinate) and Its copolymers for Packaging Applications

3.1 Introduction

The increasing popularity of ready-to-eat foods has driven significant growth in the food packaging market, which is expected to reach USD 411.3 billion by 2025.¹ Plastic packaging plays a crucial role in preserving food freshness and extending shelf life owing to its barrier properties; however, its environmental impact remains a major concern due to its low recyclability. Addressing environmental concerns, biodegradable polymers offer a promising alternative by enabling composting and decomposition within a short timeframe, unlike traditional plastics that persist in landfills for centuries.²

The suitability of biodegradable polymers for food packaging is assessed by their transport properties concerning gases and vapours since high water vapour and oxygen permeability can compromise the chemical and physical stability of packaged foods, potentially accelerating microbial growth.³ Yet, the transition to biodegradable food packaging has encountered considerable challenges. Polylactic acid (PLA), polybutylene succinate (PBS), and polybutylene adipate terephthalate (PBAT), which together made up 36.5 % of global bioplastics production in 2023,⁴ are the most considered alternatives for biodegradable food packaging; still, they have considerably high oxygen and water vapour permeability (above 100 cm³·mil/m²·day).⁵ A few biodegradable polymers, such as polyglycolic acid (PGA) and polyhydroxyalkanoates (PHAs), demonstrate high barrier properties comparable to petroleum-based alternatives like poly(ethylene terephthalate) (PET) or poly(styrene) (PS). However, their high crystallinity limits their melt processability.

To overcome these challenges, copolymerisation has been a frequently used method to improve the properties of biodegradable polymers for targeted applications.

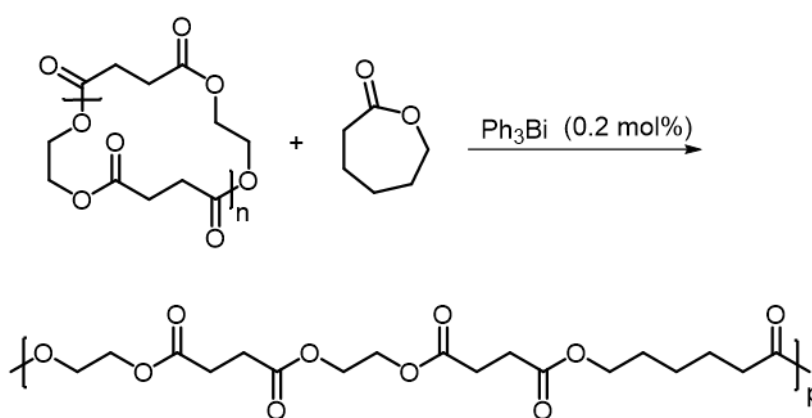
For example, Sangroniz *et al.* demonstrated that copolymerisation of lactic acid with δ -valerolactone (VL) has enhanced the ductility of PLA while the O₂ permeability was also improved with moderate VL additions (up to 19%).⁶ In another study, incorporating small amounts of ϵ -caprolactone (CL) (up to 17%) has been shown to improve the water permeability of PLA.⁷ Both poly(ϵ -caprolactone) (PCL) and poly(δ -valerolactone) (PVL) are known for their biocompatibility and environmental friendliness. They are often used in flexible moulding applications due to their low glass transition temperature (T_g), melting temperature (T_m) and high elasticity.⁸ Similarly, incorporating these inexpensive and commercially available CL and VL monomers into poly(ethylene succinate) (PES) that possess higher glass T_g and T_m could potentially optimise the properties of the resulting copolymer, along with cost reduction.

Ethylene succinate macrocycles (cyc(ES)_n) can be copolymerised with CL and VL, which differs thermodynamically from ring-opening polymerisation (ROP) of cyc(ES)_n alone. Moreover, the difference in one carbon atom between VL and CL can influence the polymerisation rate and the overall end-polymer characteristics differently as they possess different reactivities.⁹ Previously, cyc(ES)_n and CL have been copolymerised using enzymatic catalysis without further exploring the copolymers' mechanical and barrier properties.¹⁰ This chapter investigates the copolymerisation of cyc(ES)_n with VL and CL and the resulting chain microstructures over conversion. While copolymerisation of cyc(ES)_n with CL was optimised and promising results were obtained, VL struggled to achieve high conversions. A comparison of the mechanical and barrier properties of PES homopolymers and their copolymers with CL revealed their suitability for soft packaging applications demanding low oxygen permeability.

3.2 Result and Discussion

3.2.1 Copolymerisation of cyc(ES)_n with CL

In the previous chapter, superior results in monomer-to-polymer conversion, reaction rate and molecular weight were achieved at 175 °C using Ph₃Bi (0.2 mol%) as the catalyst in the ROP of cyc(ES)_n. In this chapter, using the same catalyst, the copolymerisation of cyc(ES)_n and CL was investigated (Scheme 3.1).



Scheme 3.1 Copolymerisation of cyc(ES)_n and CL in the presence of Ph₃Bi (0.2 mol% of total monomer concentration) catalyst in bulk.

Initially, the homopolymerisation of CL was conducted in bulk at 175 °C using Ph₃Bi (0.2%), where an induction period was followed by a rapid acceleration of monomer conversion (Figure 3.1). The polymerisation was monitored by the disappearance of the monomer resonance at $\delta = 4.22$ ppm (COOCH₂) and the appearance of resonance of the polymer at $\delta = 4.06$ ppm (COOCH₂) in the ¹H NMR spectrum. A noticeable increase in viscosity occurred after 1 h and 96% monomer conversion was reached in 4 h with a number average molecular weight of (*M_n*) 62.7 kg·mol⁻¹ and a dispersity of (*D_M* = *M_w*/*M_n*) 1.89. Differential scanning calorimetry (DSC) analysis revealed a glass transition temperature (*T_g*) of -62 °C and a melting temperature (*T_m*) of 65 °C, consistent with literature data.¹¹

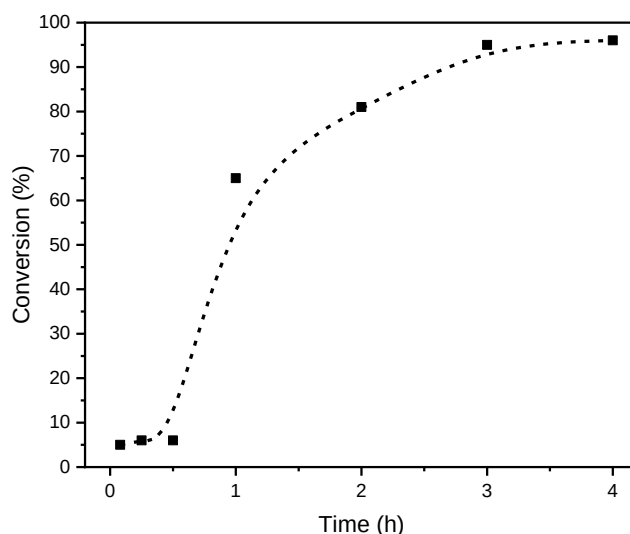


Figure 3.1 Time-monomer conversion curve of CL polymerisation in bulk at 175 °C using Ph_3Bi (0.2 mol%).

Next, copolymerisation of $\text{cyc}(\text{ES})_n$ with CL was performed, maintaining CL comonomer feed ratios at $[\text{cyc}(\text{ES})_n]:[\text{CL}] = 1:1$ under the same conditions. However, after 4 h of reaction, $\text{cyc}(\text{ES})_n$ polymerised into PES while ^1H NMR spectrum showed no incorporation of CL, despite CL's ability to homopolymerise with 97% monomer conversion under the same conditions. It was speculated that the high viscosity of the reaction mixture that resulted from the polymerisation of the $\text{cyc}(\text{ES})_n$ led to a heterogeneous mixture forming, which further hindered CL's incorporation into the copolymer.

In Chapter 2, it was observed that the polymerisation rate of $\text{cyc}(\text{ES})_n$ increased with increasing temperature. Therefore, to slow down the polymerisation of $\text{cyc}(\text{ES})_n$ and hence prevent rapid viscosity rise and poor mixing, the copolymerisation was carried out at a lower temperature of 150 °C. $[\text{cyc}(\text{ES})_n]:[\text{CL}] = 1:1$ feed ratio and Ph_3Bi (0.2%) was maintained, and the reaction proceeded for 24 h, with aliquots taken at the selected intervals. The conversion of ethylene succinate units (ES) from cyclic oligomers to linear polymers could not be accurately determined through ^1H NMR spectroscopy due to overlapping signals of $\text{cyc}(\text{ES})_n$ and PES, challenging the

measurement of the comonomers' reactivity and consumption ratios. However, following CL conversion using ^1H NMR spectra of the reaction mixture revealed that 91% of CL was consumed within 2 h at this temperature (Figure 3.2). ^1H NMR spectrum of purified copolymer after 2 h of reaction confirmed copolymerisation was complete with 50% incorporation of CL and 50% incorporation of ES units (Appendix, Figure A3.3).

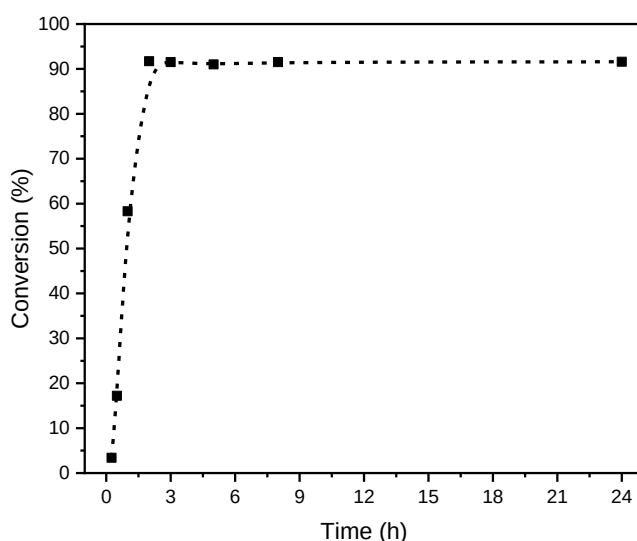


Figure 3.2 Time-CL conversion curve in copolymerisation of $[\text{cyc}(\text{ES})_n]:[\text{CL}] = 1:1$ in bulk at 150 °C using Ph_3Bi (0.2 mol%).

The chain microstructure of the copolymers could be assessed by calculating the randomness parameter of the copolymer (η) and the average sequence lengths (l) of ES and CL units the following equation;^{7, 12}

$$\eta = \frac{(ES - CL)}{2(ES)(CL)} \quad \text{Eq. 3.1}$$

$$l_{CL} = \frac{2(CL)}{(ES - CL)} \quad \text{Eq. 3.2}$$

$$l_{ES} = \frac{2(ES)}{(ES - CL)} \quad \text{Eq. 3.3}$$

where (ES) and (CL) are the two comonomer molar fractions, representing cumulative compositions, and (ES-CL) is the ES-CL average dyad relative molar fraction which was calculated by the ratio of the integral for that dyad over the sum of all dyad integrals:

$$(ES - CL) = 2 \left(\frac{(I_{a'} + I_{b'})/2}{\left(\frac{I_a + I_b + I_{a'} + I_{b'}}{2}\right) + I_g + I_c} \right) \quad \text{Eq. 3.4}$$

where I_i is the integral of the signal at i shift. (Figure 3.3).

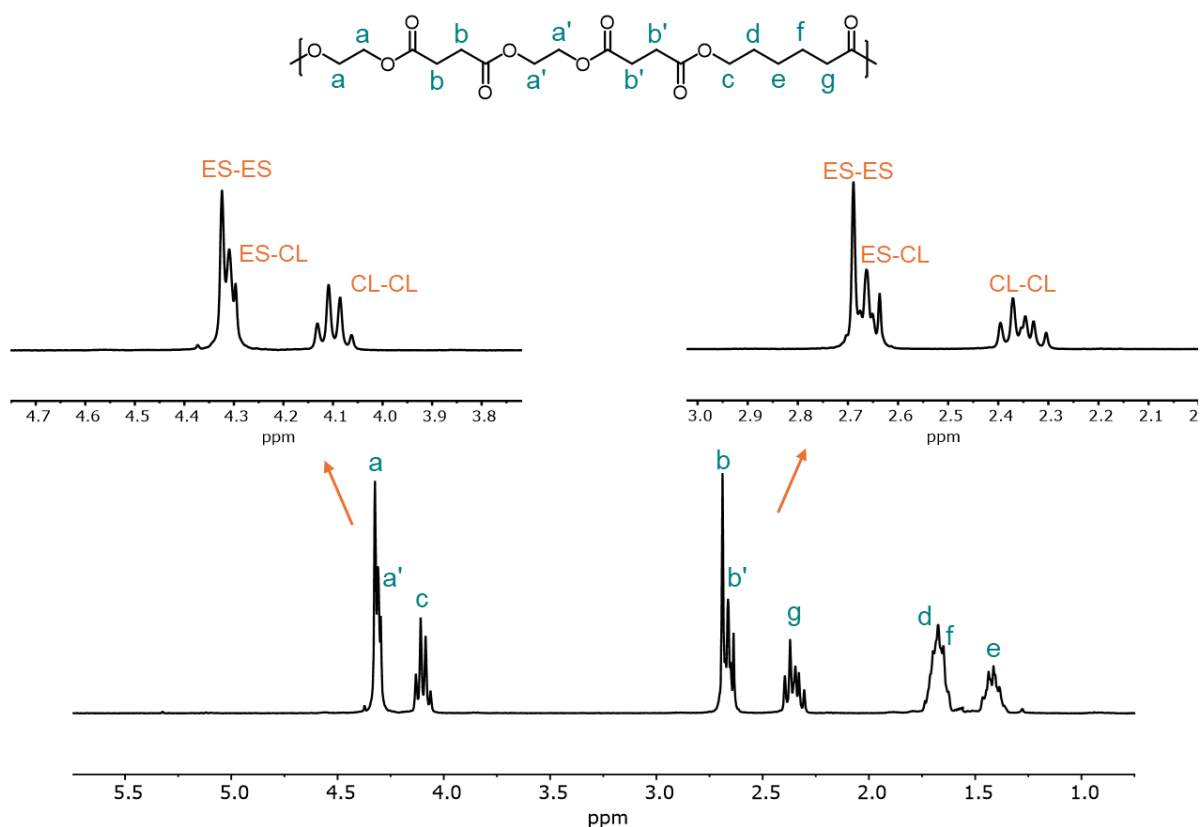


Figure 3.3 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of $[\text{cyc}(\text{ES})_n]:[\text{CL}] = 1:1$ copolymerisation at 150 °C, using Ph_3Bi (0.2 mol%) in bulk after 8 h of reaction.

The randomness parameter (η) is a critical metric for describing the chain microstructure of a copolymer. When η approaches 0, the copolymer exhibits block-like characteristics, whereas η values near 1 indicate random copolymerisation, and η

approaching 2 suggests an alternating structure.¹² Initially, the copolymer displayed a more blocky structure early in the reaction, with $\eta = 0.47$ at 1 h, indicating preferential reactivity of one monomer over the other (Figure 3.4a). At this stage, CL consumption was about 60%. By 2 h, when CL was fully consumed, the resulting copolymer, with a composition of PES₅₀-co-PCL₅₀ and M_n of 62.3 kg·mol⁻¹ ($\bar{D}_M = 1.62$) maintained a blocky nature as $\eta = 0.76$ (Table 3.1, Entry 1). Longer reaction time resulted in a more random structure ($\eta \geq 1$), likely because transesterification reactions redistribute ester bonds and mix the sequences of ES and CL. Consequently, the average sequence length (l) of ES and CL units also decreased over time (Figure 3.4b).

Although the copolymer exhibited a blocky structure at 2 h, only one T_g was observed at -49 °C. As the structure transitioned to a more random arrangement, T_g increased to -40 °C, likely due to the shortening of CL segment lengths and a corresponding reduction in free volume (Table 3.1, Entry 2). Additionally, size exclusion chromatography (SEC) of the polymers revealed a noticeable increase in dispersity from $\bar{D}_M = 1.62$ at 2 h to $\bar{D}_M = 2.75$ at 24 h, along with a decrease in M_n , while the copolymer composition remained unchanged.

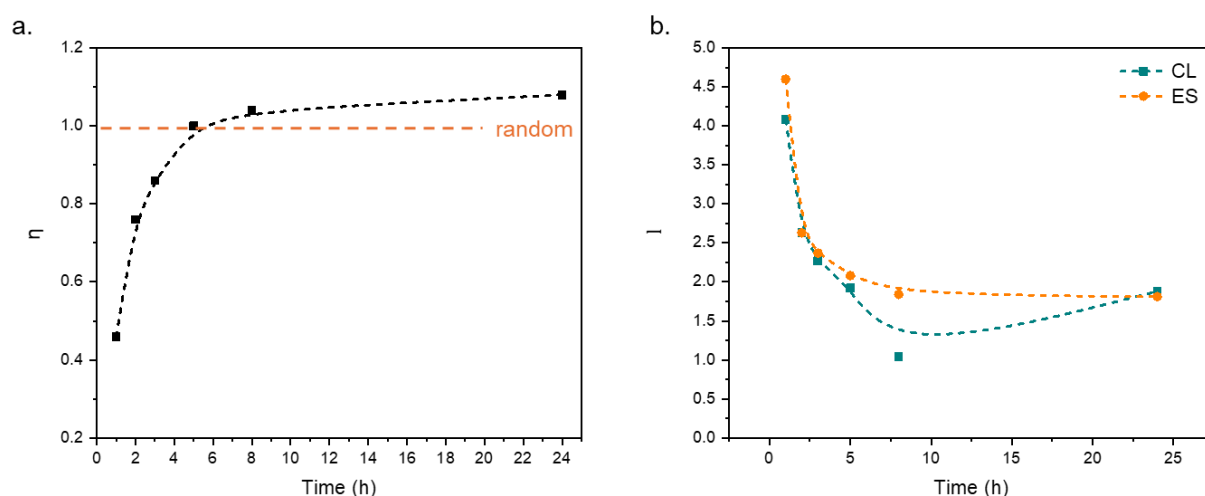


Figure 3.4 a. The randomness character during reaction of [cyc(ES)_n]:[CL] = 1:1 copolymerisation at 150 °C, using Ph₃Bi (0.2 mol%) in bulk; b. The number-average sequence length (l) of ES and CL during the reaction.

Table 3.1 Characteristics of PES₅₀-co-PCL₅₀ polymers changing over time.

Entry	Time (h)	^a M_n (kg·mol ⁻¹)	^a $\bar{D}_M$	^b η	^c T_g (°C)
1	2	62.3	1.62	0.76	-49
2	5	65.7	2.35	1.00	-40
3	8	67.9	2.44	1.04	-40
4	24	59.8	2.75	1.08	-40

^a Determined from SEC in CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.

^b Calculated from the ¹H NMR spectrum (CDCl₃, 400 MHz) of the reaction mixture.

^c Determined from DSC at a heating rate of 5 °C/min.

Next, a series of copolymers were synthesised with decreased CL feed ratios. Those reactions were allowed to proceed for 5 h to enhance randomness and potentially raise T_g , as a higher T_g is advantageous for barrier properties. However, all copolymers with decreased CL composition displayed blocky structures (Table 3.2, Entries 1,2 and 3). It was observed that, aside from the 50% CL feed ratio, CL incorporation was 2-5% lower than its feed ratio, which could be attributed to the miscibility problem of ES with CL monomers as observed previously. In addition, a trend of a decrease in M_n was observed with an increase in the CL ratio.

Table 3.2 Characteristics of series of copolymerisation of cyc(ES)_n and CL at different ratios at 150 °C using 0.2 mol% Ph₃Bi after 5h of reaction.

Entry	Feed Ratio (%) cyc(ES) _n :CL	^a Composition of Polymer	^b M_n (kg·mol ⁻¹)	^b $\bar{D}_M$	^b η
1	90:10	PES ₉₂ -co-PCL ₈	78.5	1.98	0.52
2	80:20	PES ₈₅ -co-PCL ₁₅	71.4	2.02	0.45
3	75:25	PES ₈₀ -co-PCL ₂₀	68.7	2.32	0.5
4	50:50	PES ₅₀ -co-PCL ₅₀	65.7	2.35	1.04

^a Calculated from the ¹H NMR spectrum (CDCl₃, 400 MHz) of the reaction mixture.

^b Determined from SEC in CHCl₃ (0.5% NEt₃) eluent, calibrated against polystyrene standards.

3.2.2 Copolymerisation of $\text{cyc}(\text{ES})_n$ with VL

VL homopolymerisation was initially conducted at 175 °C, as it was initially applied for CL homo and copolymerisation. The monomer conversion was followed by ^1H NMR spectroscopic analysis by monitoring the disappearance of monomer resonance at $\delta = 4.35$ ppm (COOCH_2) and the appearance of polymer resonance at $\delta = 4.08$ ppm (COOCH_2). Monomer conversion at this temperature was much slower than CL homopolymerisation, with M_n of $23.6 \text{ kg}\cdot\text{mol}^{-1}$ ($\bar{D}_M = 2.00$) after 65% monomer conversion at 4 h. DSC analysis of PVL revealed a T_g of -58 °C and a T_m of 57 °C, consistent with literature data.¹³

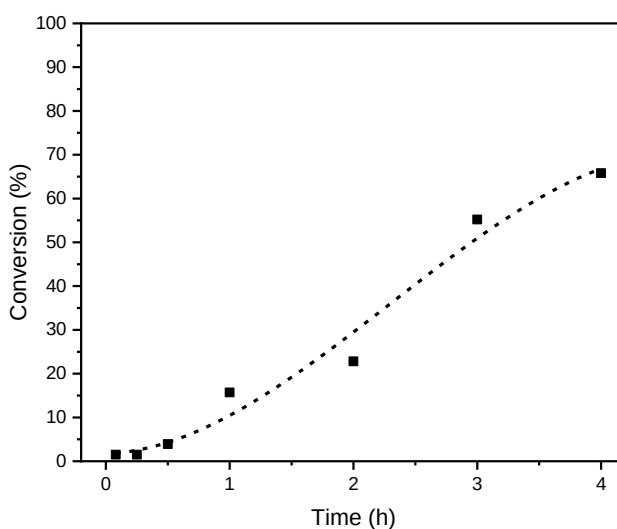
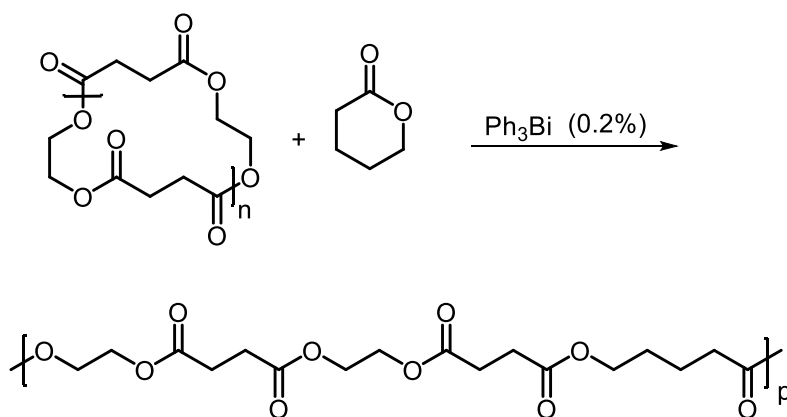


Figure 3.5 Time-monomer conversion curve of VL polymerisation in bulk at 175 °C using Ph_3Bi (0.2 mol%).

Given VL's slow conversion, a heterogeneous reaction medium was expected, in line with what was observed in the copolymerisation of $\text{cyc}(\text{ES})_n$ and CL at 175 °C. Thus, the first copolymerisation of $\text{cyc}(\text{ES})_n$ and VL was performed at 150 °C with the ratio of $[\text{cyc}(\text{ES})_n]:[\text{VL}] = 1:1$ (Scheme 3.2). The VL conversion reached 82% after 2 h, fluctuated and ultimately decreased to 61% after 24 h, with only 20% VL incorporation in the precipitated copolymer (Figure 3.6a). The decrease in monomer conversion

suggests a polymerisation-depolymerisation equilibrium was reached, while the low VL incorporation indicates that cross propagation from ES to VL was limited. Adjusting the reaction temperature to 130 °C improved the VL conversion to 87% at 8 h and increased its incorporation to 50%. However, it was speculated that lower temperatures were also related to less favourable conditions for $\text{cyc}(\text{ES})_n$, as evidenced by a low M_n of $10.5 \text{ kg} \cdot \text{mol}^{-1}$ ($D_M = 1.96$). Given these findings, subsequent studies prioritised the copolymerisation of $\text{cyc}(\text{ES})_n$ and CL.



Scheme 3.2 Copolymerisation of $\text{cyc}(\text{ES})_n$ and VL in the presence of Ph_3Bi (0.2 mol% of total monomer concentration) catalyst in bulk.

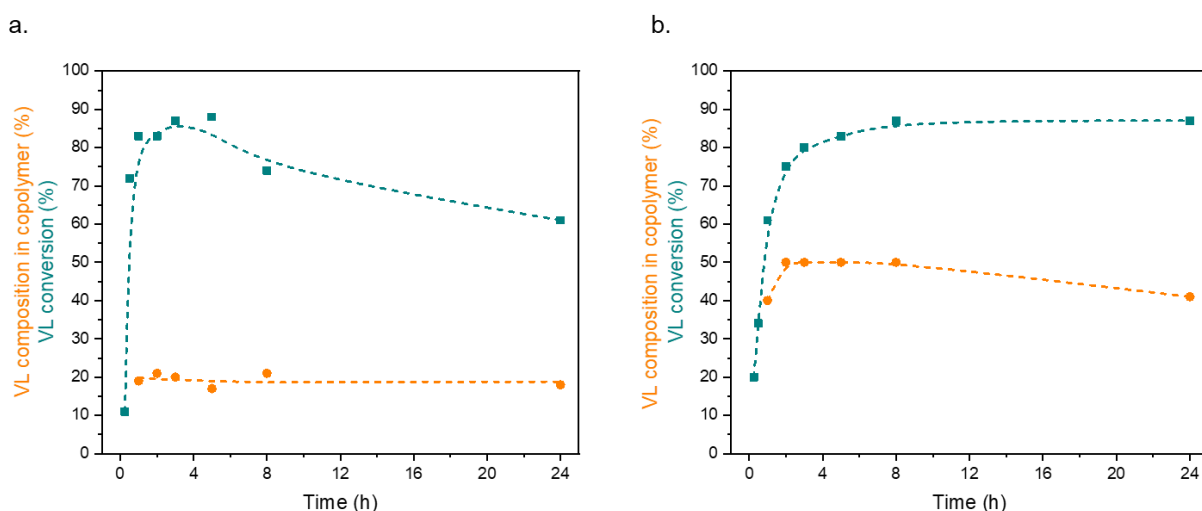


Figure 3.6 VL conversion and composition in copolymer vs time graphs using 0.2 mol% Ph_3Bi a. at 150 °C; b. at 130 °C.

3.2.3 Thermomechanical Properties of PES-co-PCL copolymers

The onset thermal degradation temperatures ($T_{d,5\%}$) for PES, PCL and their copolymers showed a trend as the composition varies (Table 3.3). Pure PES started to degrade at 317 °C, while PCL at 281 °C. For the PES-PCL copolymers, $T_{d,5\%}$ initially decreased as small amounts of PCL were incorporated into the PES matrix, with PES_{92-co-PCL}₈ showing the lowest degradation temperature of 262 °C. This could result from localised weaker points being introduced with a low concentration of PCL into the PES-dominated matrix, accelerating the PES degradation. However, as the PCL content increased, $T_{d,5\%}$ raised, and PES_{50-co-PCL}₅₀ showed a degradation temperature of the mid-range of both homopolymers.

Table 3.3 Thermal properties of non-processed PES, PCL and their copolymers.

Polymer	^a T_g (°C)	^a T_m (°C)	^b X_c (%)	^c $T_{d5\%}$ (°C)
PES	-5	103	28	317
PES _{92-co-PCL} ₈	-16	97	6.6	262
PES _{85-co-PCL} ₁₅	-19	90	4	287
PES _{80-co-PCL} ₂₀	-22	80	-	299
PES _{50-co-PCL} ₅₀	-40	-	-	302
PCL	-62	57	51	281

^a Determined from the second heating of DSC thermogram at heating rate of 5 °C/min.

^b Calculated according to Eq 3.5.

^c Determined from TGA thermogram at heating rate of 10 °C/min.

Increasing the PCL content in the PES-PCL copolymer resulted in decreased T_g and T_m , as expected. A fully amorphous polymer was achieved with a composition of 50% PCL. The degree of crystallinity (X_c) was determined according to the following equation;

$$X_c(\%) = \left(\frac{\Delta H_m - \Delta H_{cc}}{w\Delta H_m^0} \right) \times 100 \quad \text{Eq. 3.5}$$

where ΔH_m is the experimental melting enthalpy, ΔH_{cc} is the cold crystallisation enthalpy, and w is the weight fraction of material. ΔH_m^0 , the enthalpy of melting of 100% crystalline PES and PCL were taken as 180 J/g and 139 J/g, respectively.^{14, 15} At a heating rate of 5 °C/min, PES exhibited crystallinity without cold crystallisation, achieving an X_c of 28%. However, the addition of PCL significantly slowed down the crystallisation of the PES chain, leading to predominant cold crystallisation. Consequently, the actual crystallinity degrees were considerably low, 6.6% and 4% for PES_{92-co}-PCL₈ and PES_{85-co}-PCL₁₅, respectively. In the PES_{20-co}-PCL₂₀ copolymer, the crystallinity phase only formed during heating. Notably, when PES_{85-co}-PCL₁₅ films were processed by compression moulding, they exhibited increased crystallinity and no cold crystallisation, indicating that the applied thermal and pressure conditions facilitated crystallisation during cooling (Figure 3.8).

Given its higher thermal stability and comparable crystallinity to PES_{92-co}-PCL₈, PES_{85-co}-PCL₁₅ was scaled up to 3 g for tensile and barrier tests. Tensile tests on dog-bone-shaped samples were performed to assess the ultimate tensile strength (σ_B), elongation at break (ϵ_B), Young's modulus (E), and ultimate toughness (U_T) of the copolymer relative to PES. While PES exhibited σ_B of 36.6±11 MPa, ϵ_B of 279±46 %, E of 548±82 MPa, and $U_T = 79\pm28 \text{ MJ}\cdot\text{m}^{-3}$, PES_{85-co}-PCL₁₅, a softer and more ductile material, displayed σ_B of 20±1.5 MPa, ϵ_B of 360±63 %, E of 309±46 MPa, and U_T of 61±18 MJ·m⁻³. The stress-strain curves for both PES and PES_{85-co}-PCL₁₅ displayed a sharp yield point with yield stresses (σ_Y) of 20 MPa and 10 MPa, respectively. Following this yield, both materials were observed to undergo strain hardening, where

stress increases until fracture. This strain hardening was accompanied by stress fluctuations, appearing as periodic increases and decreases in stress during non-uniform necking, where deformation localises in specific regions (Figure 3.7a). This phenomenon, known as stress oscillation,¹⁶ was visually apparent in the form of alternating transparent and opaque bands perpendicular to the direction of deformation (Figure 3.7b).

While the stress oscillation mechanism is still under investigation and can vary for different polymers, it was suggested that it results from a crystalline transition through lamellar thickening under tensile deformation for PES.¹⁷ As lamellae thicken, they form momentarily stronger and stiffer regions that dissipate and reform, producing the oscillatory stress pattern on the stress-strain curve. The stress-induced crystallisation was also observed in PES₈₅-co-PCL₁₅ copolymer with an increased X_c from 26% to 35%, indicating the formation of uniform but smaller or imperfect crystals, which melt at a lower temperature while maintaining a narrow melting range (Figure 3.8). Moreover, in PES₈₅-co-PCL₁₅, stress oscillations were notably more frequent and of higher amplitude than in PES (Figure 3.7a). This difference is likely due to the presence of PCL chains, allowing for more flexible regions and chain mobility that are more prone to stretch, thereby reducing strain on the PES itself.¹⁸ This behaviour can be particularly beneficial for soft packaging applications, as it combines stress-induced crystallisation, which temporarily strengthens the polymer matrix, with flexible amorphous regions that accommodate stretching. The balanced flexibility and reinforced structure could make it a promising candidate for durable and flexible packaging films that have structural integrity under repeated handling and stress.

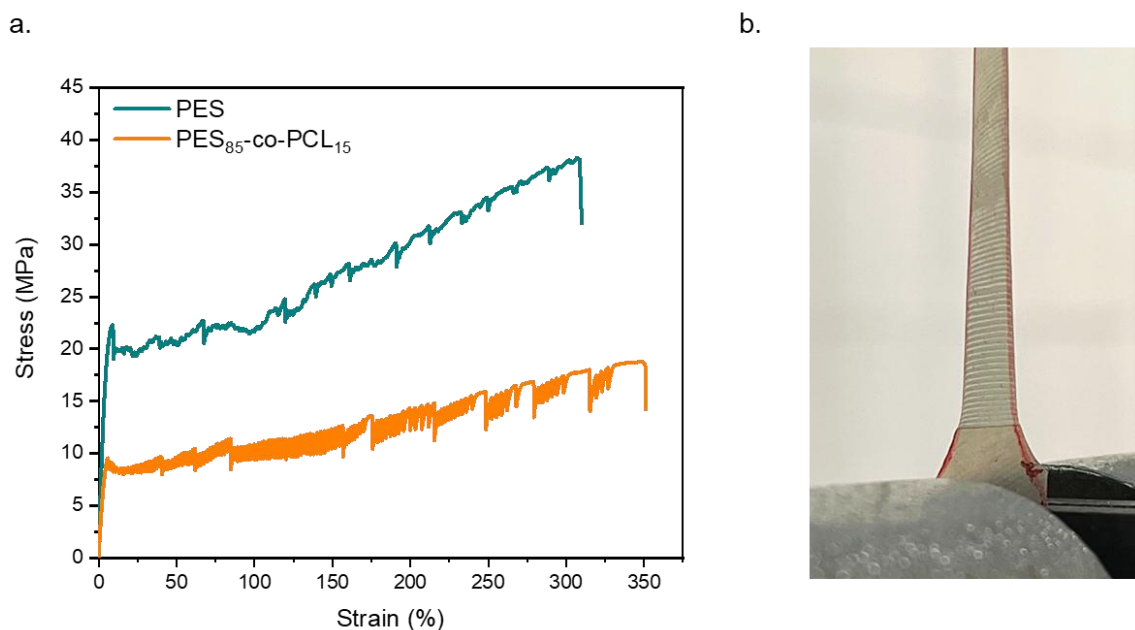


Figure 3.7 a. Exemplary stress vs strain curves of PES and PES₈₅-co-PES₁₅ (1 mm/min, ambient temperature); b. Visual of PES₈₅-co-PES₁₅ films under tensile showing stress oscillatory bands.

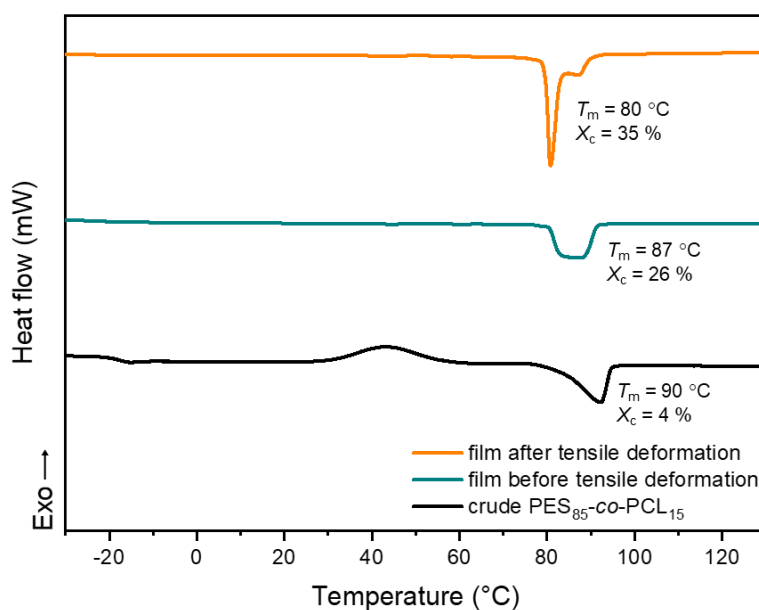


Figure 3.8 DSC thermograms at a heating rate of 5 °C/min for PES₈₅-co-PCL₁₅: crude polymer (2nd heating), compression-moulded film (before deformation), and the same film after deformation.

3.2.4 Barrier Properties of PES and PES₈₅-co-PCL₁₅

Oxygen permeability (PO_2) and water vapour transmission rate (WVTR) were measured for PES and PES₈₅-co-PCL₁₅, given that oxygen and water can induce both

physical and chemical changes in food products. The results were compared with poly(hydroxybutyrate) (PHB), PLA, PET, low-density poly(ethylene) (LDPE),¹⁹ PBAT,²⁰ and PCL,⁷ which were tested using the same equipment in our group, as well as with PBS^{21, 22} and poly(propylene) (PP)²³ permeability data from the literature tested under similar temperature and humidity conditions.

PES demonstrated exceptional oxygen barrier properties, with a PO_2 of just 0.008 Barrer, lower than many widely produced biodegradable polymers (Figure 3.9). Remarkably, the PES homopolymer exhibited superior barrier performance even when compared to PHB, a well-known representative of PHA that boasts high barrier properties but suffers from brittleness and low thermal stability.²⁴ Additionally, PES outperformed conventional petroleum-based packaging polymers like LDPE, PP, and PET. However, when PES was copolymerised with PCL, the oxygen permeability of the copolymer increased to 0.07 Barrer. This is consistent with pure PCL having high oxygen permeability, and the copolymer exhibited a reduction in both T_g and crystallinity. Despite this increase, the oxygen permeability of PES_{85-co}-PCL₁₅ remained significantly lower than those of the biodegradable and non-biodegradable polymers mentioned earlier, with the added advantage of improved ductility.

Regarding WVTR, PES exhibited values comparable to other biodegradable polyesters. The difference between oxygen and water permeability performance can be attributed to the interaction of water molecules with polar functional groups *via* hydrogen bonding and dipole-dipole interactions. The WVTR of the PES_{85-co}-PCL₁₅ copolymer decreased substantially, showing values higher than both pure PCL and PES, likely due to a reduction in crystallinity.

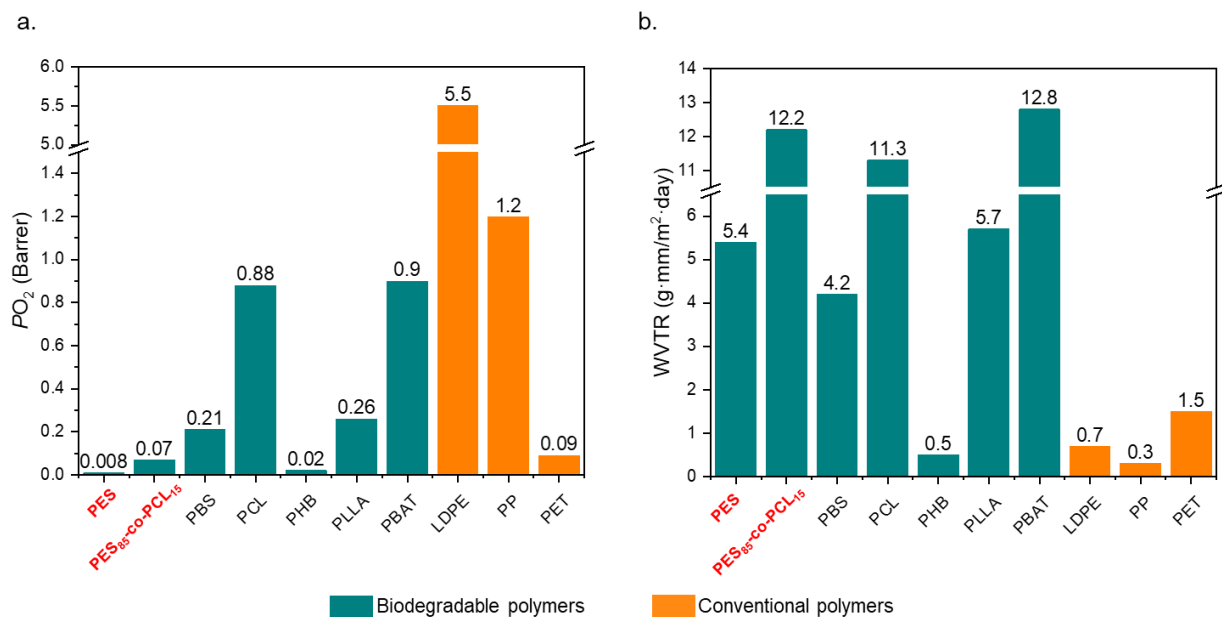


Figure 3.9 Barrier properties of PES and PES₈₅-co-PCL₁₅ compared to commercial biodegradable polymers and conventional polymers: a. Oxygen permeability (PO_2); b. Water Vapour Transmission Rate (WVTR).

3.3 Conclusion

The copolymerisation of cyc(ES)_n with CL and VL demonstrated notable findings regarding the synthesis and properties of biodegradable copolymers for sustainable packaging applications. While the homopolymerisation of CL and VL proceeded successfully, challenges in copolymerisation arose due to the different reactivity rates and miscibility. Particularly, the rapid polymerisation rate of cyc(ES)_n hindered CL and VL incorporation at high temperatures, necessitating adjustments in the reaction conditions to achieve a more random copolymer structure and effective integration of comonomer units. The investigation into VL copolymerisation at different temperatures revealed limited success, while CL proved a more suitable comonomer under the chosen conditions.

Small additions of CL showed distinct effects on $T_{d,5\%}$ and caused major reductions in crystallinity. However, $\text{PES}_{85}\text{-co-PCL}_{15}$ exhibited stress-induced crystallisation during tensile testing, increasing crystallinity and providing both flexibility and reinforcement under stress. In terms of barrier properties, PES exhibited excellent oxygen barrier performance, outperforming biodegradable polymers like PHB and conventional materials such as LDPE and PET. Therefore, PES could be a viable biodegradable alternative for packaging applications that require low oxygen permeability. Although copolymerisation with CL decreased thermal and barrier properties, it could offer balanced flexibility, ductility, and barrier effectiveness, as O_2 barrier properties of $\text{PES}_{85}\text{-co-PCL}_{15}$ copolymer remained more effective than many other alternatives.

3.4 Appendix

3.4.1 Proton (^1H) NMR Spectra

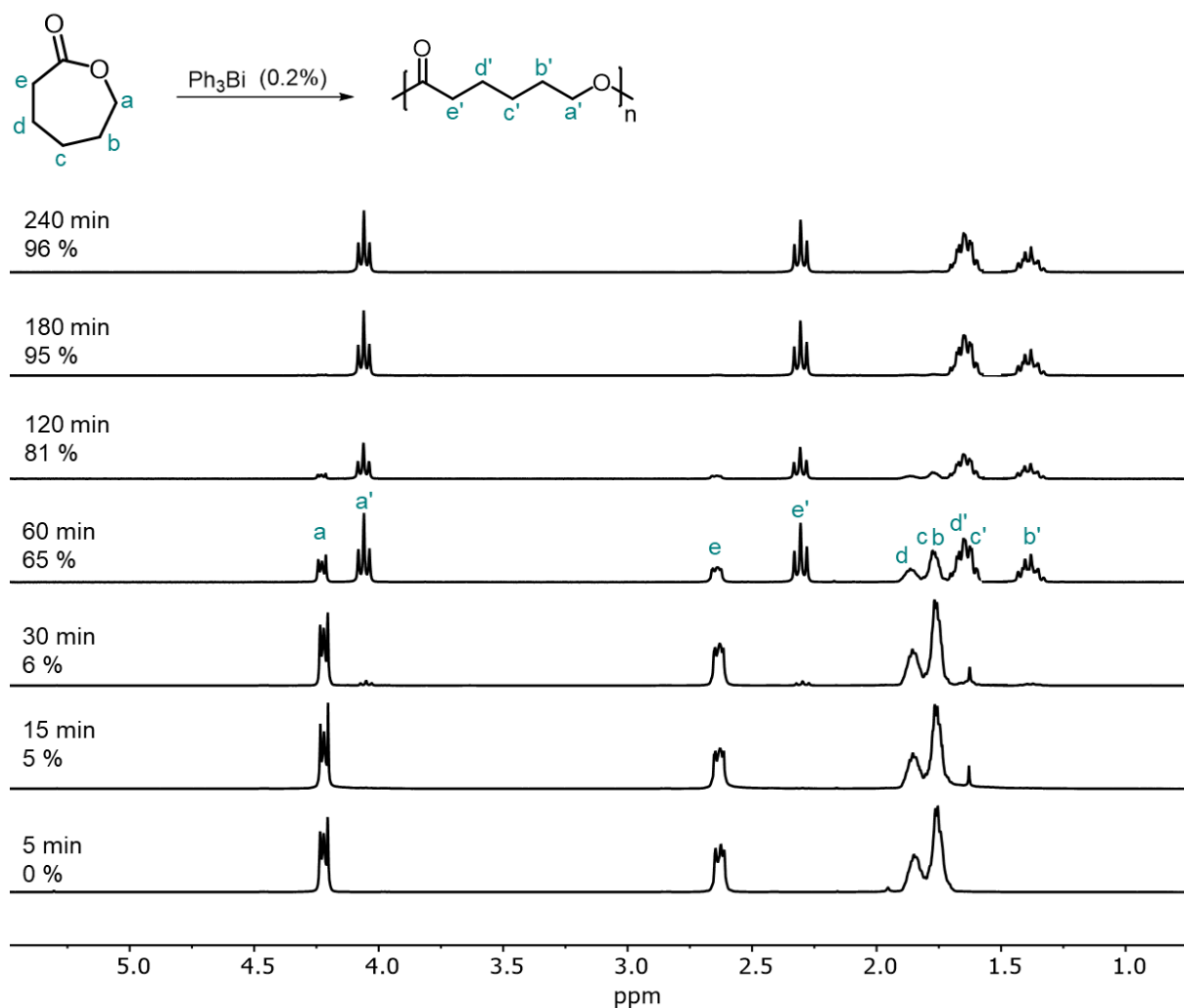


Figure A3.1 Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of crude reaction mixtures of the CL polymerisation using Ph_3Bi (0.2 mol%) at 150 °C in bulk taken at different time points throughout its kinetic study. The time and CL conversion are given next to each spectrum.

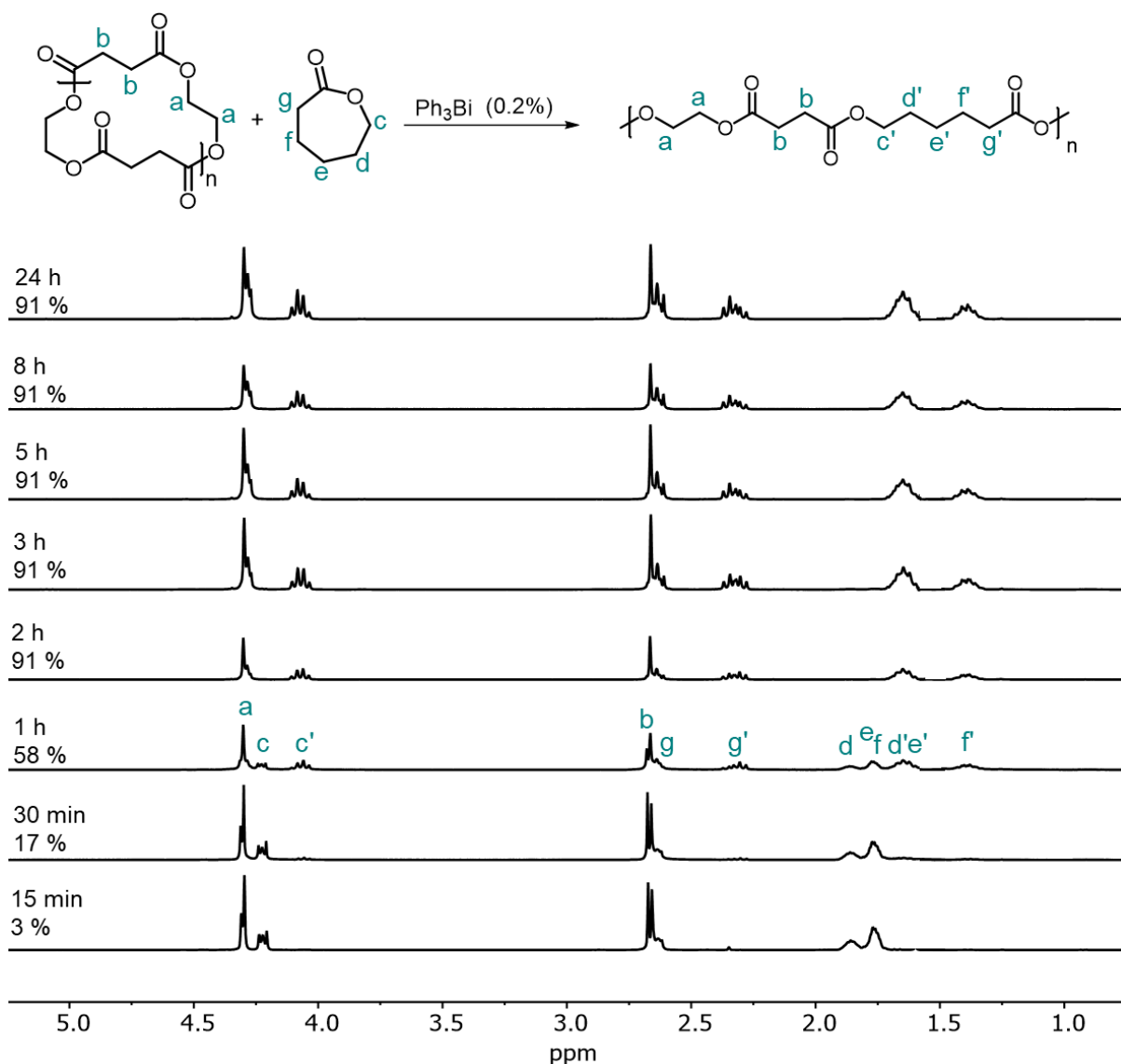


Figure A3.2 Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of crude reaction mixtures of the model copolymerisation of $[\text{cyc}(\text{ES})_n]:[\text{CL}] = 1:1$ using Ph_3Bi (0.2 mol%) at 150 °C in bulk taken at different time points throughout its kinetic study. The time and CL conversion are given next to each spectrum.

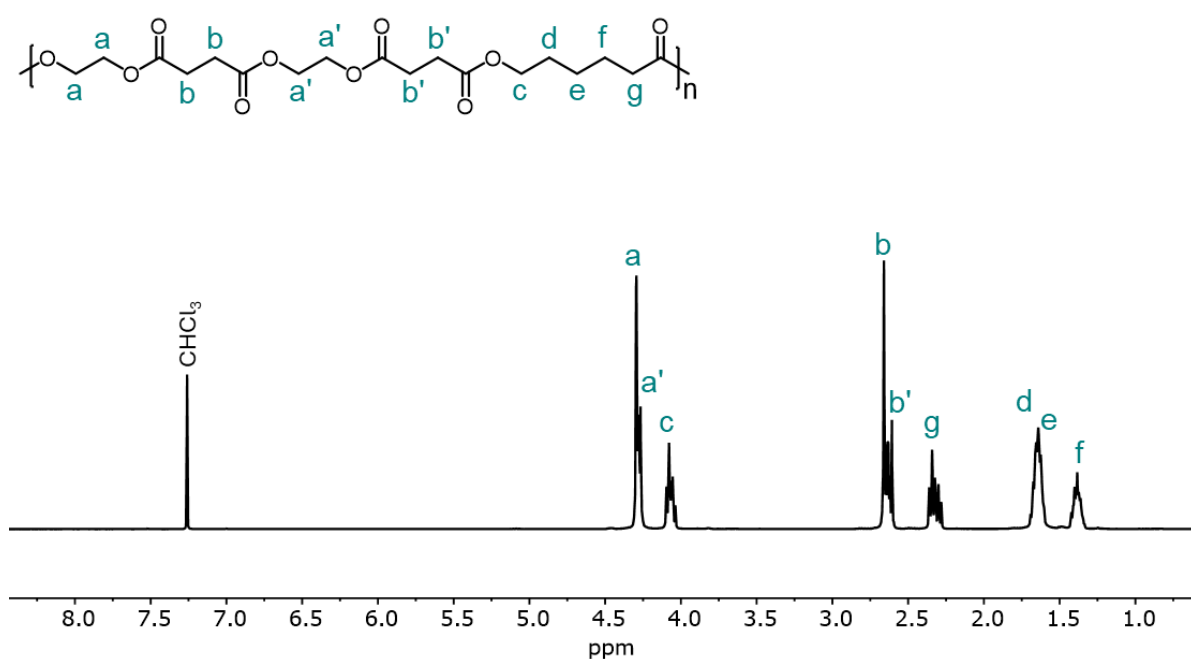


Figure A3.3 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of PES₅₀-co-PCL₅₀.

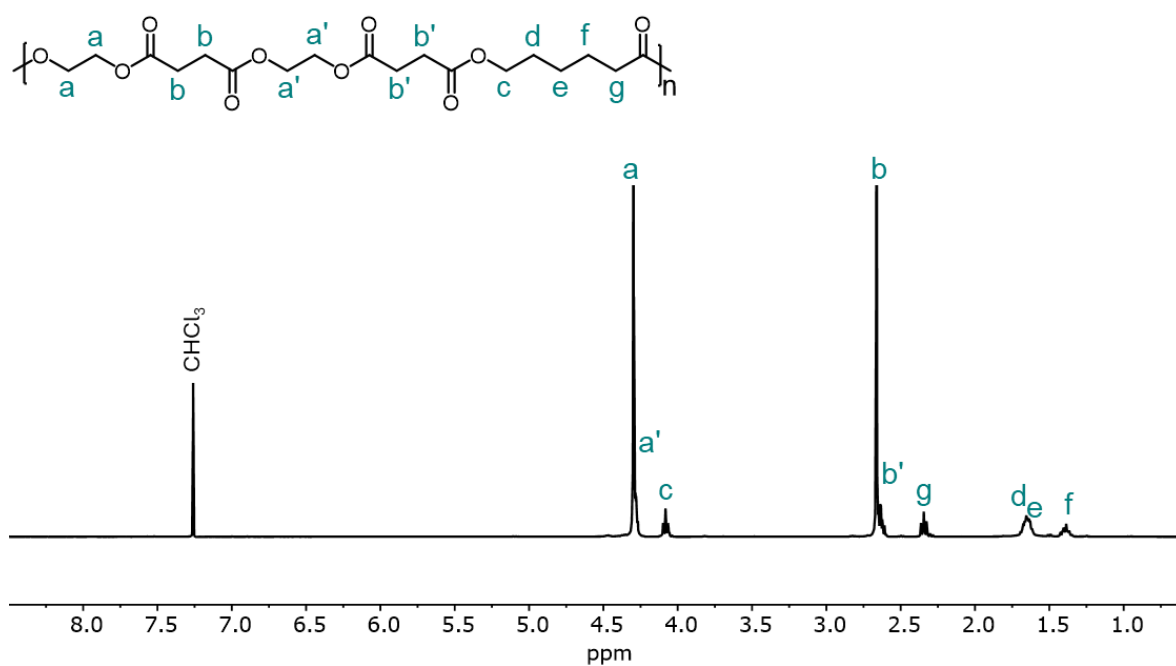


Figure A3.4 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of PES₈₀-co-PCL₂₀.

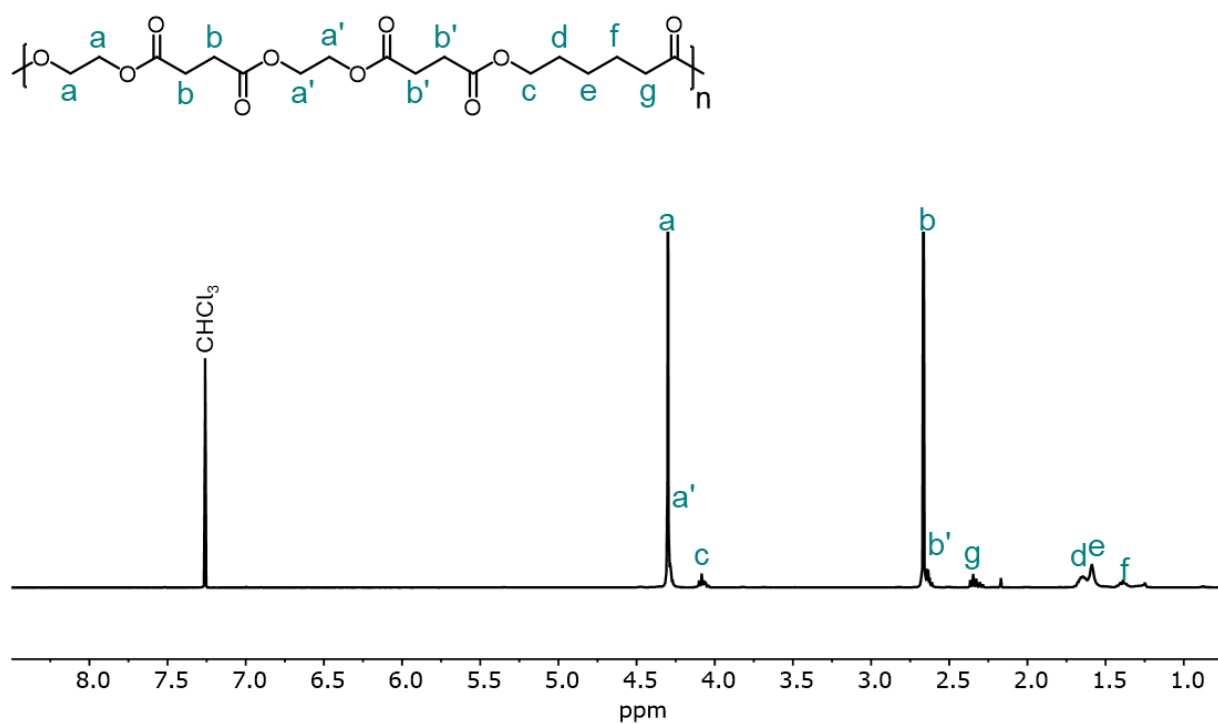


Figure A3.5 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of PES₈₅-co-PCL₁₅.

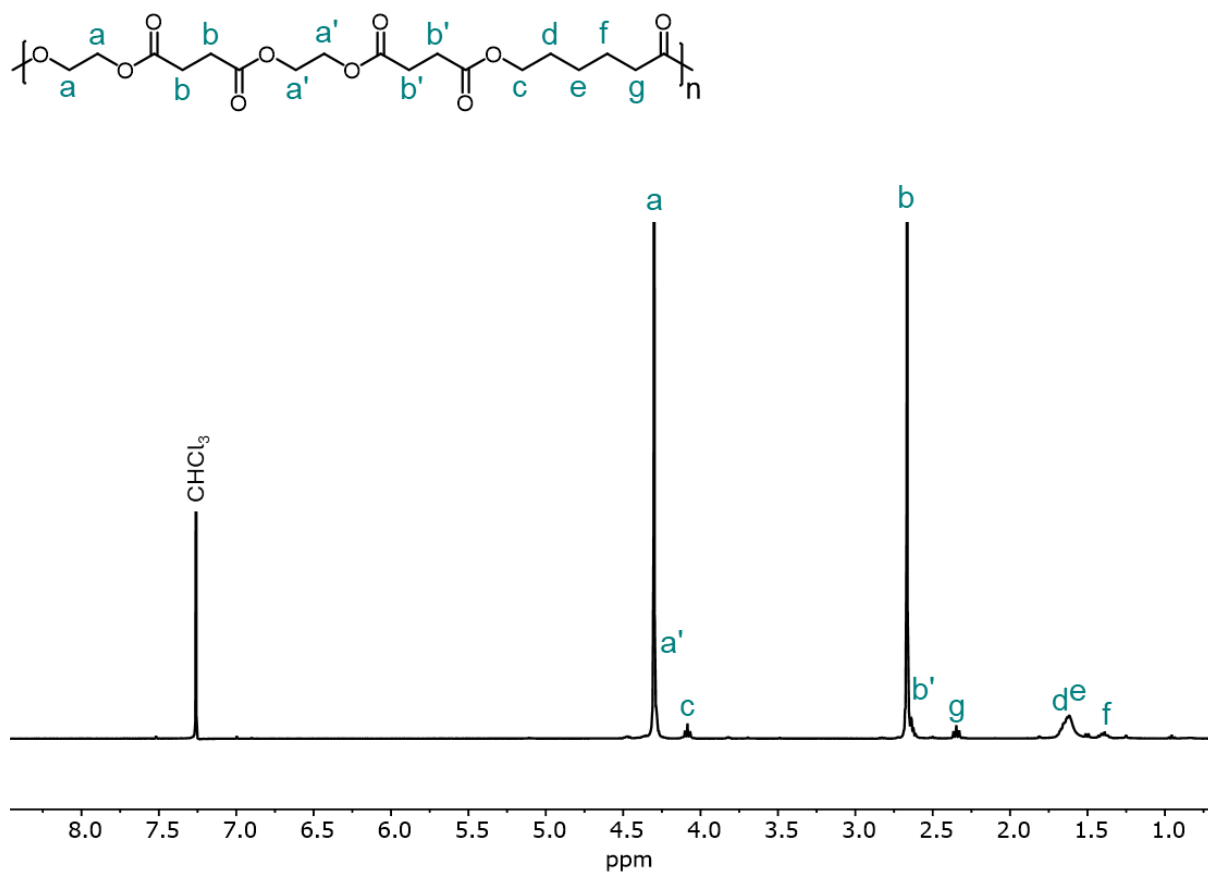


Figure A3.6 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of PES₉₂-co-PCL₈.

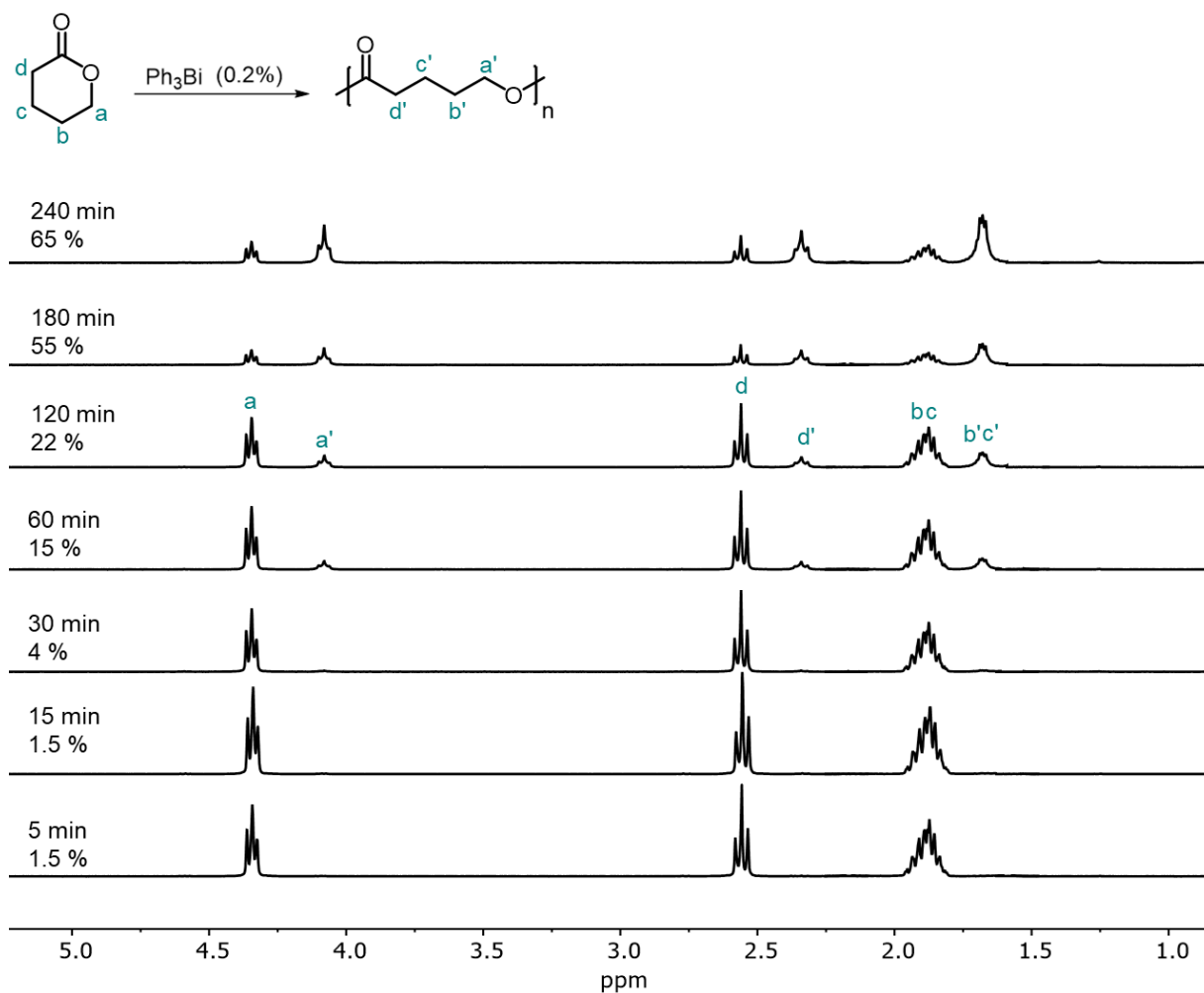


Figure A3.7 Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of crude reaction mixtures of the VL polymerisation using Ph_3Bi (0.2 mol%) at 150 °C in bulk taken at different time points throughout its kinetic study. The time and VL conversion are given next to each spectrum. Polymer and monomer peaks were labelled at 2 h as they exist together.

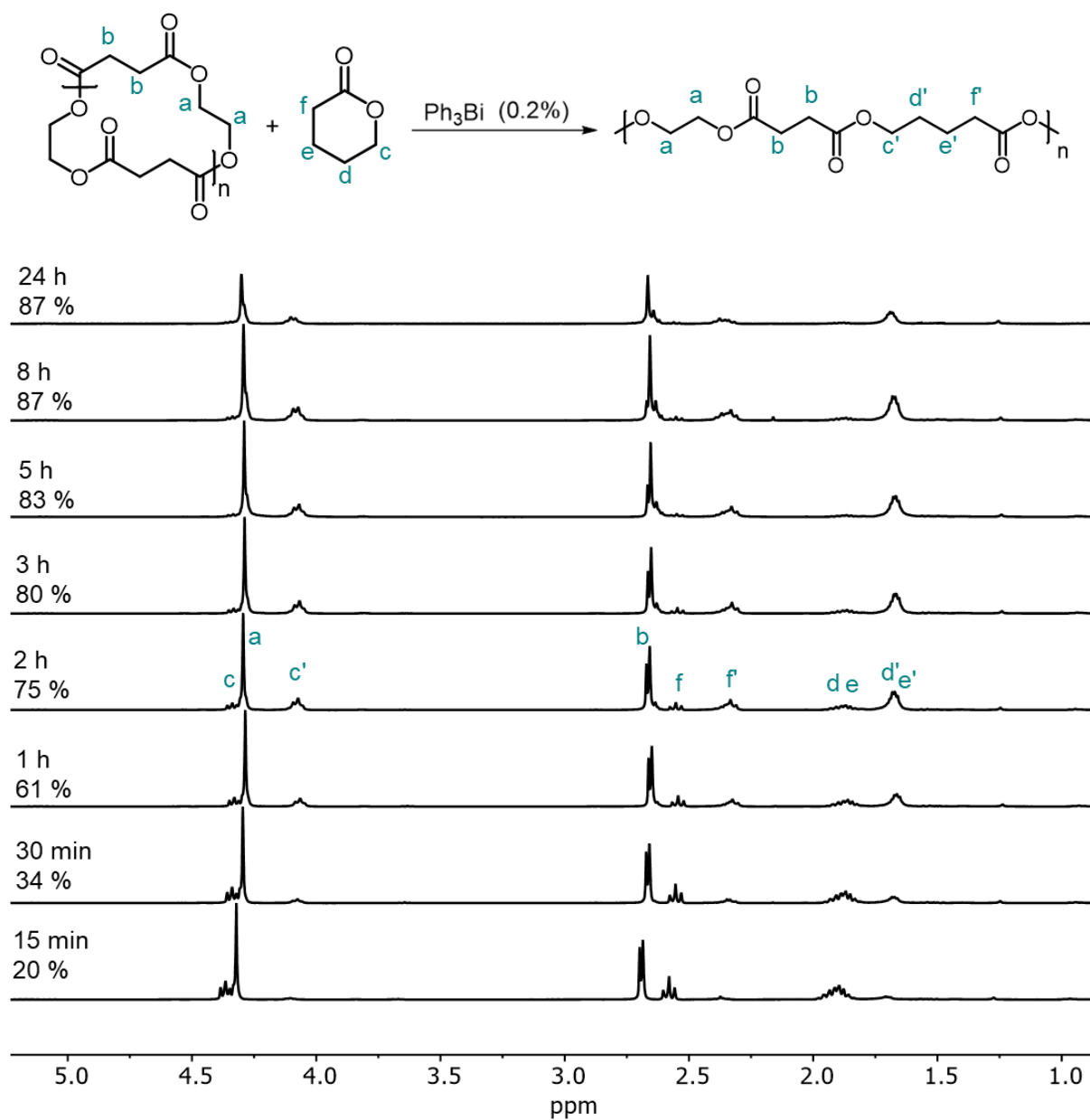


Figure A3.8 Stacked ¹H NMR spectra (400 MHz, 298 K, CDCl₃) of crude reaction mixtures of the model copolymerisation of [cyc(ES)_n]:[VL] = 1:1 using Ph₃Bi (0.2 mol%) at 150 °C in bulk taken at different time points throughout its kinetic study. The time and VL conversion are given next to each spectrum. Polymer and monomer peaks were labelled at 2 h as they exist together.

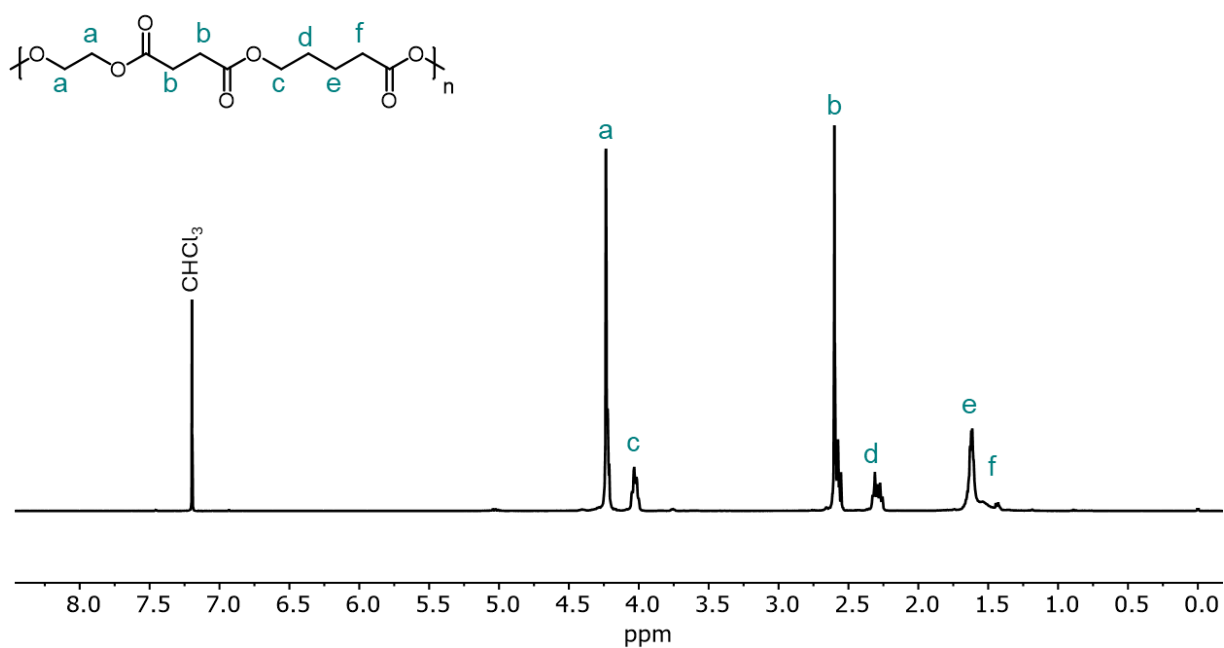


Figure A3.9 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of PES₅₀-co-PVL₅₀.

3.4.2 Carbon (¹³C) NMR Spectra

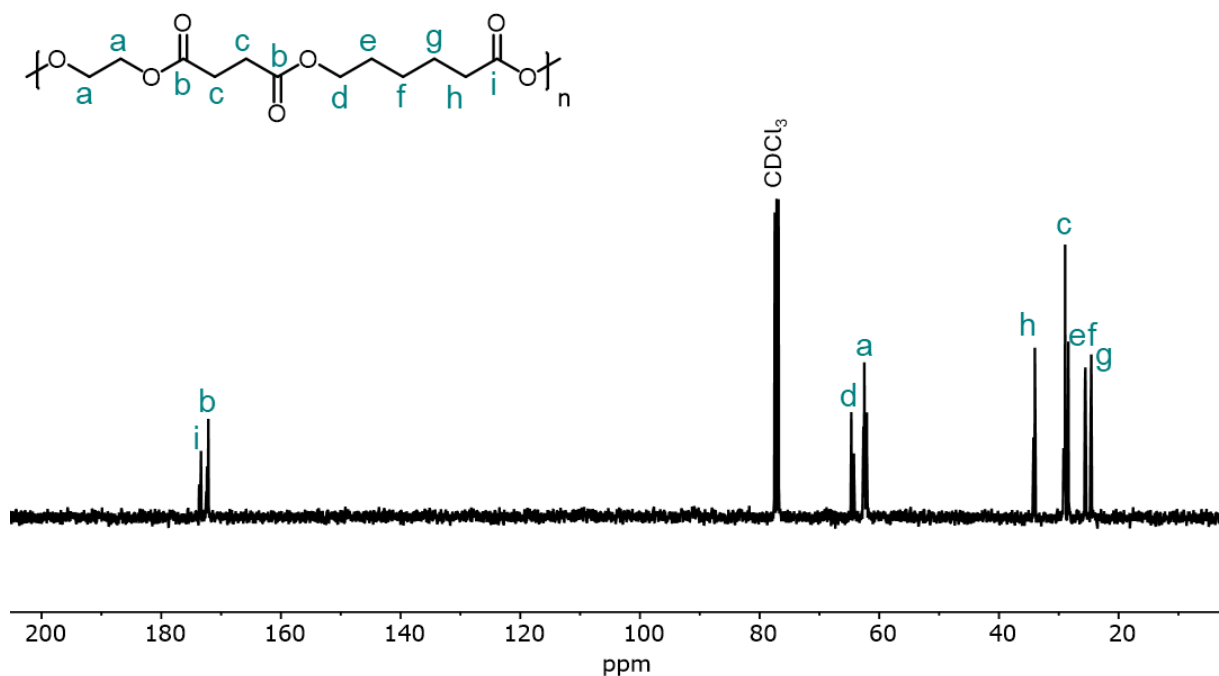


Figure A3.10 ¹³C NMR spectrum (101 MHz, 298 K, CDCl₃) of PES₅₀-co-PCL₅₀.

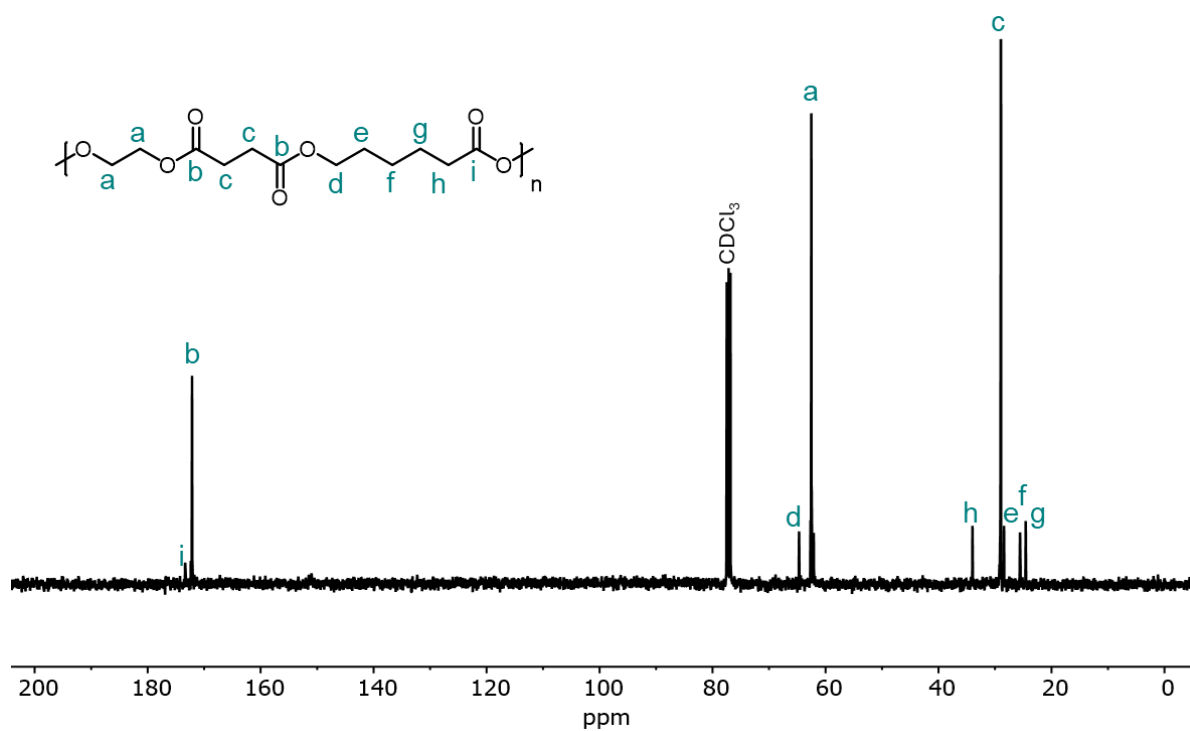


Figure A3.11 ¹³C NMR spectrum (101 MHz, 298 K, CDCl₃) of PES₈₀-co-PCL₂₀.

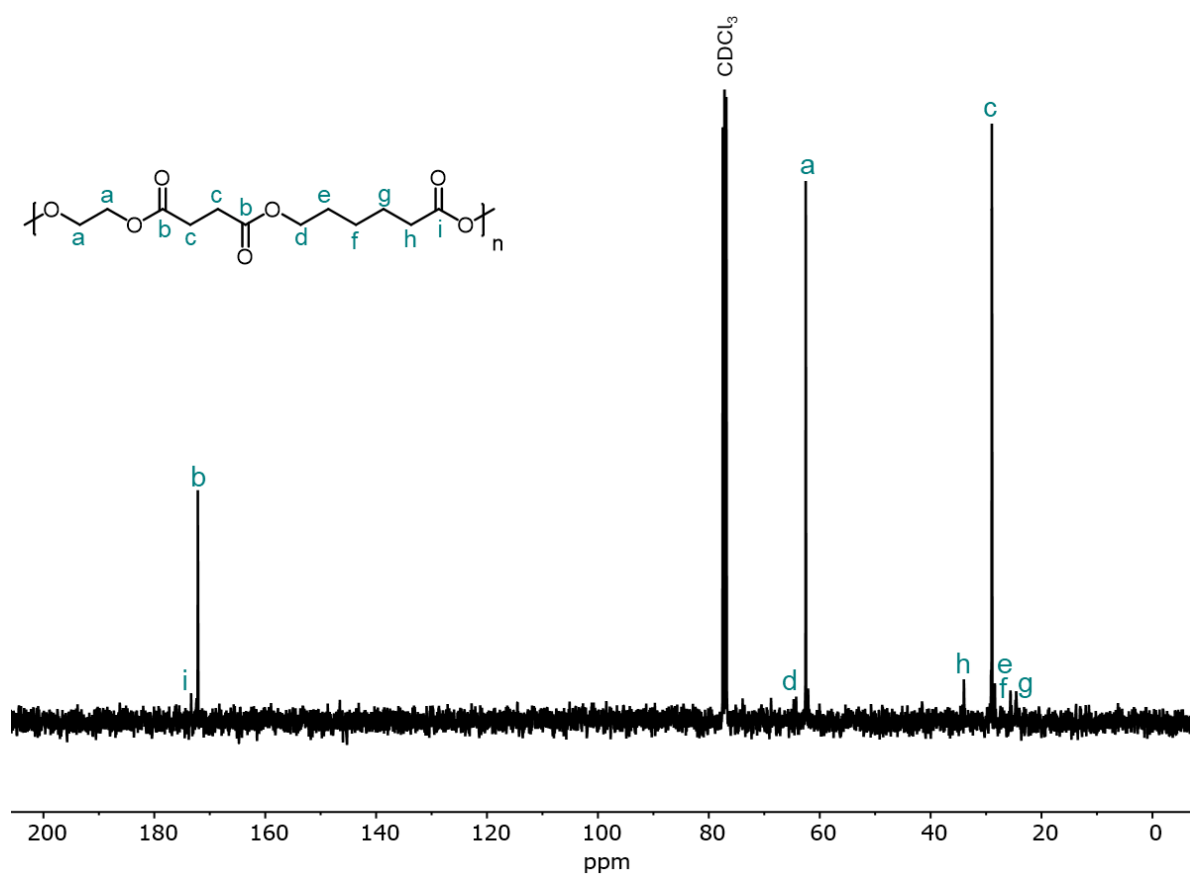


Figure A3.12 ¹³C NMR spectrum (101 MHz, 298 K, CDCl₃) of PES₈₅-co-PCL₁₅.

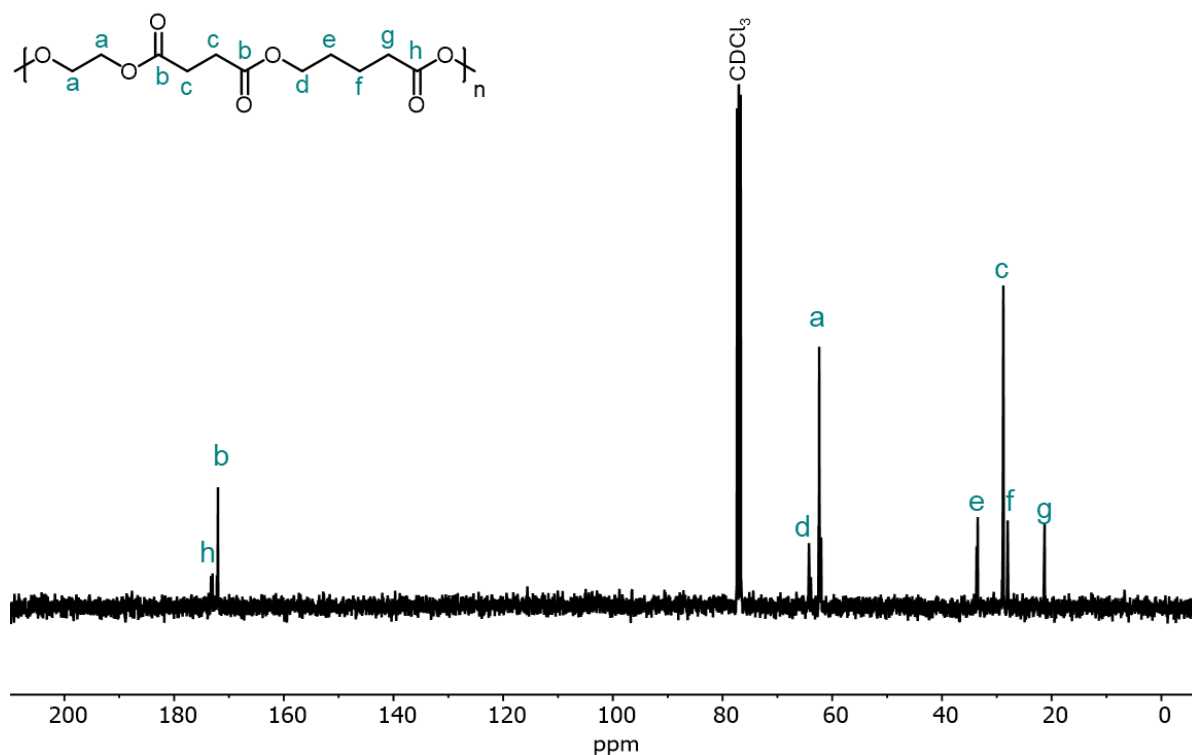


Figure A3.13 ^{13}C NMR spectrum (101 MHz, 298 K, CDCl_3) of $\text{PES}_{50}\text{-co-PVL}_{50}$.

3.4.3 SEC Chromatograms

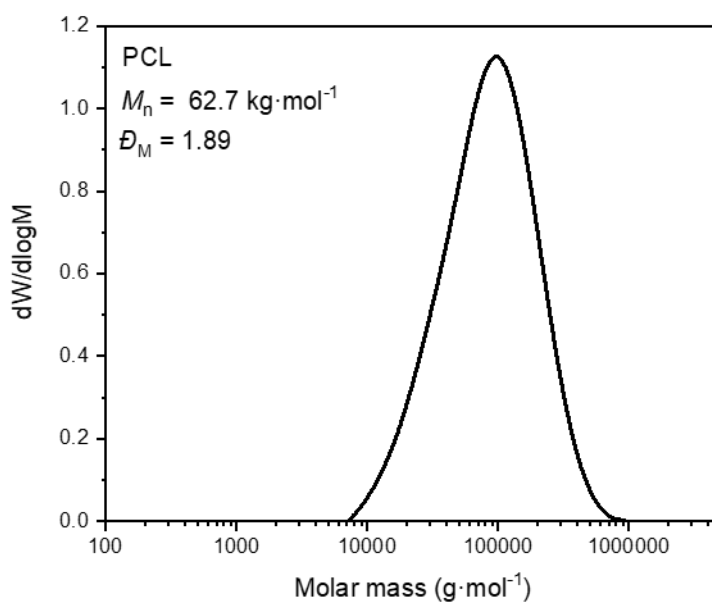


Figure A3.14 SEC chromatogram of PCL calibrated against PS standards in CHCl_3 + 0.5% NEt_3 .

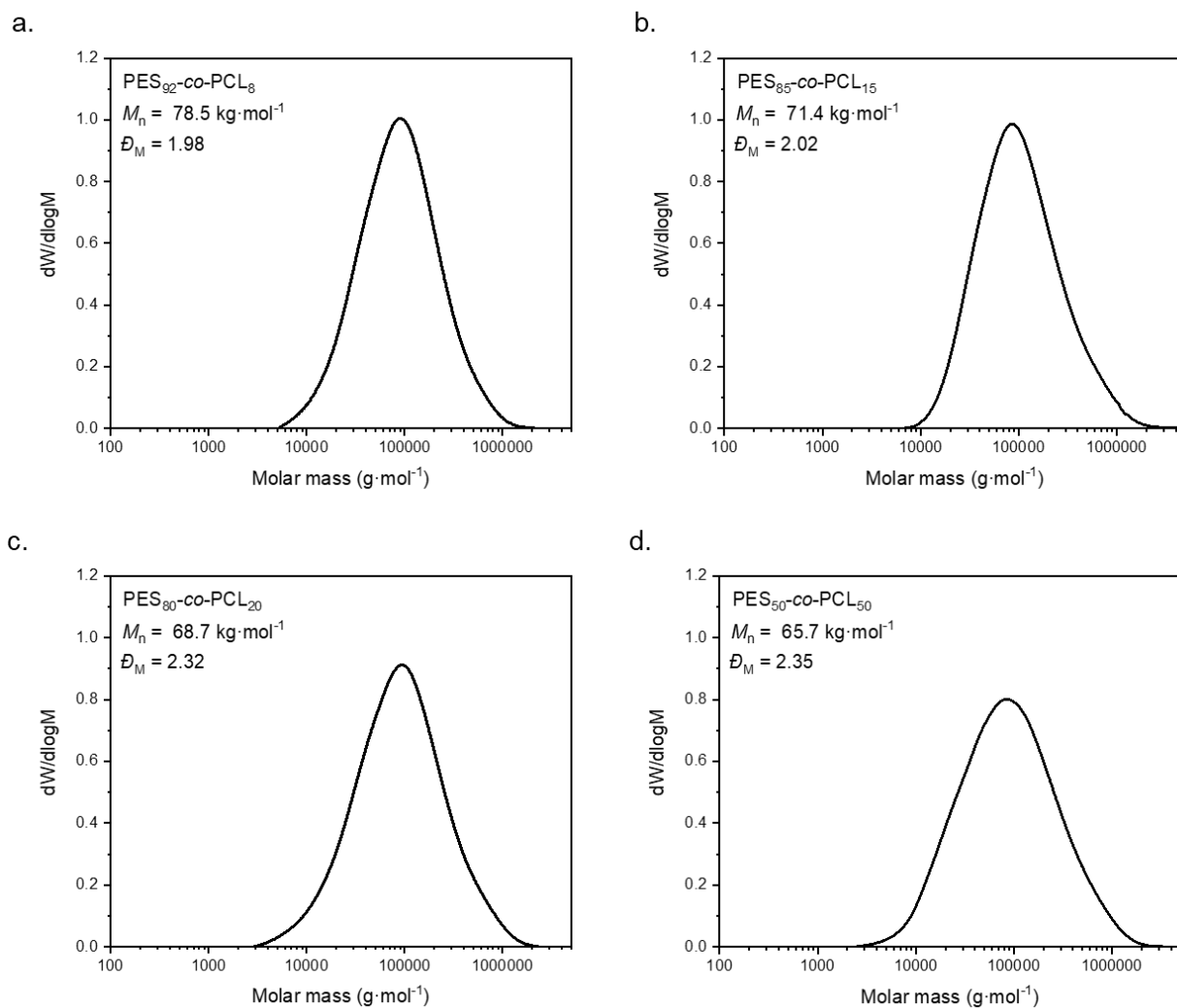


Figure A3.15 SEC chromatograms of PES-PCL copolymers calibrated against PS standards in $\text{CHCl}_3 + 0.5\% \text{ NEt}_3$ a. $\text{PES}_{92}\text{-co-PCL}_8$; b. $\text{PES}_{85}\text{-co-PCL}_{15}$; c. $\text{PES}_{80}\text{-co-PCL}_{20}$; d. $\text{PES}_{50}\text{-co-PCL}_{50}$.

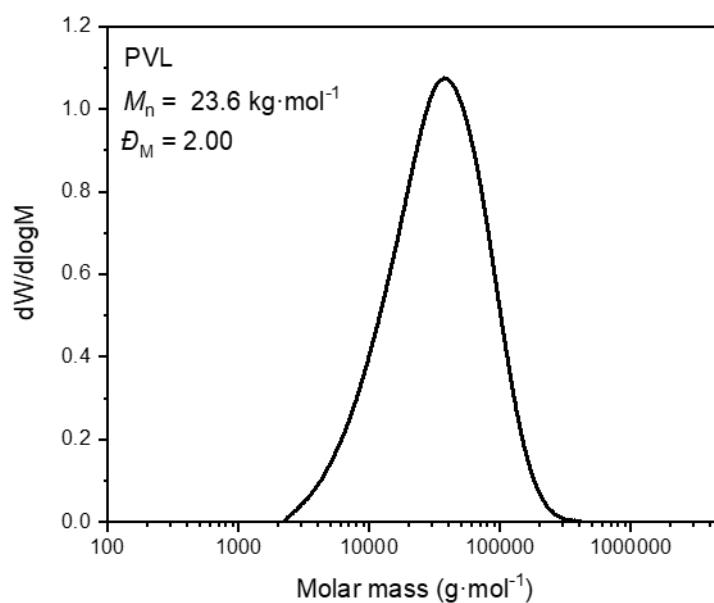


Figure A3.16 SEC chromatogram of PVL calibrated against PS standards in $\text{CHCl}_3 + 0.5\% \text{NEt}_3$.

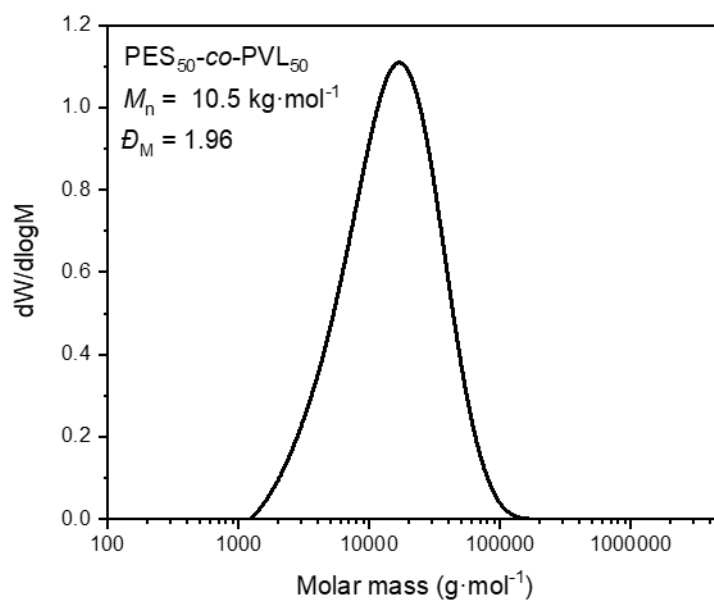


Figure A3.17 SEC chromatogram of $\text{PES}_{50}\text{-co-PVL}_{50}$ calibrated against PS standards in $\text{CHCl}_3 + 0.5\% \text{NEt}_3$.

3.4.4 Thermomechanical Properties

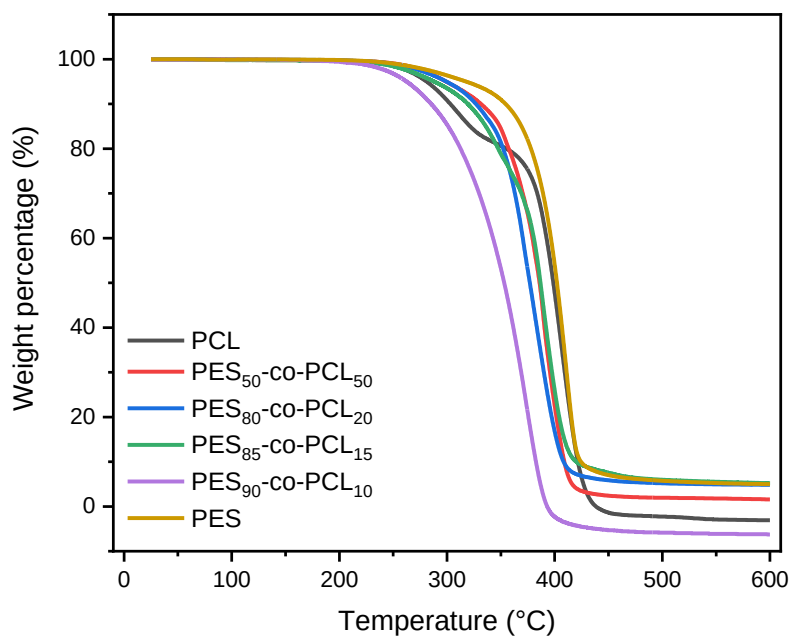


Figure A3.18 TGA thermograms of PES, PCL and their copolymers at a heating rate of 10°C/min.

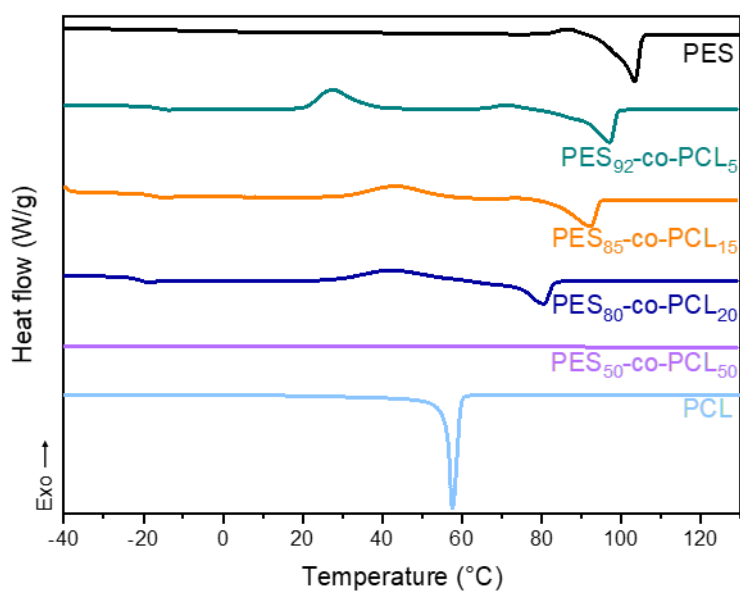


Figure A3.19 DSC thermograms of PES, PCL and their copolymers at a heating rate of 5 °C/min.

Table A3.1 Tensile test results of PES₈₅-co-PCL₁₅.

Entry	E (MPa)	σ_Y (MPa)	σ_B (MPa)	ϵ_B (%)	U_T (MJ/m ³)
1	279	10	19	349	53.1
2	287	10	20	302	48.2
3	309	11	22	428	81.9

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Chapter 4: Structure-Property Relationship in Network Polyesters Derived from Cyclic and Linear Ethylene Fumarate Oligomers

4.1 Introduction

Unsaturated polyesters are a versatile class of polymers, used as a foundation for constructing polymer networks or enabling post-polymerisation modifications. Maleic acid/anhydride is among the most common monomers used in unsaturated polyester synthesis, which partially isomerises to fumaric ester units during polycondensation.¹ Due to their tuneable properties, unsaturated polyesters based on maleate and fumarate have found extensive applications in biomedical and tissue engineering.² For instance, poly(propylene fumarate) (PPF) has been studied for drug delivery systems, benefiting from its biocompatibility and controlled degradability.³⁻⁵ Additionally, PPF has been widely applied in additive manufacturing, enabling the creation of materials with tailored shapes and mechanical properties.⁶⁻⁹ Beyond PPF, poly(propylene glycol-co-fumaric acid), oligo(poly(ethylene glycol) fumarate) and poly(caprolactone-co-fumarate) have been explored for applications in membranes, bone and tissue engineering.¹⁰⁻¹³

In addition to these advancements in unsaturated polyesters containing maleate/fumarate groups, further exploration of structural variations could unlock new functional properties. To this end, tin-mediated esterification, reported in the previous chapters for the synthesis of ethylene succinate macrocycles, was here adapted to synthesise novel ethylene fumarate macrocycles (*cyc*(EF)_n).¹⁴ This synthesis resulted in partial *trans*-to-*cis* isomerisation during ring closure, creating a unique opportunity to explore stereochemical effects. Their linear counterparts (*lin*(EF)_n) were prepared by ring-opening polymerisation (ROP) of *cyc*(EF)_n, yielding 100% *trans* oligomers, as well as by polycondensation of maleic acid and ethylene glycol, allowing controlled *cis/trans* isomerisation. Access to cyclic and linear structures, combined with the ability

to control *cis/trans* isomerism, provided a unique opportunity to investigate the influence of molecular topology and stereochemistry on the properties of crosslinked networks.

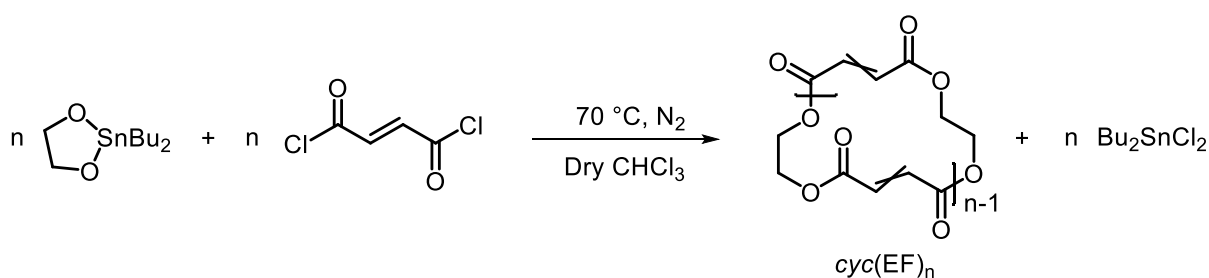
Cyclic and linear oligomers play distinct roles in developing polymer networks due to unique topological and structural features that can significantly influence material properties. While there is limited research directly comparing the properties of networks based on cyclic vs linear oligomers, existing studies demonstrate the advantages of gels based on cyclic topology over their linear counterparts. One critical benefit is the absence of structural defects in networks based on cyclic topologies, such as loops and dangling chain ends, which are common in networks formed from linear oligomers and do not contribute to the elasticity.¹⁵ Cyclic oligomers, when crosslinked with at least two connections per oligomer precursor, result in networks devoid of dangling chain ends, enhanced viscoelasticity and mechanical strength. Additionally, the cyclic topology introduces a secondary intramolecular crosslink, which further enhances network stability and mechanical properties. For instance, Trachsel *et al.* demonstrated that transferring the topological effects from cyclic poly (2-oxazoline) to crosslinked hydrogels resulted in materials with unique properties, including swelling capacity, while maintaining superior mechanical properties.¹⁶ Similarly, Zhang *et al.* found that gels formed from cyclic poly(5-hydroxy-1-cyclooctene) exhibited increased gel fraction, swelling ratio, and modulus at higher initial polymer concentrations, in contrast to the expected trends for linear polymer gels.¹⁷ These findings underline the potential of cyclic oligomers for developing advanced polymer networks.

Inspired by these works, this chapter explores the combined effects of topology and stereochemistry within crosslinked ethylene fumarate networks. The variations in the *cis/trans* isomeric ratio within cyclic and linear oligomers add a layer of structural parameters, enabling a comprehensive investigation into the relationship between molecular structure and network properties. Specifically, four distinct samples were prepared for this study: cyclic oligomers with 90% and 80% *trans* content and linear oligomers with equivalent *trans* ratios. As the ROP of *cyc*(ES)_n obtained only 100% *trans* oligomers, *lin*(EF)_n with 90% and 80% *trans* content were synthesised *via* polycondensation. By synthesising and crosslinking tailored oligomers, this study allows for a direct comparison of the influence of oligomer topology and stereochemistry on network characteristics and thermomechanical performance, offering insights into how structural variations can be leveraged to achieve targeted material properties.

4.2 Result and Discussion

4.2.1 Synthesis and characterisation of $\text{cyc}(\text{EF})_n$

The $\text{cyc}(\text{EF})_n$ was synthesised by the condensation of 2,2-dibutyl-1,3,2-dioxastannolane (DOX) with fumaryl chloride, the same technique as described in Chapter 2, yielding 65% after purification steps (Scheme 4.1).¹⁴ High-performance liquid chromatography mass spectrometry (HPLC MS) analysis of $\text{cyc}(\text{EF})_n$ revealed a range of cyclic species, from trimers to octamers, with a decreasing abundance (Figure 4.1).



Scheme 4.1 Synthesis of $\text{cyc}(\text{EF})_n$ through tin-mediated esterification.

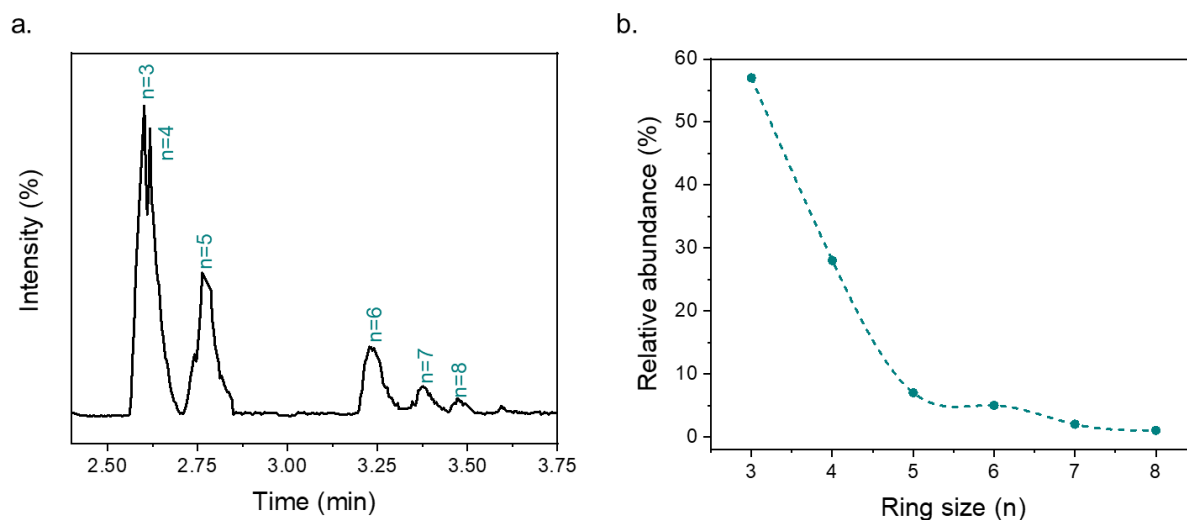


Figure 4.1 a. HPLC chromatogram of $\text{cyc}(\text{EF})_n$; b. Ring size distribution based on HPLC-MS results.

^1H NMR spectrum of $\text{cyc}(\text{EF})_n$ revealed *trans* to *cis* isomerisation during the ring closure process (Figure 4.2). *Trans* to *cis* ratio was quantified from *cis* alkene peaks at

$\delta = 6.77$ ppm and *trans* alkene peaks at $\delta = 6.88$ ppm in the ^1H NMR spectrum, typically obtaining 10% *cis* content in each $\text{cyc}(\text{EF})_n$ batch. Although the *trans* alkene is thermodynamically more stable than *cis* alkene groups, it was hypothesised that partial isomerisation to *cis* alkene may occur to facilitate ring formation. The separation of the *cis* and *trans* containing $\text{cyc}(\text{EF})_n$ was possible based on their solubility differences. At room temperature, the *cis* containing $\text{cyc}(\text{EF})_n$ was soluble in dichloromethane, whereas the *trans* containing $\text{cyc}(\text{EF})_n$ dissolved only in chloroform. The separation based on the solubility difference yielded a fraction with 20% *cis* content, comprising about 25% of the total $\text{cyc}(\text{EF})_n$ weight. Furthermore, the *cis* groups in $\text{cyc}(\text{EF})_n$ were isomerised to fumarate form using diethylamine, as previously reported (Scheme 4.2).¹⁸

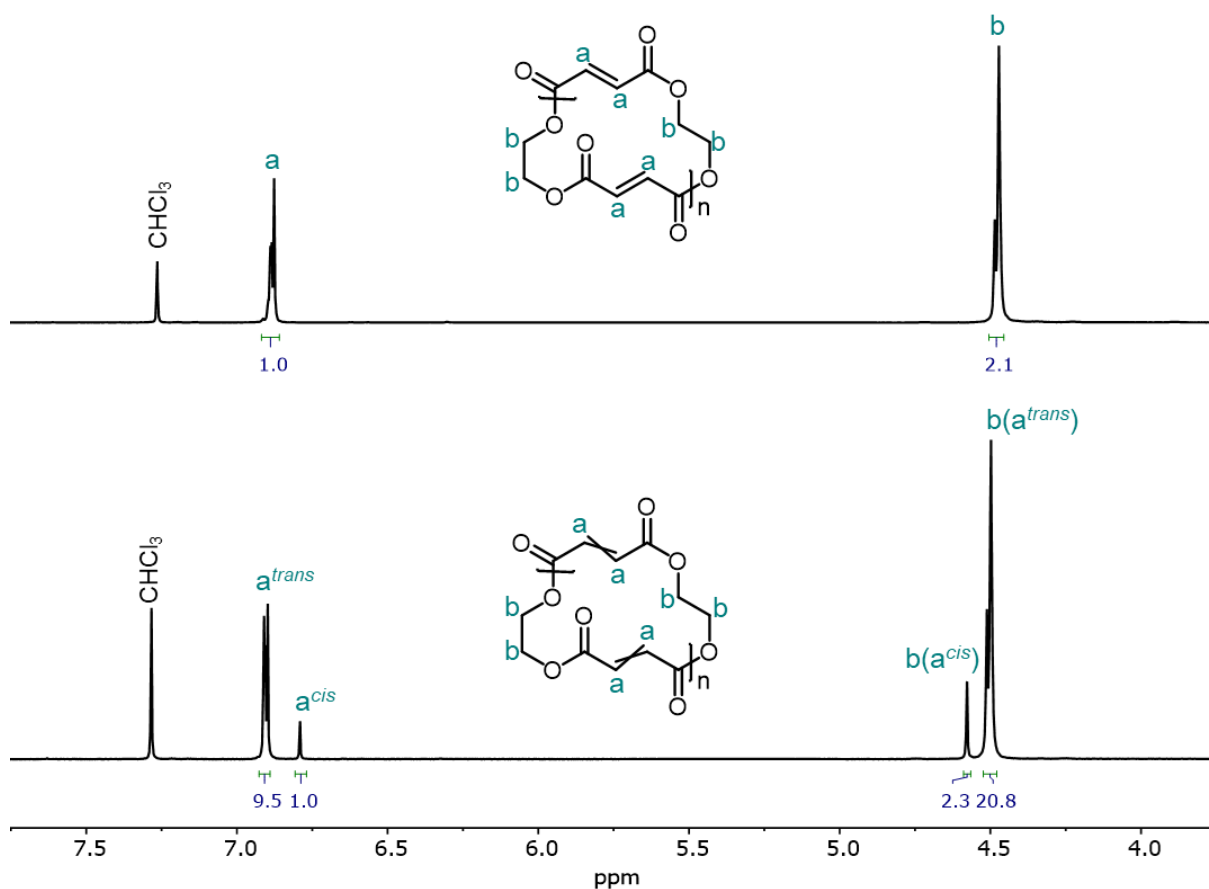
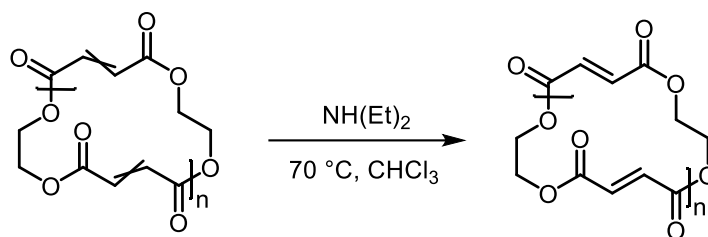


Figure 4.2 Stacked ^1H NMR spectra (400 MHz, 298 K, CDCl_3) of $\text{cyc}(\text{EF})_n$ containing 9.5% *cis* groups (bottom) and 100% *trans* $\text{cyc}(\text{EF})_n$ (top).

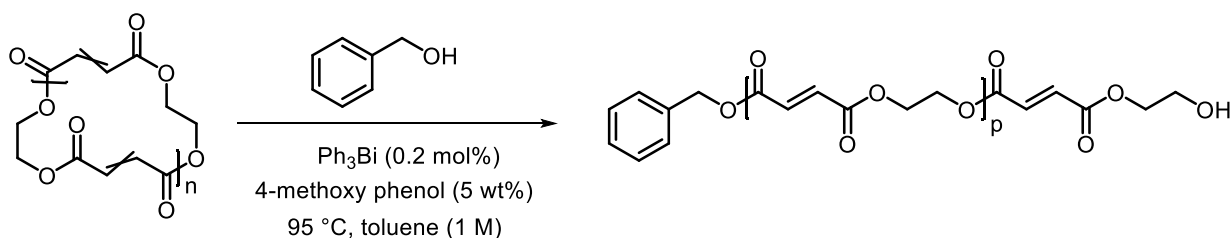


Scheme 4.2 Isomerisation of *cis* alkene groups in *cyc*(EF)_n.

4.3.2 Synthesis and characterisation of *lin*(EF)_n

4.3.2.1 ROP of *cyc*(EF)_n

The ROP of *cyc*(EF)_n was initially performed using 0.2 mol% Ph₃Bi catalyst in bulk, with 4-methoxyphenol added as a radical scavenger to prevent crosslinking. Despite varying scavenger concentrations (1-5 wt%) and temperatures (175, 150 and 135 °C), unwanted crosslinking persisted under these conditions. Ultimately, successful polymerisation without unwanted crosslinking was achieved at 95 °C in toluene with 5 wt% 4-methoxyphenol (Scheme 4.3).



Scheme 4.3 ROP of *cyc*(EF)_n.

In the absence of an added initiator, the resulting polymer exhibited a number average molecular weight (M_n) of 5500 g·mol⁻¹ with dispersity ($\mathcal{D}_M = M_w/M_n$) of 1.89, with matrix-assisted laser desorption/ionisation time-of-flight mass spectroscopy (MALDI-ToF MS) analysis confirming predominantly cyclic structures (Table 4.1, Entry 1; Appendix Figure A4.5). Introducing benzyl alcohol as an initiator promoted linear oligomer formation. The resulting *lin*(EF)_n showed the characteristic end groups peaks at $\delta = 4.35$ ppm ($-\text{CH}_2\text{CH}_2\text{OH}$) and 3.89 ppm ($-\text{CH}_2\text{CH}_2\text{OH}$), whilst the initiator signals

observed at $\delta = 5.23$ ppm ($-\text{OCH}_2-$) and 7.37 ppm ($-\text{C}_6\text{H}_5$) (Figure 4.3). The degree of polymerisation (DP) was determined by the integration ratio of the peak of the repeating alkene unit at $\delta = 6.89$ ppm ($\text{CH}=\text{CH}$) and the peak of the repeating CH_2 protons at $\delta = 4.47$ ppm ($-\text{OCH}_2\text{CH}_2\text{O}-$) to the peak of the chain ends. The targeted DP was achieved at a high initiator ratio (Table 4.1, Entry 3); however, a lower initiator ratio did not yield a higher DP, likely due to constraints arising from the poor solubility of higher molecular weight ethylene fumarate in toluene (Table 4.1, Entry 2). Discrepancies in M_n values between SEC analysis and ^1H NMR spectroscopy likely arise from differences in calibration standards and the hydrodynamic volume of cyclic vs linear oligomers. Notably, all *cis* alkene in $\text{cyc}(\text{EF})_n$ were isomerised to *trans* configurations during ring expansion or ring opening, yielding 100% *trans* cyclic or linear ethylene fumarate oligomers. However, poor solubility of the 100% *trans* $\text{cyc}(\text{EF})_n$ and $\text{lin}(\text{EF})_n$ severely limited their application in resin formulations. This limitation led to inhomogeneous crosslinking reactions, with all attempts resulting in brittle and deformed films. As a result, further optimisation of ROP for these oligomers was not pursued. Instead, efforts were made to tailor the *cis/trans* isomer ratio to balance solubility and mechanical performance, ensuring compatibility with crosslinking processes.

Table 4.1 Summary of Ph_3Bi (0.2 mol%) catalysed polymerisation of $\text{cyc}(\text{EF})_n$ with benzyl alcohol as an initiator at 95 °C in toluene (1 M).

Entry	[M]:[I]	DP	^a M_n^{NMR} ($\text{g}\cdot\text{mol}^{-1}$)	^b M_n^{SEC} ($\text{g}\cdot\text{mol}^{-1}$)	^b M_w^{SEC} ($\text{g}\cdot\text{mol}^{-1}$)	^b D_M
1	100:0	-	-	5500	10420	1.89
2	100:1	17	2520	7550	11310	1.49
3	100:10	11	1670	2360	4580	1.93

^a Calculated from the formula: $M_n = (DP \cdot M_{\text{repeating unit}}) + M_{\text{initiator}}$. DP was determined by integrating end-groups using ^1H NMR spectroscopy (400 MHz, 298 K, CDCl_3).

^b Determined by SEC analysis in CHCl_3 (0.5% NEt_3) as eluent and calibrated against polystyrene standards.

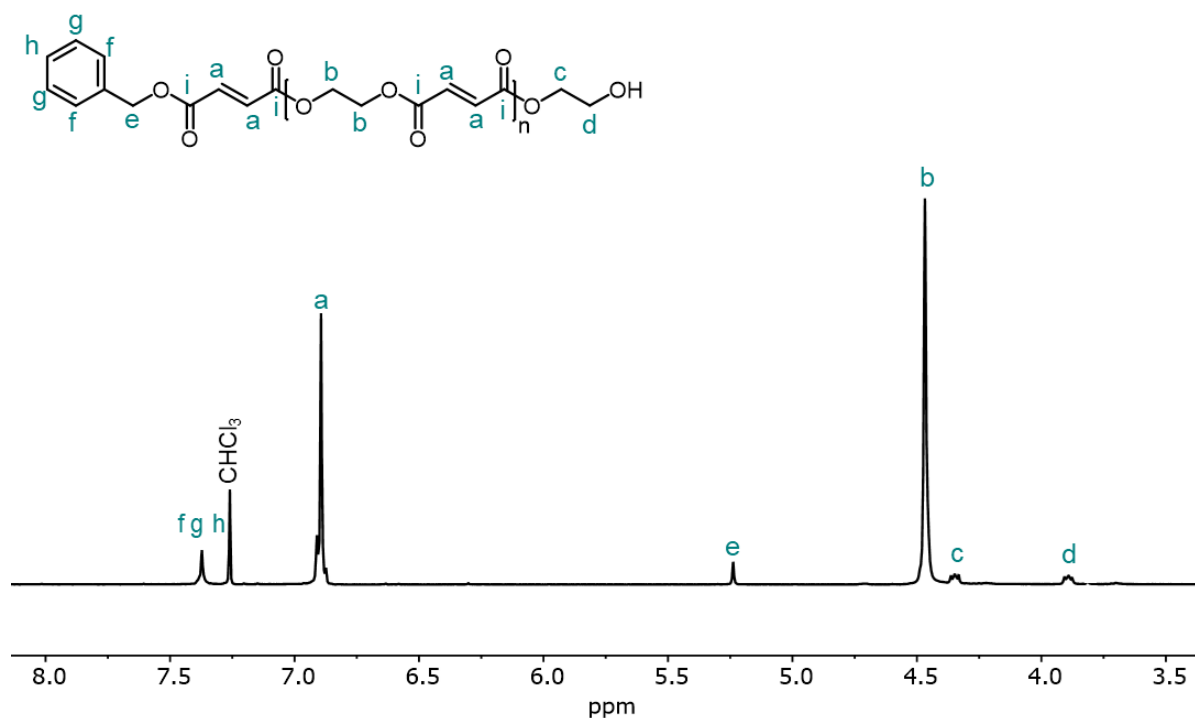
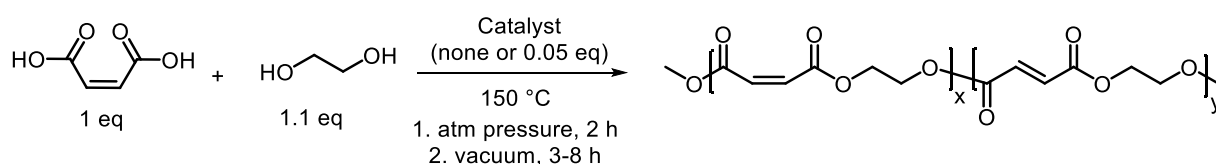


Figure 4.3 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of $\text{lin}(\text{EF})_n$ (Table 4.1, Entry 3).

4.3.2.2 Polycondensation of Maleic Acid and Ethylene Glycol

To address the poor solubility of the 100% *trans* oligomers, which limited their utility in resin formulations, $\text{lin}(\text{EF})_n$ containing *cis* groups were synthesised via a two-step polycondensation of maleic acid and ethylene glycol. Precise temperature control was essential during polycondensation to avoid unwanted crosslinking while achieving adequate molecular weight. Thus, the reaction temperature was maintained at 150 °C, above the minimum temperature required to keep maleic acid and ethylene glycol molten throughout the reaction and promote their polycondensation (Scheme 4.4).



Scheme 4.4 Polycondensation reaction of maleic acid and ethylene glycol.

First, the polycondensation was conducted without a catalyst with initial prepolymer formation under atmospheric pressure for 2 h. Vacuum was then applied

until the reaction mixture became viscous. The characteristic peak disappearance of the ethylene glycol protons at $\delta = 3.75$ ppm ($\text{HOCH}_2\text{CH}_2\text{OH}$) and the concomitant appearance of the CH_2 protons next to the ester group at $\delta = 4.43$ ppm ($-\text{OOCCH}_2\text{CH}_2\text{COO}-$) in the ^1H NMR spectra enabled determination of the monomer conversion over time (Figure 4.4). While the end group protons at $\delta = 3.89$ ppm ($-\text{CH}_2\text{CH}_2\text{OH}$) were used to determine DP, the vinyl protons at $\delta = 6.33$ and 6.87 ppm ($\text{CH}=\text{CH}$) corresponding to the *cis* and *trans* configurations, respectively, were used to calculate the isomerisation ratio. The polycondensation without a catalyst resulted in linear oligomers with M_n of $1540 \text{ g}\cdot\text{mol}^{-1}$ and a 97% conversion after 8 h (Table 4.2, Entry 1). Maleic acid is known to isomerise into fumaric acid during polycondensation, greatly influenced by the temperature.¹⁹ Throughout the reaction, the proportion of the *trans* alkene progressively increased with time, ultimately reaching a final *trans* composition of 40%.

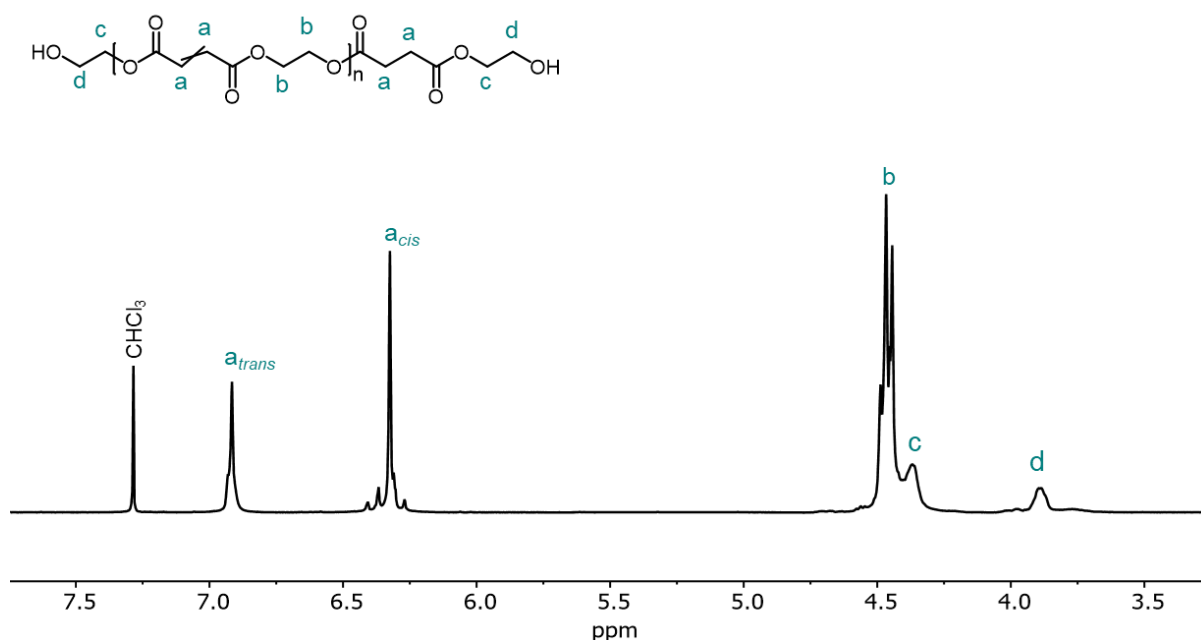


Figure 4.4 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of linear oligomers from the polycondensation of maleic acid and ethylene glycol without catalyst (Table 4.2, Entry 1).

Since $\text{cyc}(\text{EF})_n$ was obtained with 80% and 90% *trans* compositions, similar *cis/trans* ratios were targeted for $\text{lin}(\text{EF})_n$ to enable a direct comparison between films based on cyclic and linear oligomers. The $\text{lin}(\text{EF})_n$ with 40% *trans* composition, was subjected to isomerisation using diethylamine, which increased the *trans* composition from 40% to 70% in about 6 h, although the process lacked precise control.

To simplify the procedure and achieve the targeted *cis/trans* ratios in $\text{lin}(\text{EF})_n$, organocatalysts, such as nicotinic acid, proline and betaine, were employed directly in polycondensation (Figure 4.5). Previous studies within our group demonstrated that these catalysts can significantly accelerate the monomer conversion while simultaneously adjusting the *cis/trans* isomerisation ratio in the polycondensation of maleic acid. Their efficiency is attributed to their tailored nucleophilicity and basicity, which influence both reaction kinetics and isomerisation degree of the final oligomers (unpublished results, manuscript submitted).

The polycondensation of maleic acid and ethylene glycol catalysed by nicotinic acid resulted in complete isomerisation of *cis* to *trans* alkenes and 95% monomer conversion within 3 h (Table 4.2, Entry 2). This rapid isomerisation is attributed to the tertiary amine functionality of nicotinic acid, which is highly nucleophilic and further stabilised by electron delocalisation across its aromatic ring. Similarly, proline, acting as both a base and a nucleophile, facilitated a high conversion after 7 h under vacuum, producing oligomers with 90% *trans* composition (Table 4.2, Entry 3). Betaine, on the other hand, enabled faster monomer conversion (4 h) and yielded an oligomer with 80% *trans* composition (Table 4.2, Entry 4). These catalysts allowed more precise control over the *cis/trans* ratios, eliminating the need for a post-isomerisation step while maintaining target *trans* composition in $\text{lin}(\text{EF})_n$.

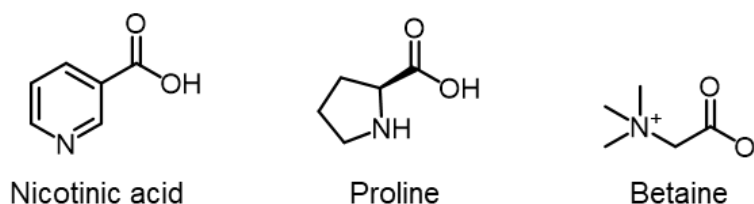


Figure 4.5 Isomerisation catalysts used in polycondensation of maleic acid and ethylene glycol.

Table 4.2 Summary of polycondensation of maleic acid and ethylene glycol at 150 °C using different catalysts.

Entry	Catalyst	Time in 2 nd step (h)	^a Conversion (%)	^a DP	^a M _n (g·mol ⁻¹)	^a Trans (%)
1	None	8	97	6	910	40%
2	Nicotinic Acid	3	95	5	770	100%
3	Proline	7	96	7	1050	90%
4	Betaine	4	97	7	1050	80%

^a Determined by ¹H NMR spectroscopy (400 MHz, 298 K, CDCl₃).

^b Calculated from the formula: $M_n = (DP \cdot M_{\text{repeating unit}}) + M_{\text{ethylene glycol}}$.

4.3.3 Kinetic Studies for Photocrosslinking

For the photocrosslinking of ethylene fumarate oligomers, *cyc*(EF)_n or *lin*(EF)_n were incorporated into a resin containing trimethylolpropane tris(3-mercaptopropionate) (TMPMP) at a stoichiometric thiol (-SH) to alkene (C=C) ratio, Irgacure 1173 (4 wt%) as a photoinitiator and chloroform (50 wt%). Fourier transform infrared spectroscopy (FTIR) was initially used to determine the kinetics of UV curing by monitoring the disappearance of alkene double bond stretch at 1642 cm⁻¹ (Figure 4.6). The maximum curing conversions were 80% and 75% for resin based on *cyc*(EF)_n with 100% *trans* composition and the resin based on *cyc*(EF)_n with 90% *trans* composition, respectively. However, the weak absorption signals of the alkene and thiol groups limited the quantitative accuracy of FTIR spectroscopic analysis, making the determination of photocrosslinking conversion inconsistent for other formulations.

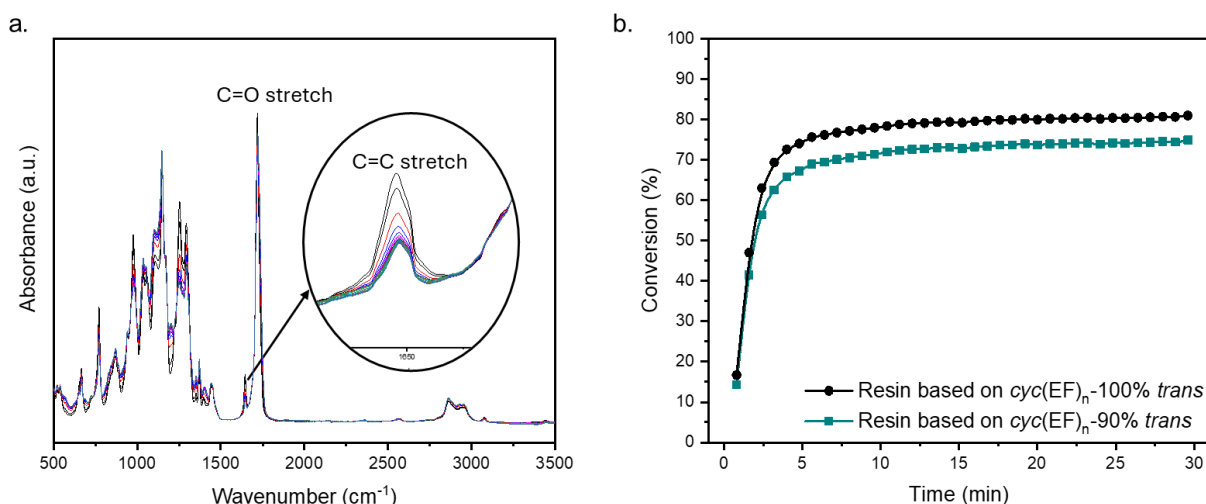
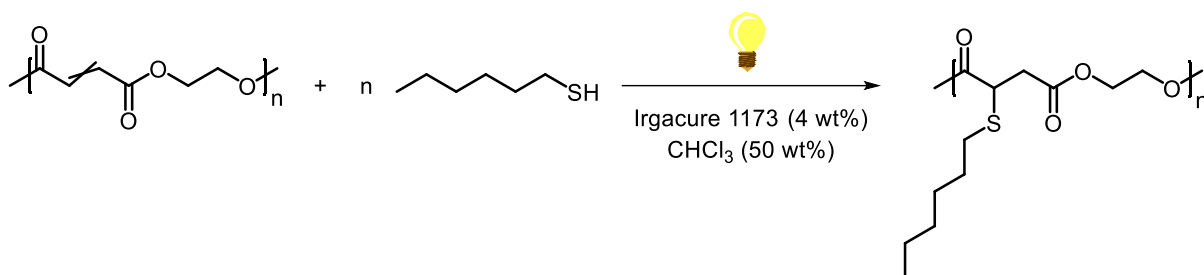


Figure 4.6 FTIR spectra of the resin based on the $\text{cyc}(\text{EF})_n$ with 100% *trans* composition photocuring over time, showing the C=C disappearance at 1647 cm^{-1} ; b. Thiol-ene conversion of resins based on 100% *trans* $\text{cyc}(\text{EF})_n$ and 90% *trans* $\text{cyc}(\text{EF})_n$.

Therefore, the model kinetic studies to monitor thiol-ene conversion over time were performed using ^1H NMR spectroscopy, replacing the trifunctional TMPMP in the resin with monofunctional hexyl mercaptan (Scheme 4.5). The thiol-ene conversion was determined from the characteristic peak disappearance of hexyl mercaptan protons at $\delta = 2.51\text{ ppm}$ ($\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{SH}$) and the concomitant appearance of protons at $\delta = 2.68\text{ ppm}$ ($\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{S-CH-}$) in the ^1H NMR spectra (Appendix, Figure A4.8).



Scheme 4.5 Thiol-ene reaction of ethylene fumarate oligomers (cyclic or linear).

The thiol-ene reactions of $\text{cyc}(\text{EF})_n$ of 100% *trans* and 90% *trans* compositions with 1-hexyl mercaptan achieved 95% and 82% conversion, respectively (Figure 4.7). Despite the differences in overall conversion, trends observed in conversion rate in the

FTIR spectroscopic studies for the photocuring of these two oligomers with TMPMP align with the kinetic model studies. The differences in overall conversion between the crosslinked system and the non-crosslinked model system are likely caused by the reduced mobility of the reacting thiol groups in the crosslinked network.

Both thiol-ene reactions of the cyclic and linear oligomers demonstrated an increase in conversion rate with higher *trans* content, which aligns with expectations since *cis* alkenes generally exhibit higher steric strain, leading to slower reaction rates (Figure 4.7).²⁰ Typically, during thiol-ene reactions, the *cis*-ene has been shown to isomerise to the *trans*-ene early in the reaction *via* the insertion-isomerisation-elimination mechanism, and subsequently consumed as *trans*-ene which is the slow and rate determining step.²¹ As a result, although conversion rates may differ slightly, the overall conversion is expected to remain comparable. Notably, *cis*-ene peaks of ethylene fumarate oligomers disappeared in ¹H NMR spectra of crude reaction within 15 minutes (Appendix, Figure A4.8) and the overall thiol-ene conversion was higher in oligomers with greater *trans* content. While the reason behind this is unclear at present, it may be rationalised by considering that the overall reaction kinetics were slow for a thiol-ene reaction, and the additional isomerisation step required for *cis* alkenes slowed the reaction even further (Figure 4.7). This could introduce opportunities for side reactions, decreasing the effective concentration of reactive species available for complete thiol-ene conversion, and depending on the rate, decrease the overall conversion further.

Distinct trends were also observed in the reaction kinetics between cyclic and linear oligomers. Cyclic oligomers reacted rapidly during the first 10–15 minutes, with the conversion rate slowing thereafter, whereas linear oligomers showed a more

gradual increase in conversion over time. This contrast highlights the potential influence of molecular topology on reaction kinetics, though the exact reasons remain unclear. One possibility is that the restricted ring topology of cyclic oligomers imposes steric constraints and introduces strain, making the alkene more eager to react. Alternatively, cyclic and linear oligomers might interact differently with the solvent, potentially enhancing the accessibility of the double bond in cyclic oligomers. To clarify these effects, further studies comparing the reaction kinetics in various solvents are needed.

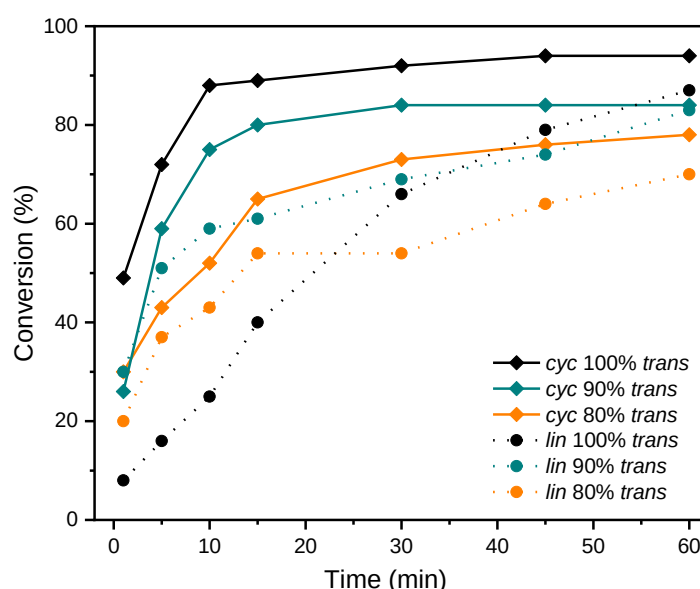
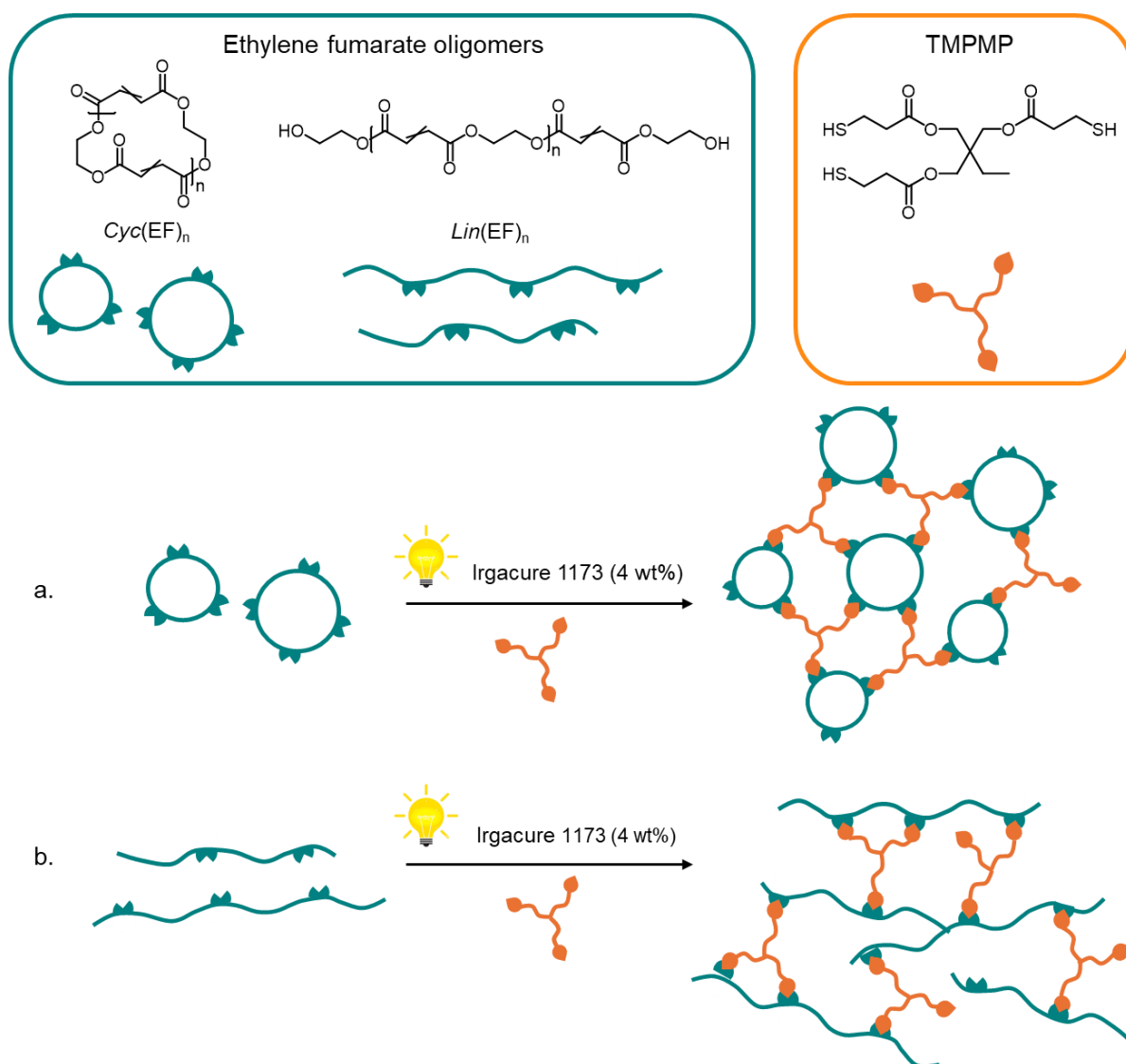


Figure 4.7 Thiol-ene conversion of ethylene fumarate oligomers and hexyl mercaptan determined by ^1H NMR spectra.

4.3.4 Network polyesters of $\text{lin}(\text{EF})_n$ and $\text{cyc}(\text{EF})_n$

Resins, prepared by mixing ethylene fumarate oligomers and TMPMP at a stoichiometric thiol ($-\text{SH}$) to alkene ($\text{C}=\text{C}$) ratio, Irgacure 1173 (4 wt%) and chloroform (50%) at room temperature, were photocured in a pre-cut silicone rectangular or dog-bone-shaped mould with a UV light source for 1 h (Scheme 4.6). Crosslinked films were post-cured in an oven at $80\text{ }^\circ\text{C}$ for 24 h to remove the solvent and washed by soaking in THF for 24 h to remove the uncrosslinked materials.



Scheme 4.6 Network formation based on TMPMP and ethylene fumarate oligomers a. $Cyc(EF)_n$; b. $Lin(EF)_n$.

4.3.4.1 Network Characterisation

The formation and structure of the crosslinked network were assessed through gel fraction, swelling ratio, and crosslinking density measurements. The gel fraction of the crosslinked samples was determined as the mass ratio of the dried gel after the washing protocol to the initial gel mass following post-curing. All crosslinked films demonstrated high gel content, indicating efficient photocuring (Table 4.3). Swelling ratios are calculated as the solvent volume ratio at equilibrium swelling to the dried gel mass. Due to differences in the solubility parameters of ethylene fumarate oligomers

across organic solvents, the swelling ratio of all the films followed the trend: THF > acetone > ethyl acetate > toluene. Networks formed by 80% *trans* content in both cyclic and linear topologies exhibited comparable swelling ratios. However, the network formed by *cyc*(EF)_n with 90% *trans* content consistently showed lower swelling ratios across all solvents, indicating that it had a tighter network structure. In contrast, the network formed by *lin*(EF)_n with 90% *trans* content had the highest swelling ratios, nearly triple those of *cyc*(EF)_n with 90% *trans* content in each solvent, reflecting a less dense and more flexible network.

Table 4.3 Gel fraction and swelling ratios of crosslinked films based on *cyc*(EF)_n and *lin*(EF)_n.

Ethylene Fumarate Oligomers	^a Gel fraction (%)	^b Swelling Ratio (cm ³ /g)			
		THF	Acetone	Ethyl Acetate	Toluene
<i>cyc</i> (EF) _n -80% <i>trans</i> content	98	35	21	13	5
<i>cyc</i> (EF) _n -90% <i>trans</i> content	97	25	11	8	3
<i>lin</i> (EF) _n -80% <i>trans</i> content	98	38	19	12	6
<i>lin</i> (EF) _n -90% <i>trans</i> content	98	62	35	24	8

^a The gel fraction was calculated by the mass ratio between the dried gel after the washing protocol and the initial gel mass following post-curing.

^b The swelling ratio was obtained by the ratio of the solvent volume at equilibrium swelling to the mass of the dried gel. Volume/mass was used because each solvent has a different density.

To better understand the contrasting trends in swelling ratios between cyclic and linear networks as a function of *trans* content, the crosslinking density (*d*) of the networks was determined from the modulus of the rubbery plateau ($E'_{rubbery}$) obtained from dynamic mechanical thermal analysis (DMTA) and applying Eq. 4.1 (Figure 4.8).²²

$$d = \frac{E'_{rubbery}}{3R(T_g + 40)} \quad \text{Eq. 4.1}$$

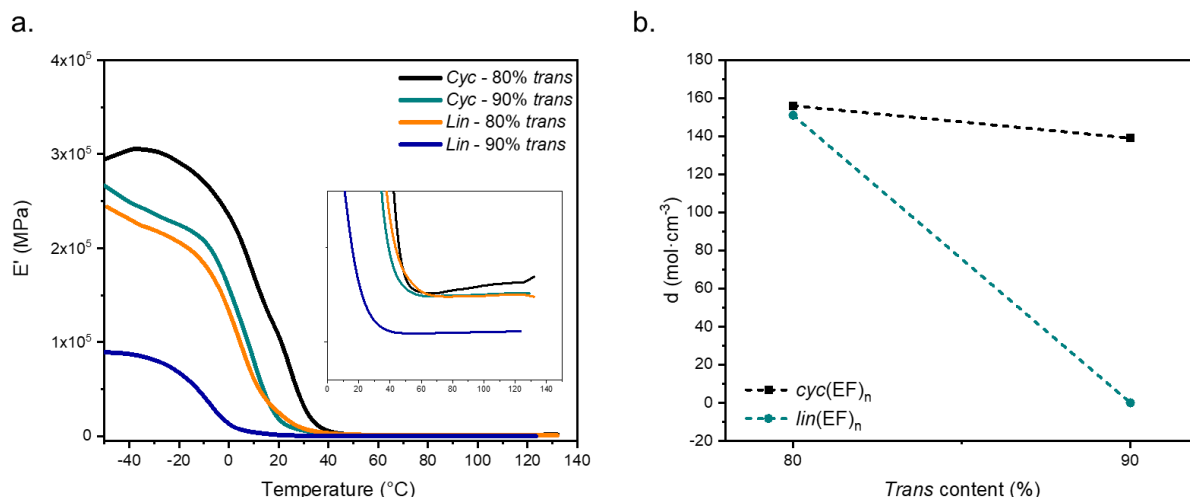


Figure 4.8 a. Storage modulus vs temperature of crosslinked films analysed in bending mode in DMTA; b. The crosslinking density of the films was determined by Eq 4.1.

The networks based on $\text{cyc}(\text{EF})_n$ with 80% *trans* content, $\text{cyc}(\text{EF})_n$ with 90% *trans* content, and $\text{lin}(\text{EF})_n$ with 80% *trans* content exhibit very high crosslinking densities (159, 139, and 151 mol·cm $^{-3}$, respectively), suggesting the presence of intramolecular crosslinking within same oligomer chains. This was possibly due to the ring topology of cyclic oligomers inherently restricting chain mobility and increasing the likelihood of intramolecular crosslinking during curing. Similarly, the higher *cis* content in $\text{lin}(\text{EF})_n$ with 80% *trans* composition introduced kinks that might promote intramolecular crosslinking, enabling a more dense network. For the linear networks, the dramatic decrease in crosslinking density of the network based on $\text{lin}(\text{EF})_n$ with 90% *trans* content (0.032 mol·cm $^{-3}$) was notable, which explained the highest swelling ratio among all films. This reduction in crosslinking density, despite the expected higher thiol-ene conversion at increased *trans* content, suggested that the more linear structure of $\text{lin}(\text{EF})_n$ with 90% *trans* content compared to $\text{lin}(\text{EF})_n$ with 80% *trans* content might reduce the chance for intramolecular crosslinking, resulting in a looser network.

When comparing the networks based on $\text{cyc}(\text{EF})_n$ with 80% *trans* content and $\text{lin}(\text{EF})_n$ with 80% *trans* content, both exhibited similar swelling ratios despite their comparable crosslinking densities. Zhang *et al.* and Trachsel *et al.* demonstrated that networks based on high molecular weight cyclic polymers exhibit higher swelling ratios than those derived from their linear counterparts when the intramolecular crosslinking within individual cyclic polymer chains was eliminated.^{16, 17} These characteristics result in larger mesh sizes within the network, allowing for greater solvent uptake. In the case of $\text{cyc}(\text{EF})_n$, the oligomers have significantly lower molecular weights and potential intramolecular crosslinking, likely reducing the effective mesh size even further.

4.3.4.2 Thermomechanical Properties

Differential scanning calorimetry (DSC) analysis was performed for uncrosslinked $\text{cyc}(\text{EF})_n$ and $\text{lin}(\text{EF})_n$ oligomers, revealing distinct thermal behaviours during the second heating influenced by topology and *cis/trans* content (Figure 4.9). In general, $\text{cyc}(\text{EF})_n$ displayed a higher glass transition temperature (T_g) than $\text{lin}(\text{EF})_n$, attributed to the absence of free chain ends in cyclic structure, which reduces its flexibility. In $\text{cyc}(\text{EF})_n$, T_g increased by approximately 5 °C for every 10% increase in *trans* content, highlighting the role of *cis* groups in enhancing the chain mobility within the cyclic topology. $\text{Lin}(\text{EF})_n$ followed a similar trend of increase in T_g with increased *trans* content, but the effect was less pronounced, with a rise of 2 °C per 10% *trans* content increase.

Notably, the crystallisation behaviour of $\text{cyc}(\text{EF})_n$ and $\text{lin}(\text{EF})_n$ showed an opposite trend as a function of their *cis-trans* isomer ratios. While $\text{cyc}(\text{EF})_n$ with 100% and 90% *trans* compositions remained amorphous, as the rigid cyclic structure restricted molecular mobility, $\text{cyc}(\text{EF})_n$ with 80% *trans* composition exhibited cold

crystallisation at 70 °C and melting at 118 °C, likely due to the flexibility introduced by 20% *cis* content, which allowed sufficient mobility for crystallisation upon heating. In contrast, *lin*(EF)_n, free from the constraints of a cyclic topology, tended toward crystallisation with increasing *trans* content as *trans* isomers promote linearity and regularity. The *lin*(EF)_n with 100% *trans* composition displayed cold crystallisation at 82 °C and melting at 117 °C, while the 90% and 80% *trans* compositions remained amorphous due to disruptions in chain regularity caused by increasing *cis* isomers.

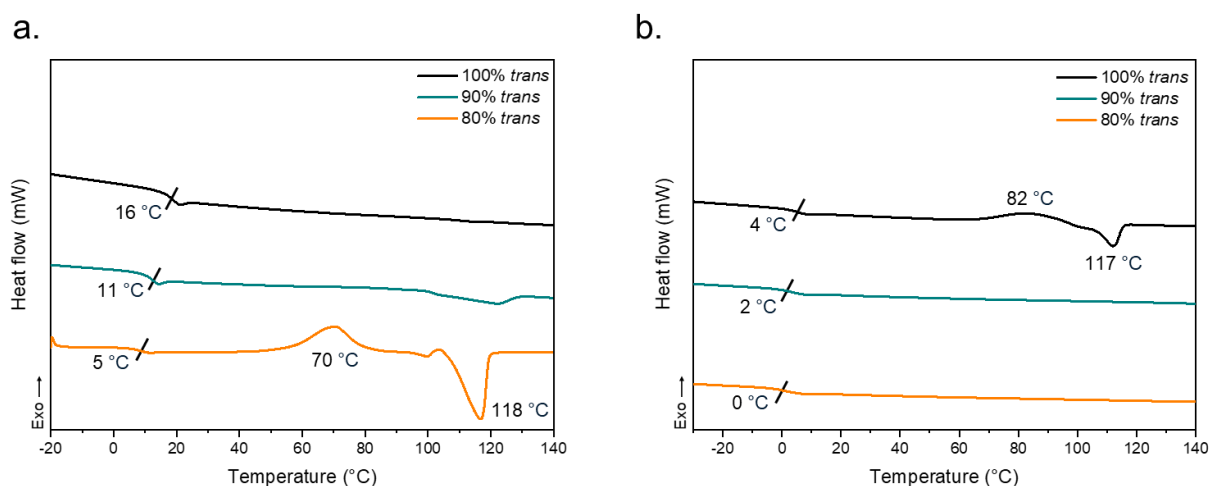


Figure 4.9 DSC thermograms at a heating rate of 5 °C/min of a. *cyc*(EF)_n and b. *lin*(EF)_n with different *cis/trans* ratios.

Upon crosslinking, all networks displayed consistent increases in T_g , with *cyc*(EF)_n-based networks showing higher T_g than *lin*(EF)_n-based networks as *lin*(EF)_n's linear structure permits greater flexibility and free volume, partially due to dangling chain ends. The $\tan \delta$ values of DMTA confirmed these trends, showing slightly higher T_g values than DSC, consistent with reduced mobility in the cyclic-based networks.

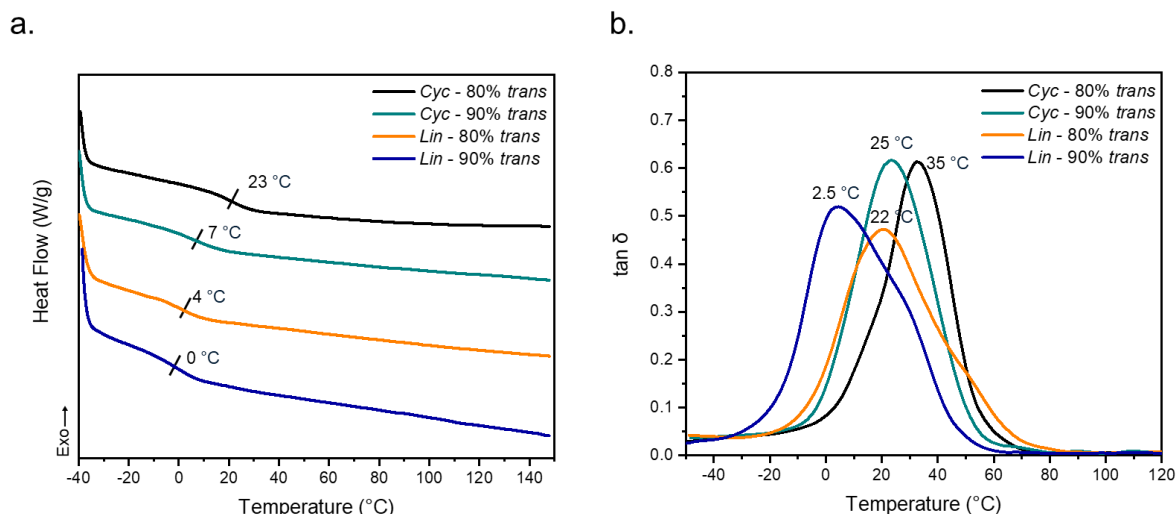


Figure 4.10 a. DSC thermogram at a heating rate of 5 °C/min and b. $\tan \delta$ results (analysed in bending mode in DMTA) of crosslinked films based on $\text{cyc}(\text{EF})_n$ and $\text{lin}(\text{EF})_n$ with different *cis/trans* ratios.

The tensile properties of the crosslinked films revealed that $\text{cyc}(\text{EF})_n$ -based networks demonstrated superior properties than $\text{lin}(\text{EF})_n$ -based networks in terms of elongation, tensile strength, and modulus (Figure 4.11). The network based on $\text{cyc}(\text{EF})_n$ with 80% *trans* content exhibited the highest elongation at break ($\epsilon_B = 33 \pm 3.6$ %), ultimate tensile strength ($\sigma_B = 9 \pm 4.3$ MPa), and Young's modulus ($E = 217 \pm 96.3$ MPa). The other samples followed the trend: $\text{cyc}(\text{EF})_n$ with 90% *trans* content ($\epsilon_B = 25.7 \pm 2.3$ %, $\sigma_B = 5.2 \pm 0.6$ MPa, $E = 49.5 \pm 9.3$ MPa) > $\text{lin}(\text{EF})_n$ with 80% *trans* content ($\epsilon_B = 14.7 \pm 4.5$ %, $\sigma_B = 2.7 \pm 0.7$ MPa, $E = 22.7 \pm 2.9$ MPa) > $\text{lin}(\text{EF})_n$ with 90% *trans* content ($\epsilon_B = 12.4 \pm 2.9$ %, $\sigma_B = 1.2 \pm 0.2$ MPa, $E = 13.2 \pm 1$ MPa). The results suggested that the substantial advantage of cyclic topology in retaining network integrity under stress, especially with *cis* content within cyclic structures, may impart localised flexibility that distributes stress. The enhanced mechanical properties of the $\text{cyc}(\text{EF})_n$ -based networks over linear ones are evident when comparing $\text{cyc}(\text{EF})_n$ with 80% *trans* content to $\text{lin}(\text{EF})_n$ with 80% *trans* content. As these two networks have similar crosslinking densities, the advantage of the cyclic topology in maintaining network

integrity under stress is reflected. *Lin*(EF)_n with 90% *trans* content exhibited the lowest mechanical performance, consistent with its significantly lower crosslinking density.

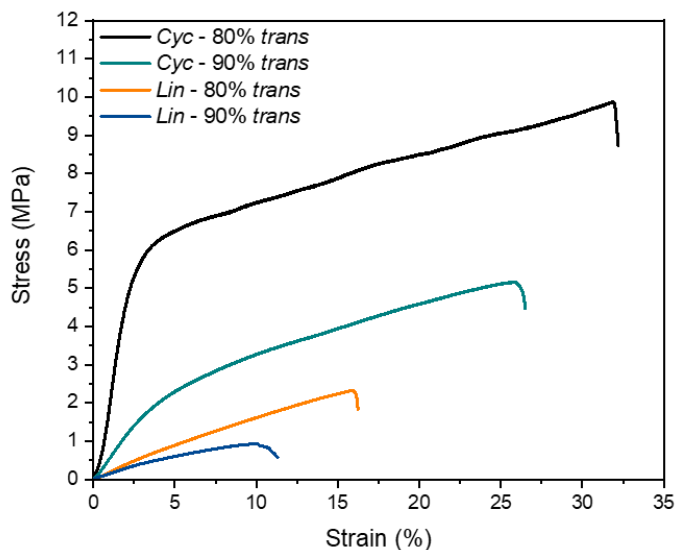


Figure 4.11 Representative stress vs strain plot (1 mm/min, ambient temperature) of crosslinked films based on *cyc*(EF)_n and *lin*(EF)_n with different *cis/trans* ratios.

4.3 Conclusion

This chapter explored the synthesis, characterisation, and photocrosslinking of cyclic and linear ethylene fumarate oligomers to assess how molecular topology and *cis/trans* isomerism influence the properties of crosslinked networks. The oligomers were incorporated into resins and crosslinked *via* thiol-ene photocuring. The resulting networks exhibited varying degrees of crosslinking, swelling, and thermomechanical behaviour, which were impacted by the topology and *cis/trans* content of the oligomers. Overall, networks based on cyclic oligomers exhibited improved crosslinking efficiency and mechanical stability compared to linear counterparts, consistent with existing literature that suggests cyclic topologies reduce network defects and enhance performance. Additionally, the *cis/trans* ratio in $\text{cyc}(\text{EF})_n$ was found to influence the swelling ratio and tensile properties, with higher flexibility observed in networks with increased *cis* content. However, the formation of intramolecular crosslinking limited the comparison of properties of the networks. Future research could explore modifying formulations, such as adjusting crosslinker ratios or employing alternative crosslinkers, to minimise intramolecular linkages and achieve more uniform crosslinking. Further studies on these systems' long-term stability and recyclability will be essential to assess their practical potential for real world applications.

4.4 Appendix

4.4.1 Proton (^1H) NMR Spectra

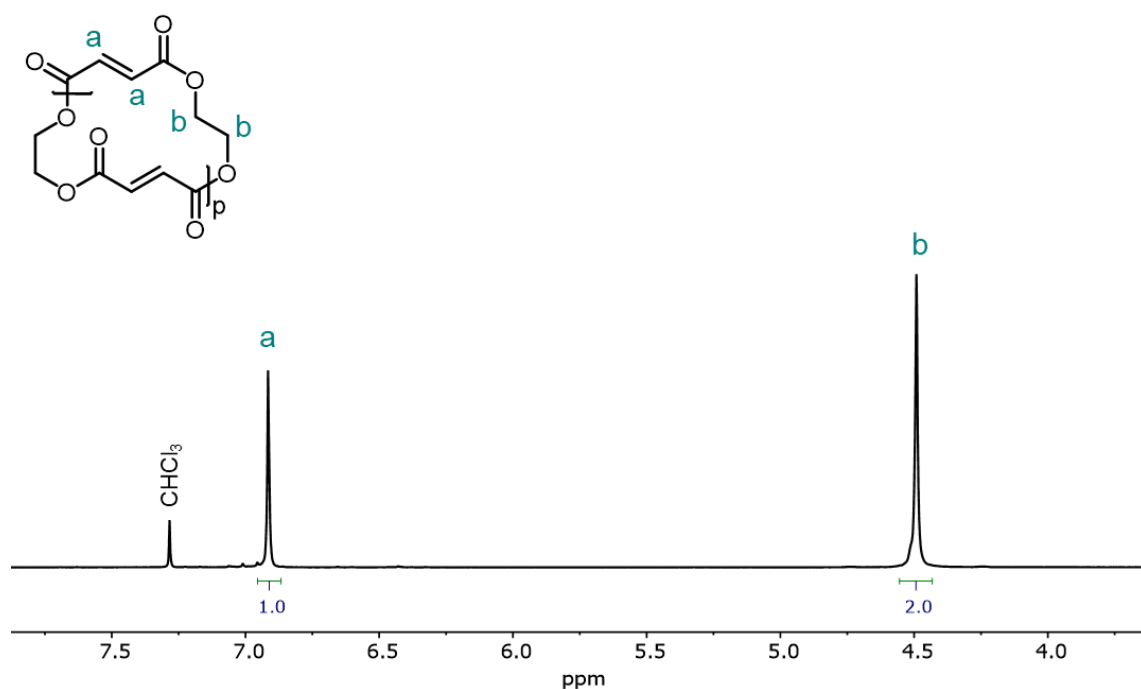


Figure A4.1 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of the product from the ROP of $\text{cyc}(\text{EF})_n$ without initiator (Table 4.1, Entry 1). No end group was observed.

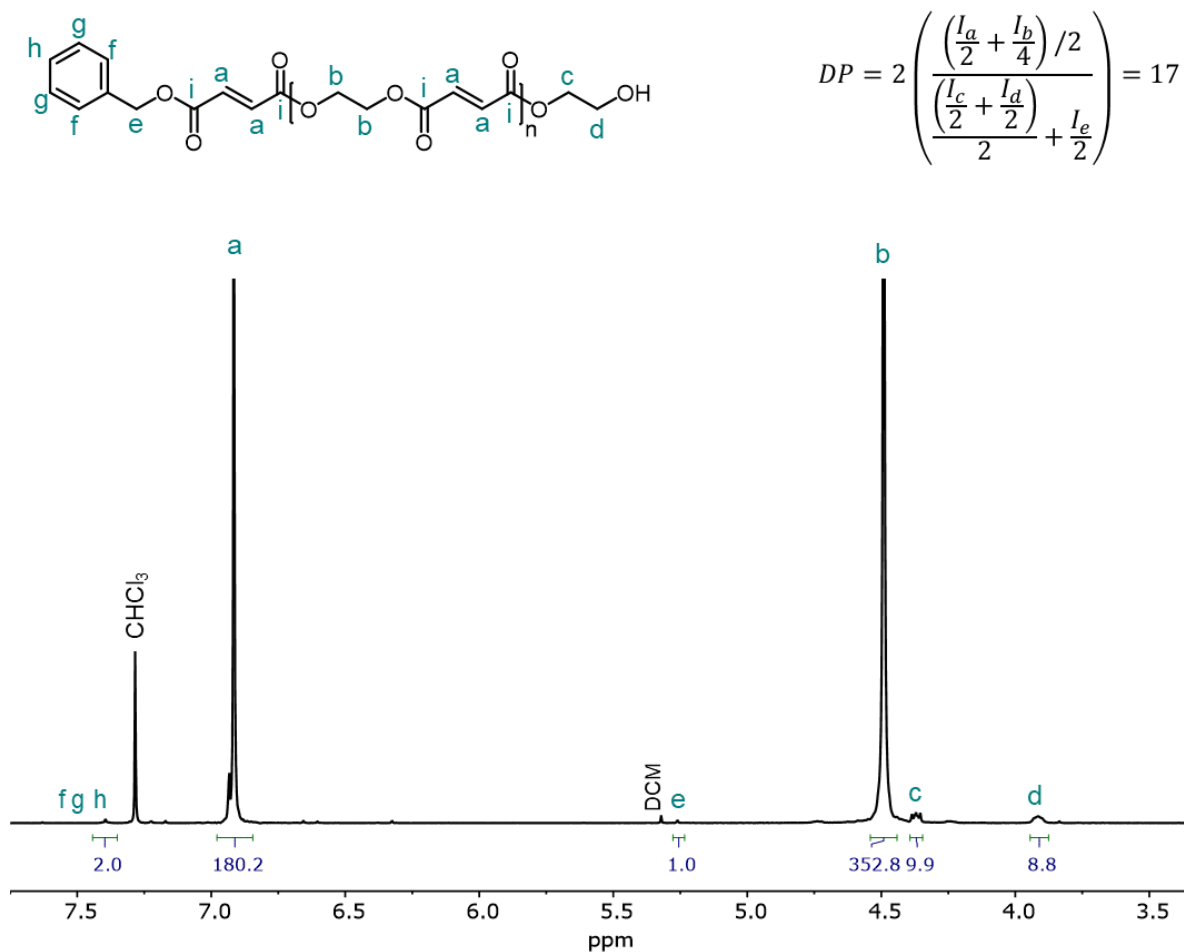


Figure A4.2 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of the product from the ROP of cyc(EF)_n with benzyl alcohol as initiator ([M]:[I]=100:1) (Table 4.1, Entry 2).

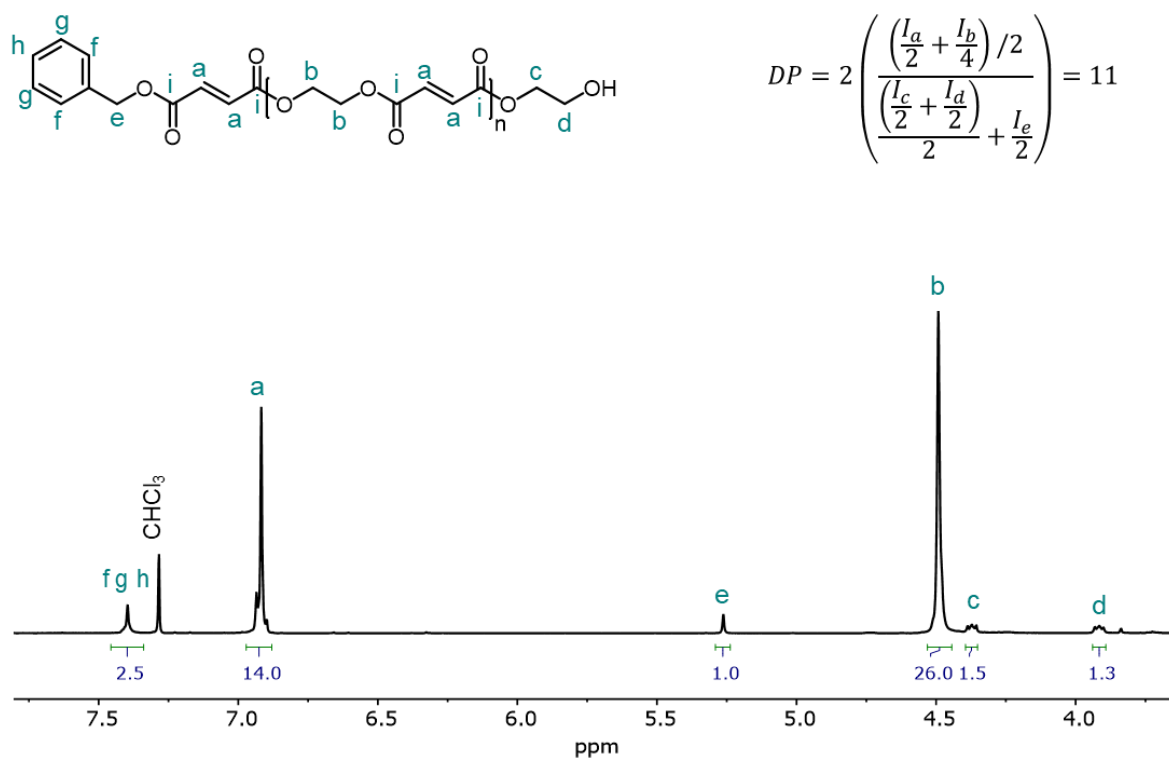


Figure A4.3 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of the product from the ROP of $\text{cyc}(\text{EF})_n$ with benzyl alcohol as initiator ($[\text{M}]:[\text{I}]=10:1$) (Table 4.1, Entry 3).

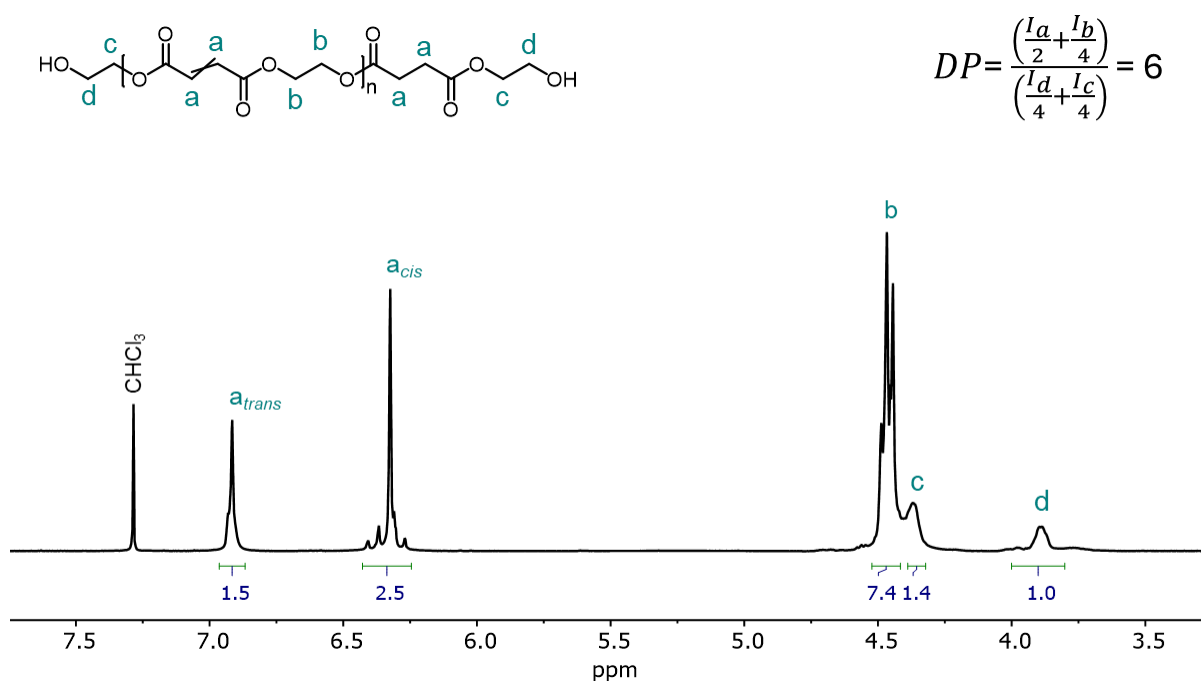


Figure A4.4 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of the product from the polycondensation of ethylene glycol and maleic acid without a catalyst (Table 4.2, Entry 1).

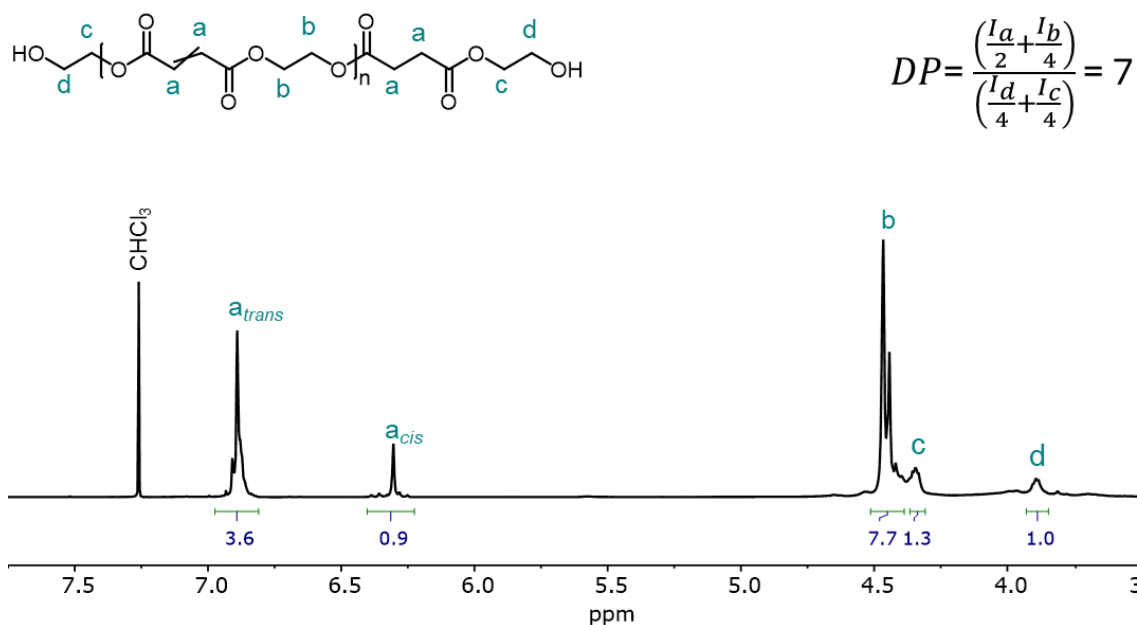


Figure A4.5 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of the product from the polycondensation of ethylene glycol and maleic acid in the presence of betaine as a catalyst (Table 4.2, Entry 2).

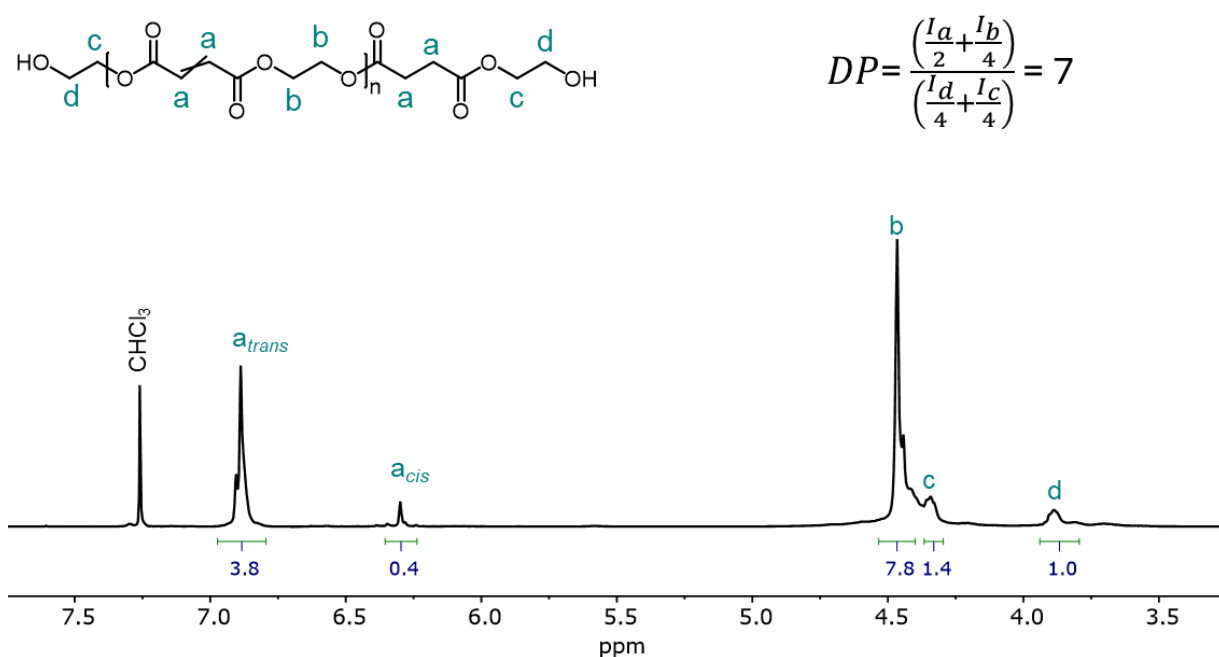
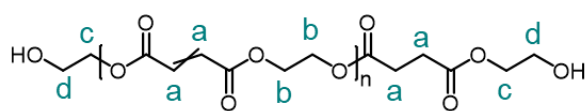


Figure A4.6 ¹H NMR spectrum (400 MHz, 298 K, CDCl₃) of the product from the polycondensation of ethylene glycol and maleic acid in the presence of proline as a catalyst (Table 4.2, Entry 3).



$$DP = \frac{\left(\frac{I_a + I_b}{2} + \frac{I_c}{4}\right)}{\left(\frac{I_d}{4} + \frac{I_c}{4}\right)} = 5$$

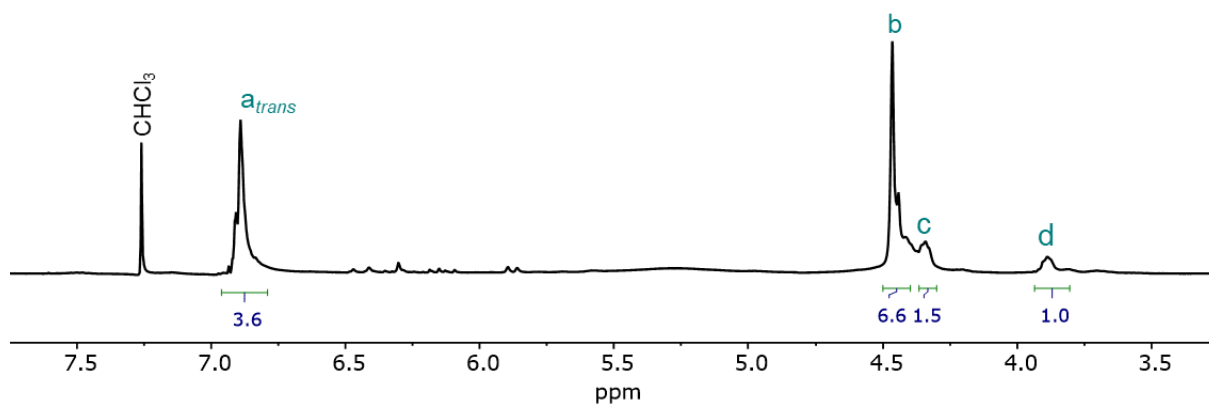


Figure A4.7 ^1H NMR spectrum (400 MHz, 298 K, CDCl_3) of the product from the polycondensation of ethylene glycol and maleic acid in the presence of nicotinic acid as a catalyst (Table 4.2, Entry 4).

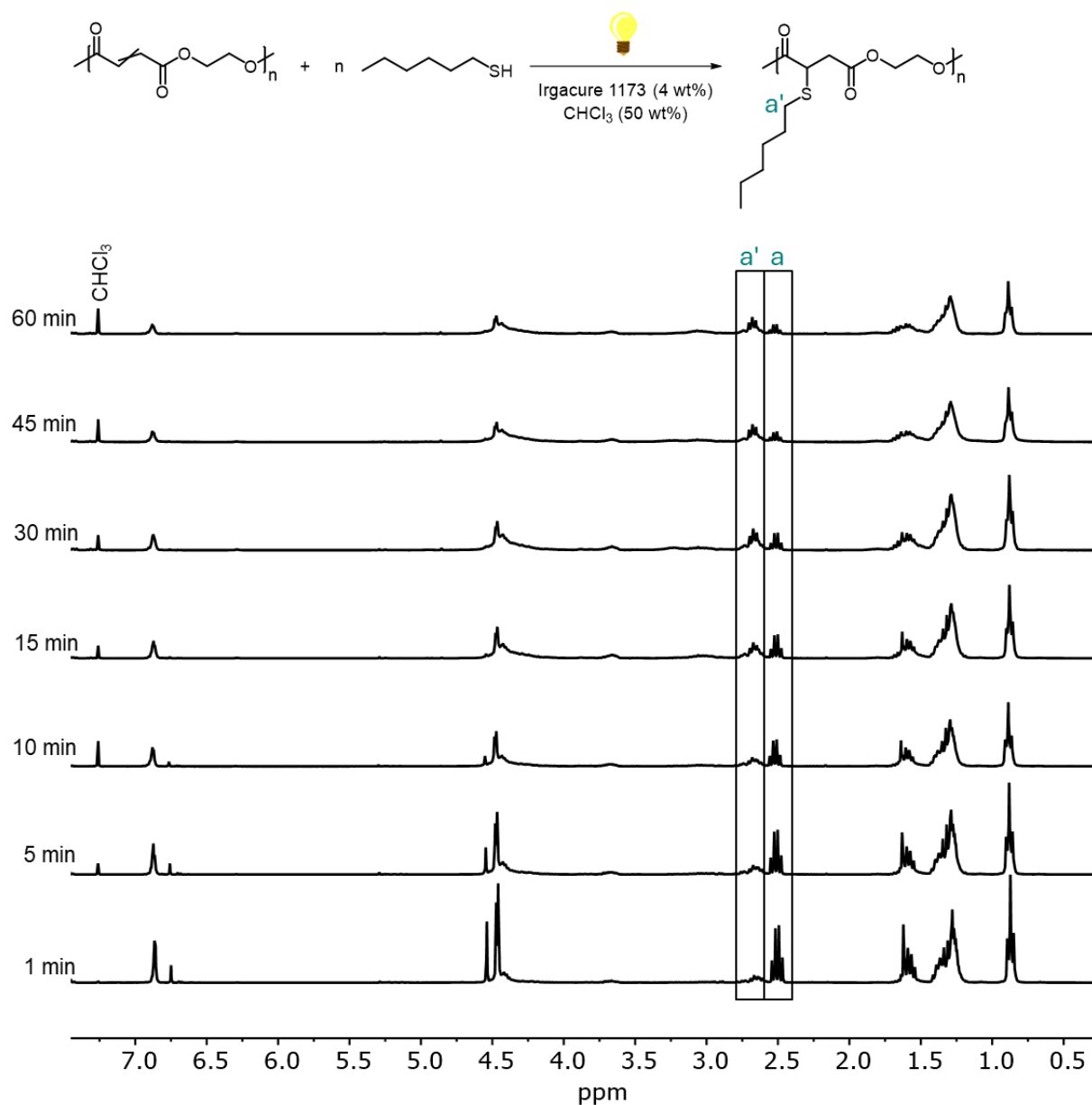


Figure A4.8 ¹H NMR spectra (400 MHz, 298 K, CDCl₃) of crude reaction mixtures of the model thiol-ene reaction of *cyc*(EF)_n-80% *trans* taken at different time points throughout its kinetic study. The time is given next to each spectrum.

4.4.2 Carbon (^{13}C) NMR Spectra

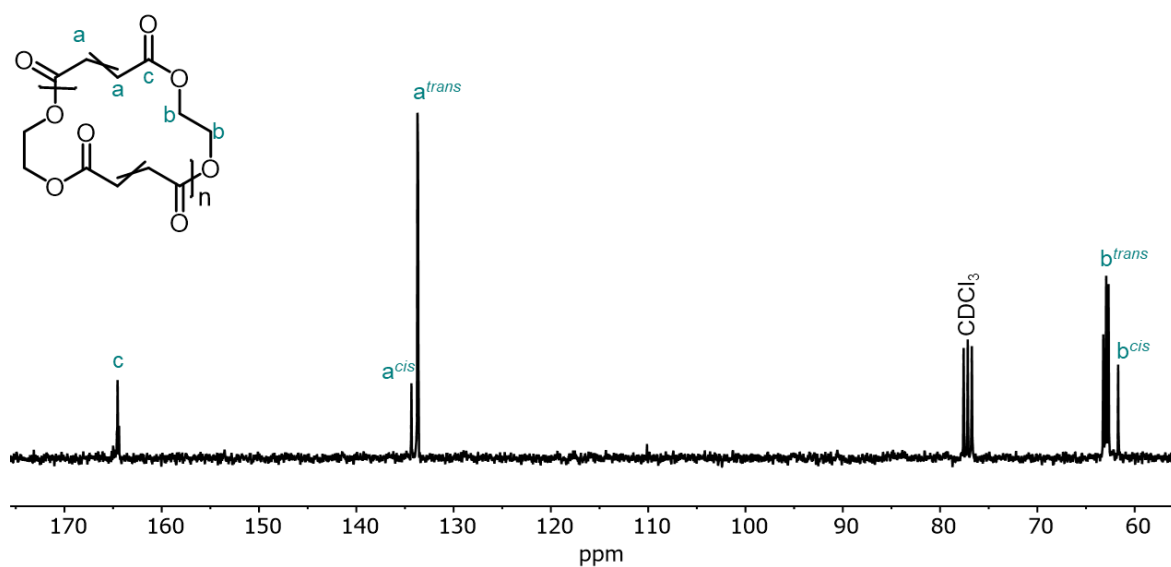


Figure A4.9 ^{13}C NMR spectrum (101 MHz, 298 K, CDCl_3) of $\text{cyc}(\text{EF})_n$.

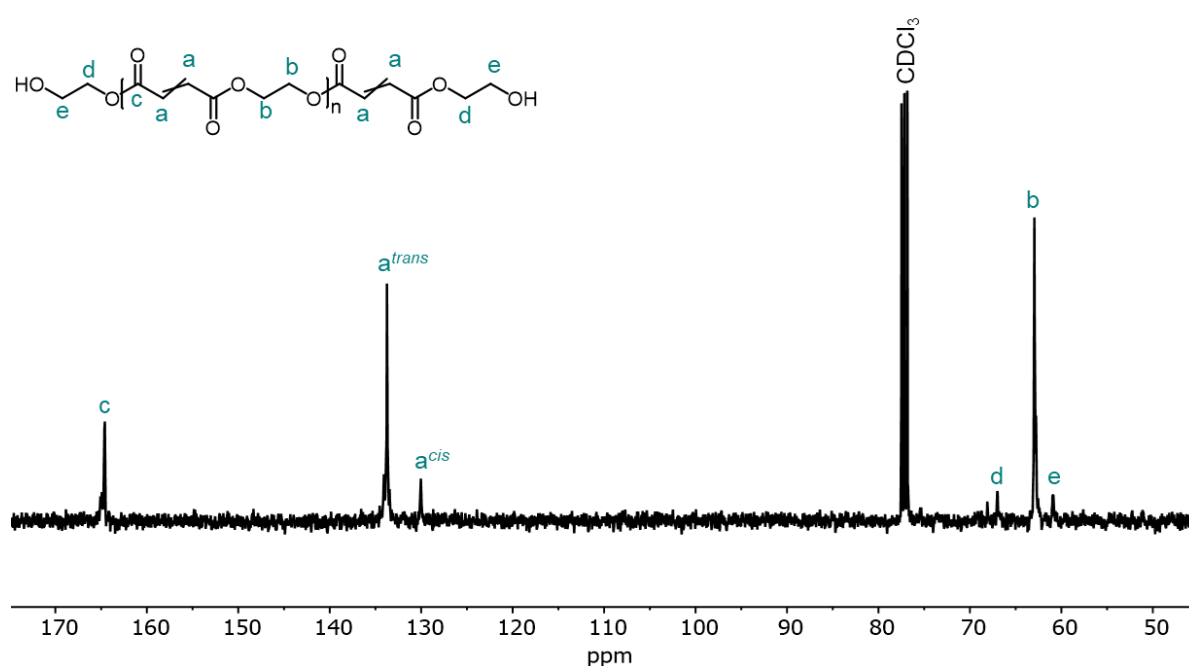


Figure A4.10 ^{13}C NMR spectrum (101 MHz, 298 K, CDCl_3) of $\text{lin}(\text{EF})_n$.

4.4.3 MALDI-ToF MS Spectra

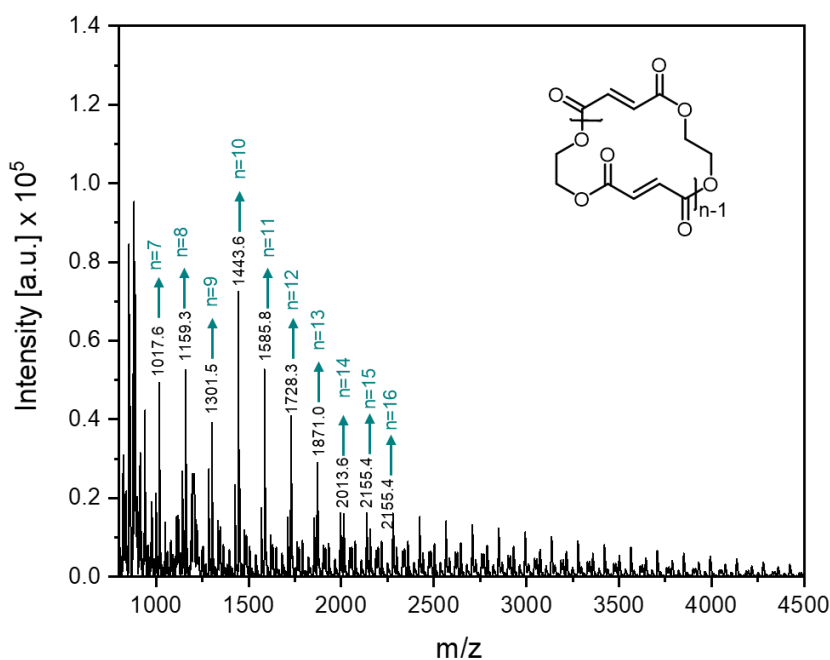


Figure A4.11 MALDI-ToF spectrum of cyc(EF)_n polymerised without initiator (Table 4.1, Entry 1).

4.4.3 Thermomechanical Properties

Table A4.1 Tensile test results of the network based on *cyc(ES)_n-80% trans* (1 mm/min, ambient temperature).

Entry	E (MPa)	σ_B (MPa)	ϵ_B (%)
1	307	10.8	37.4
2	248	9.2	31.1
3	96	6.5	30.2

Table A4.2 Tensile test results of the network based on *cyc(ES)_n-90% trans* (1 mm/min, ambient temperature).

Entry	E (MPa)	σ_B (MPa)	ϵ_B (%)
1	50.2	4.7	23.3
2	58.7	5.6	25.9
3	49.5	4.8	28

Table A4.3 Tensile test results of the network based on *lin(ES)_n-80% trans* (1 mm/min, ambient temperature).

Entry	<i>E</i> (MPa)	σ_B (MPa)	ϵ_B (%)
1	20.8	2.8	15.9
2	26.1	3.4	18.5
3	21.3	1.9	9.6

Table A4.4 Tensile test results of the network based on *lin(ES)_n-90% trans* (1 mm/min, ambient temperature).

Entry	<i>E</i> (MPa)	σ_B (MPa)	ϵ_B (%)
1	13.1	1.4	15.7
2	12.2	1.2	10.9
3	13.2	1.2	20.4

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Chapter 5: Conclusion

The aim of this thesis was to investigate sustainable polymers with tailored properties, focusing on biodegradable polyesters and fumarate-based oligomers to address the environmental challenges posed by fossil-based, non-degradable plastics. Chapters 2 and 3 centred on the synthesis, characterisation and optimisation of poly(ethylene succinate) (PES) and its copolymers for packaging applications, while Chapter 4 explored a new research direction involving ethylene fumarate-based oligoesters. This concluding chapter summarises the key findings from Chapters 2–4, and outlines future directions to advance the field.

A primary challenge addressed was overcoming the limitations of polycondensation for producing high molecular weight PES. In Chapter 2, ring-opening polymerisation (ROP) of ethylene succinate macrocycles ($\text{cyc}(\text{ES})_n$) was demonstrated as a viable alternative. By employing triphenyl bismuth (Ph_3Bi) as an efficient catalyst with low toxicity, PES with molecular weights exceeding its critical molecular weight (M_c) was achieved under solvent-free conditions in shorter reaction times and lower temperatures than polycondensation. The resulting PES exhibited mechanical properties comparable to commercial polymers, making it a strong candidate for industrial applications. Furthermore, the depolymerisation of PES into cyclic oligomers demonstrated its potential for a closed-loop system, though challenges remain in identifying greener solvents and optimising energy efficiency.

Chapter 3 built upon the findings of Chapter 2 by exploring the copolymerisation of PES with ϵ -caprolactone (CL) and valerolactone (VL) to further tailor material properties and potentially reduce cost through incorporating commercially available, inexpensive lactones. While VL incorporation showed limited success, the addition of CL proved to be more promising. However, the incorporation of CL significantly

reduced crystallinity and thermal properties. Notably, the stress-induced crystallisation observed in PES₈₅-co-PCL₁₅ under tensile stress balanced flexibility and mechanical reinforcement. While the O₂ barrier properties of pure PES were excellent, PES₈₅-co-PCL₁₅ maintained oxygen barrier effectiveness superior to many commercial alternatives, along with improved ductility, highlighting its potential for applications requiring high biodegradability, flexibility and low oxygen permeability. Future work could explore other cyclic esters that can copolymerise more compatible with cyc(ES)_n and enhance mechanical properties.

In Chapter 4, the focus shifted to ethylene fumarate-based oligomers to explore new directions in biobased polymer design. The synthesis of cyclic and linear ethylene fumarate oligomers enabled a comparative study of their topology and *cis/trans* composition effects on the properties of crosslinked networks. Thiol-ene photocuring was employed to generate crosslinked materials, revealing that cyclic oligomers offered superior crosslinking efficiency and mechanical stability, likely due to their reduced network defects. The *cis/trans* ratio was also shown to influence network flexibility and swelling properties. The occurrence of intramolecular crosslinking, however, highlighted the need for further optimisation of formulations and crosslinking strategies to achieve uniform properties and better compare these networks.

Across these chapters, common themes emerge, such as the importance of molecular structure in defining material properties and the role of the polymerisation techniques in the desired performance. The synthesis of macrocyclic oligoesters of ethylene succinate (cyc(ES)_n) and ethylene fumarate (cyc(EF)_n) demonstrated the potential of innovative chemistries for PES production *via* ROP and for exploring network properties of fumarate based systems depending on topological and structural

differences. Looking forward, several key areas warrant further investigation. For PES, advancing depolymerisation methods to improve efficiency, yield, and environmental compatibility will be critical for establishing fully closed-loop systems. Expanding the range of comonomers in copolymerisation studies may further broaden the material's application potential. For fumarate-based networks, refining crosslinking formulations and exploring their long-term durability and degradability will enhance their viability for functional applications.

Chapter 6: Experimental

6.1 Materials

All solvents were purchased from Sigma-Aldrich, Fisher Scientific or Alfa Aesar and used without further purification unless otherwise stated. Silica gel (SiO_2 40-60 μm) was purchased from Apollo Scientific and used as received for column chromatography. 1,2-ethanediol, (99.8%), methanesulfonic acid (MSA, 99%), (dimethylamino)pyridine (DMAP, 98%), γ -Valerolactone (GVL, $\geq 99\%$), maleic acid ($\geq 99\%$), diethylamine ($\geq 99.5\%$), 1,6-hexanedithiol (97%), trimethylolpropane tris(3-mercaptopropionate) (TMPMP, $>95.0\%$), 4-methoxyphenol (99%), L-proline ($>99\%$) and betaine ($\geq 98\%$) were supplied by Sigma-Aldrich and used as received. Dibutyltin(IV) oxide (Bu_2SnO , 98%), succinyl chloride (95%), fumaryl chloride (95%) and nicotinic acid (99%) were purchased from Fisher Scientific and used as received. Tin(II) ethylhexanoate ($\text{Sn}(\text{Oct})_2$) was purchased from Sigma-Aldrich and distilled before being stored in the glove box. ϵ -caprolactone (97%), δ -valerolactone, and benzyl alcohol (99%) were supplied by Sigma-Aldrich and dried over CaH_2 for 48h before their distillation under reduced pressure and were stored on molecular sieves. Triphenyl bismuth (Ph_3Bi) ($>98\%$) was purchased from Fisher Scientific and used as received. DOX^1 and DMAP:MSA^2 catalysts were prepared according to literature procedures. Irgacure 1173 photoinitiator was purchased from Sigma-Aldrich and stored in the dark prior to use.

6.2 Instruments

6.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{13}C NMR spectra were recorded at 298 K on Bruker DPX-300 or DPX-400 spectrometer. Chemical shifts are reported in ppm. Chemical shifts were referenced to the residual solvent at $\delta = 7.26$ ppm on the ^1H NMR spectrum and at 77.16 ppm on the ^{13}C NMR spectrum for CDCl_3 . The data obtained was processed and analysed using MestReNova 12.0.3 software. The signals are characterised as s = singlet, d = doublet, dt = doublet of triplets, tdd = triplet of doublet of doublets, q = quartet and m = multiplet. The coupling constant J is recorded in Hertz (Hz).

6.2.2 High-Performance Liquid Chromatography Mass Spectrometry (HPLC-MS)

The ring size distribution analysis consisted of a chromatographic separation in an ultrahigh performance liquid chromatography (UPLC, Acquity system from Waters Chromatography S.A.) coupled to a high-resolution mass spectrometer (Synapt G2 from Waters Chromatography S.A., time-of-flight analyser (ToF) by an electrospray ionisation source in positive mode (ESI^+). The chromatographic separation was achieved using an Acquity UPLC BEH C18 column (1.7 μm , 2.1 x 50 mm i.d.) with an Acquity UPLC BEH C18 1.7 μm VanGuard pre-column (2.1 x 5 mm) (Waters Chromatografia S.A.) and a binary A/B gradient (solvent A: water with 0.1 % formic acid and solvent B: methanol). The gradient program was established as follows: initial conditions were 5 % B, raised to 100 % B over 2.5 min, held at 100 % B until 4 min, decreased to 5 % B over the next 0.1 min, and held at 5 % B until 5 min for re-equilibration of the system before the next injection. A flow rate of 0.25 mL/min was used, the column temperature was 30 $^{\circ}\text{C}$, the autosampler temperature was 4 $^{\circ}\text{C}$ and the injection volume 2 μL . High-resolution mass data were acquired in SCAN mode,

using a mass range of 100–2000 u in resolution mode (FWHM $\approx$ 20,000) and a scan time of 0.1 s. The source temperature was set to 120 °C and the desolvation temperature to 350 °C. The capillary voltage was 0.7 kV and the cone voltage 15 V. Nitrogen was used as the desolvation and cone gas at flow rates of 600 L/h and 10 L/h, respectively. Before analysis, the mass spectrometer was calibrated with a sodium formate solution. A leucine-enkephalin solution was used to correct lock mass, monitoring the ions at a mass-to-charge ratio (m/z) 556.2771 and 278.1141. All the acquired spectra were automatically corrected during acquisition based on the lock mass. Samples were prepared by dissolving in dichloromethane at 10 mg/mL concentration and diluted to 25 μ g/mL in methanol for the analysis.

6.2.3 Matrix-Assisted Laser Desorption/Ionisation Time-of-Flight Mass Spectrometry (MALDI ToF MS)

MALDI ToF MS analysis was carried out in a Bruker Ultraflex Extreme mass spectrometer using a nitrogen laser delivering 2 ns pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Spectra acquisition was performed in the MS reflector positive-ion mode. The laser power was adjusted during the experiments. Samples were dissolved in CH₂Cl₂ (10 mg/mL). *Trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as a matrix and dissolved in CH₂Cl₂ (10 mg/mL). NaTFA was used as a cation donor (10 mg/mL dissolved in CH₂Cl₂). Samples were mixed with the matrix and salt at a 10:3:1 (matrix/polymer/salt) ratio, and approximately 0.5 μ L of this solution was spotted by hand on the ground steel target plate and allowed to dry before exposition to the laser beam. Spectra were accumulated and processed using FlexControl (v3.4) and FlexAnalysis software (v3.4).

6.2.4 Size Exclusion Chromatography

SEC measurements were performed on an Azura[®] Liquid Chromatography System device equipped with a PLgel column (10 μ m MIXED-B 300x7.5 mm). Chloroform (HPLC grade, Scharlab) buffered with 0.5% NEt₃ was used as a mobile phase at a flow rate of 1 mL/min. All samples were prepared at a concentration of 5 mg/mL. Number average molecular weight (M_n), weight average molecular weight (M_w) and dispersity ($\mathcal{D}_M = M_w/M_n$) were determined using Azura GPC/SEC software based on poly(styrene) standards (Shodex Standards, SM-105).

6.2.5 Size Exclusion Chromatography – Multi-Angle Light Scattering (SEC-MALS)

SEC-MALS measurements were performed in *N,N*-dimethylformamide (DMF) on a system equipped with an isocratic pump (1260 Infinity II, Agilent, Santa Clara, CA, USA), a multi-angle static light scattering (MALS) detector with a 658 nm light source (DAWN HELEOS-II, Wyatt Technology, Santa Barbara, CA, USA), and a differential refractometer (DRI) detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology, Santa Barbara, CA, USA). Separations were performed using serially connected size exclusion columns (two PLgel MIXED-C columns, 10 μ m, 7.5 x 300 mm, Agilent, Santa Clara, CA, USA) at 40 °C, with DMF (containing 5 mM NH₄BF₄) as a mobile phase at a flow rate of 1 mL/min. Samples were filtered using a 0.22 μ m PTFE filter before injection. Absolute molecular weights of polymers were determined using the ASTRA 7 software (version 7.1.3, Wyatt Technology, Santa Barbara, CA, USA) and calculated from dn/dc values of each polymer sample.

6.2.6 Thermogravimetric Analysis (TGA)

TGA thermograms were obtained using A Q550 Thermogravimetric Analyser (TA Instruments). Thermograms from 25 to 600 °C were recorded at a heating rate of 10 °C/min in a N₂ environment. Decomposition temperatures were reported at the 5% weight-loss-temperature ($T_{d,5\%}$) and the maximum decomposition rate (T_{max}).

6.2.7 Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained using a STARE system DSC3 with an auto-sampler (Mettler Toledo, Switzerland). Thermograms were acquired in 40 µL aluminium pans at temperatures ranging from -40 to 150 °C, with a heating rate of 5 or 10 °C/min over two cycles of heating and cooling. In the second heating cycle of the DSC, all endothermic peaks were integrated and normalised, and the total enthalpy of melting (ΔH_m) was determined.

6.2.8 Dynamic Mechanical Thermal Analysis (DMTA)

In single cantilever bending mode, dynamic mechanical thermal analysis (DMTA) data were obtained using a TA Q800 viscoelastometer (New Castle, DE, USA). Rectangular, nominally sized specimens measuring 8 x 6.0 x 2.0 mm³ were tested. Thermal sweeps were conducted using nominally sized specimens measuring 8 x 6.0 x 2.0 mm³ cooled to -50 °C and held isothermally for roughly 5 min. Storage and loss moduli and the loss factor (ratio of E'' and E' , $\tan \delta$) were probed as the temperature was swept from -50 to 120 °C at a heating rate of 5 °C/min, 1 Hz.

6.2.9 Uniaxial Tensile Testing

Uniaxial tensile testing was performed using an Instron 5565 testing machine. The specimens were cut according to ASTM D638 type 5 with a 50-100 µm thickness.

The measurements were performed at room temperature at a constant strain rate of 1 mm/min. All tensile tests were repeated on three individual specimens, and an average of the data was taken to find the ultimate tensile stress and strain. Young's modulus (E , MPa), ultimate strength (σ_B , MPa), yield strength (σ_Y , MPa), and elongation at break or fracture strain (ϵ_B , %) were obtained from software analysis. Reported toughness values (U_T , MJ/m³) were obtained by manual calculation of the area under the averaged stress/strain curve.

6.2.10 Rheology

The rheological measurements were performed on an ARES-G2 rheometer (TA Instrument) between two aluminium 12 mm parallel plates using disc-shaped samples (12 x 1 mm) prepared by compression moulding. The linear viscoelastic region (LVR) was determined by strain sweep ranging from 0.01% to 100% at the reference temperature (120 °C). Oscillatory frequency sweeps (2 % strain, 0.1 to 100 rad/s) were performed at temperatures from 80-140 °C in increments of 20 °C, with 1 min equilibration time between runs, to simultaneously record storage and loss moduli (G' and G'' , Pa). All individual curves were overlayed by applying a Williams-Landel Ferry (WLF) time-temperature superposition at a reference temperature of 120 °C, automated by the TRIOS software.

6.2.11 Pressure-Volume-Temperature Analysis

Pressure-volume-temperature (PVT) analysis was conducted in a PVT apparatus of the piston die technique PVT 100 from Haake (Thermo Electron Corporation, Germany). The sample was in a floating measurement cylinder of 6 mm diameter, and pressure was applied hydraulically to the piston at the top of the cell with a PTFE disc seal. An identical piston and sealing system were located at the bottom of the cell.

Measurements were performed using the isobaric cooling mode in a 200-1000 bar pressure range at a cooling rate of 5 °C/min. The Tait extrapolation in the equipment software determined specific volumes at the atmospheric pressure.

6.2.12 Permeability Measurements

Water vapour transmission rate (WVTR) was measured using a permeation gravimetric cell made of poly(tetrafluoroethylene) at 25 °C according to ASTM E96-95 standart. The cell is a small container partially filled with water and the polymer film sample sealing it. Experiments are conducted in a Sartorius BP 210 D balance with 10⁻⁵ g sensitivity. The weight loss is recorded in a computer for data treatment. The permeability data shown are the average of at least four measurements. The water vapour transmission rate is obtained from the slope of the permeated mass vs time at the steady state, employing Eq 6.1.

$$WVTR \left(\frac{g \cdot mm}{m^2 \cdot day} \right) = 8.64 \times 10^5 \frac{s \cdot l}{A(a_{in} - a_{out})} \quad \text{Eq. 6.1}$$

where l is the thickness (mm), A is the surface area of the film exposed to the vapour (2.54 cm²), a_{in} and a_{out} are the water vapour activity inside and outside of the cell, that is the relative humidity expressed per unit value, and 8.64×10^5 is the conversion factor to obtain the $WVTR$ in $\left(\frac{g \cdot mm}{m^2 \cdot day} \right)$.

Oxygen transmission rate was measured using a Mocon Ox-Tran model 2/21 MH equipment following ASTM D3985 standart. The measurements were performed at 23 °C, 1 atm, and 0% relative humidity. The values are the average of two measurements. The equipment provides the oxygen transmission rate (OTR) that is related to the permeability coefficient by Eq 6.2.

$$OTR \left(\frac{cc \cdot mil}{m^2 \cdot day} \right) \times \frac{0.029398}{p(cmHg)} = P(Barrer) \quad \text{Eq. 6.1}$$

6.2.13 Fourier Transform Infrared Spectrometry

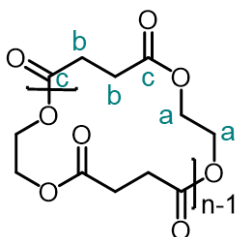
Fourier Transform Infrared Spectrometry were recorded using an FTIR spectrophotometer (Nicolet 20, Thermo Scientific Inc.) equipped with a deuterated triglycine sulfate detector. Spectra were recorded between 4000 and 500 cm^{-1} with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 32 scans.

6.3 Procedures

6.3.1 Procedures for Chapter 2

6.3.1.1 Synthesis of Cyc(ES)_n

DOX (20 g, 68 mmol) was added in a two-neck round bottom flask equipped with a magnetic stirrer and condenser from one neck and a septum from the other. 300 mL dry chloroform was transferred *via* a cannula tube into the RBF. Succinyl chloride (10.6 g, 68 mmol) diluted in 40 mL dry chloroform was added dropwise to the solution of DOX in dry chloroform at room temperature with magnetic stirring. After the addition, the reaction mixture was refluxed for 4 h at 70 °C, then cooled to room temperature. The solvent was removed on a rotary evaporator. The residue was extracted with hexane to remove dibutyltin dichloride (Bu₂SnCl₂) and purified by flashing through deactivated silica gel (treated with 1% triethylamine). cyc(ES)_n was obtained as a white solid with an 80% yield (7.8 g) with spectroscopical data in agreement with the literature.³

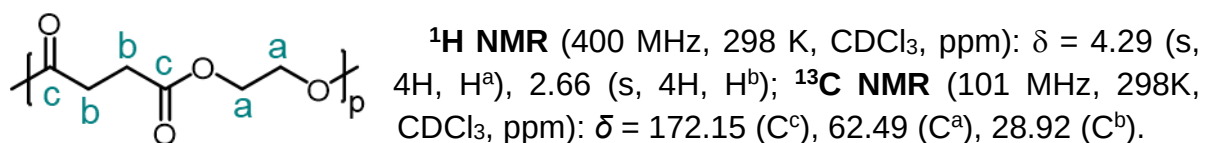


¹H NMR (400 MHz, 298 K, CDCl₃, ppm): δ = 4.29 (d, J = 5.5 Hz, 4H, H^a), 2.65 (d, J = 6.1 Hz 4H, H^b); **¹³C NMR** (101 MHz, 298 K, CDCl₃, ppm): δ = 172.02, 171.91, 171.68 (C^c), 62.61, 62.42 (C^a), 29.46, 29.30, 29.16, 29.08 (C^b).

6.3.1.2 General Procedure for ROP of cyc(ES)_n

In an argon-filled glove box, a stock solution containing the chosen organometallic catalyst (1.4 mg Sn(Oct)₂ or 1.5 mg Ph₃Bi or 1 mg DOX, 0.034 mmol) and anhydrous THF (250 μ L) was prepared. For the polymerisation with DMAP:MSA, a stock solution containing DMAP-MSA (54.5 mg, 0.17 mmol), benzyl alcohol (18 mg, 0.17 mmol), and anhydrous THF (250 μ L) was prepared. The stock solution (25 μ L)

was added to a previously dried reaction tube with a stopcock on the side arm. The cyc(ES)_n (0.5 gr, 1.73 mmol, calculated as dimers; $M_w = 288 \text{ g}\cdot\text{mol}^{-1}$) was then added to the reaction tube. The reaction tube was removed from the glovebox, connected to the Schlenk line and immersed in a pre-heated oil bath at the desired temperature. Aliquots were taken under an argon blanket. The reaction was stopped by cooling down the medium in an ice bath. For the purification, the crude polymer was dissolved in chloroform and precipitated in cold methanol. The resulting polymer was filtrated and dried under vacuum for 24 h.



SEC-MALS: $M_n = 42700 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 66690 \text{ g}\cdot\text{mol}^{-1}$, $D_M = 1.56$. **TGA** (10 °C/min): $T_{d,5\%} = 317 \text{ }^\circ\text{C}$. **DSC** (10 °C/min): $T_g = -11 \text{ }^\circ\text{C}$, $T_m = 97 \text{ }^\circ\text{C}$, $X_c = 15 \%$.

6.3.1.3 General Procedure for Depolymerisation of PES

PES (100 mg) and Bu₂SnO (3 mg, 0.012 mmol) were dissolved in a chosen solvent at a chosen concentration in a two-neck round bottom flask equipped with a magnetic stirrer and reflux condenser. The reaction was stirred at the decided temperature for a set time for depolymerisation to occur. When the desired time was reached, the reaction mixture was first cooled to room temperature and left in the fridge for 24 h. The remaining polymer precipitated during this time and was then filtered with filter paper. The solvent in the filtered reaction mixture was removed by vacuum distillation.

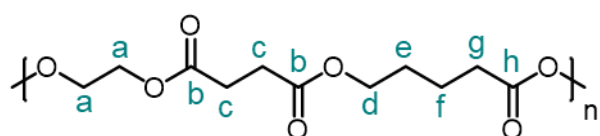
6.3.2 Procedures for Chapter 3

6.3.2.1 General procedure for polymerisation of CL and VL

In an argon-filled glove box, CL (0.5 g, 4.3 mmol) or VL (0.43 g, 4.3 mmol) and Ph_3Bi (3.7 mg, 0.0086 mmol) were added to a previously dried reaction tube with a stopcock on the side arm equipped with a magnetic stirrer. The reaction tube was removed from the glovebox, connected to the Schlenk line and immersed in a pre-heated oil bath at 175 °C. Aliquots were taken under an argon blanket. The reaction was stopped by cooling down the medium in an ice bath. For the purification, the crude polymer was dissolved in chloroform and precipitated in cold methanol. The resulting polymer was filtrated and dried under vacuum for 24 h.

6.3.2.2 General procedure for copolymerisation of VL and $\text{cyc}(\text{ES})_n$

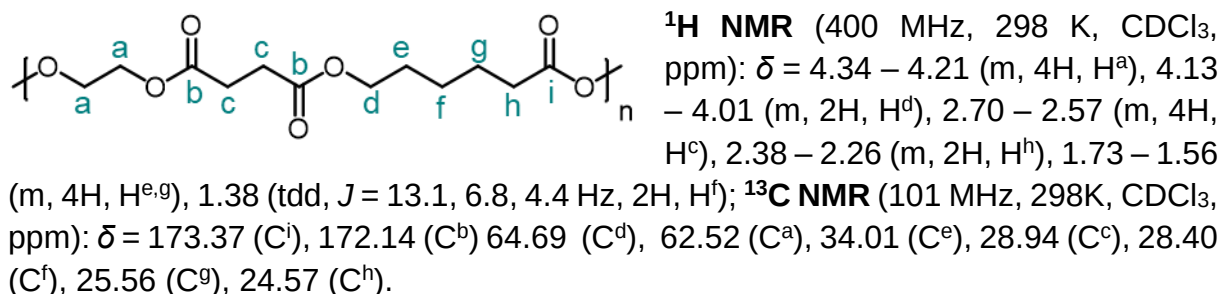
In an argon-filled glove box, $\text{cyc}(\text{ES})_n$ (0.5 gr, 3.47 mmol), VL (0.34 g, 3.47 mmol) and Ph_3Bi (6.1 mg, 0.013 mmol) were added to a previously dried reaction tube with a stopcock on the side arm equipped with a magnetic stirrer. The reaction tube was removed from the glovebox, connected to the Schlenk line and immersed in a pre-heated oil bath at 130 °C. Aliquots were taken under an argon blanket. The reaction was stopped by cooling down the medium in an ice bath. For the purification, the crude polymer was dissolved in chloroform and precipitated in cold methanol. The resulting polymer was filtrated and dried under vacuum for 24 h.



^1H NMR (400 MHz, 298 K, CDCl_3 , ppm): δ = 4.29 (s, 4H, H^a), 4.08 (q, J = 5.7 Hz, 2H, H^d), 2.65 (d, J = 6.9 Hz, 4H, H^c) 2.35 (dt, J = 10.7, 6.6 Hz, 2H, H^g), 1.68 (m, J = 3.1 Hz, 4H, $\text{H}^{e,f}$); **^{13}C NMR** (101 MHz, 298K, CDCl_3 , ppm): δ = 173.40 (C^h), 172.14 (C^b), 64.37 (C^d), 62.54 (C^a), 33.60 (C^e), 28.96 (C^c), 28.14 (C^f), 21.41 (C^g). **SEC** (CHCl_3): M_n = 10990 $\text{g}\cdot\text{mol}^{-1}$, M_w = 20830 $\text{g}\cdot\text{mol}^{-1}$, $\bar{D}_M$ = 1.89.

6.3.2.3 General procedure for copolymerisation of CL and cyc(ES)_n

All the copolymerisation reactions were prepared inside an argon-filled glove and were performed at 150 °C using 0.2 mol% Ph₃Bi to total monomer concentration. The [cyc(ES)_n]:[CL]=1 copolymerisation for the kinetic analysis was prepared by adding cyc(ES)_n (0.5 g, 3.47 mmol) and CL (0.39 g, 3.47 mmol) and Ph₃Bi (6.1 mg, 0.013 mmol) in a previously dried reaction tube with a stopcock on the side arm equipped with a magnetic stirrer. The reaction was immersed in a preheated oil bath and left for 24 h with aliquots taken under an argon blanket. For copolymers with lower CL ratios, the reaction mixture was carried out on a 0.5 g scale in a small glass vial and heated for 5 h. The reaction was stopped by cooling down the medium in an ice bath. For the purification, the crude polymer was dissolved in chloroform and precipitated in cold methanol. The resulting polymer was filtrated and dried under vacuum for 24 h.



PES₅₀-co-PCL₅₀: SEC (CHCl₃): $M_n = 68560 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 136380 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D}_M = 1.96$. TGA (10 °C/min): $T_{d,5\%} = 302 \text{ }^\circ\text{C}$. DSC (5 °C/min): $T_g = -40 \text{ }^\circ\text{C}$.

PES₈₀-co-PCL₂₀: SEC (CHCl₃): $M_n = 74500 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 145300 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D}_M = 1.95$. TGA (10 °C/min): $T_{d,5\%} = 299 \text{ }^\circ\text{C}$. DSC (5 °C/min): $T_g = -22 \text{ }^\circ\text{C}$, $T_m = 80 \text{ }^\circ\text{C}$.

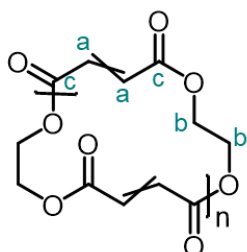
PES₈₅-co-PCL₁₅: SEC (CHCl₃): $M_n = 77670 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 170460 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D}_M = 1.96$. TGA (10 °C/min): $T_{d,5\%} = 287 \text{ }^\circ\text{C}$. DSC (5 °C/min): $T_g = -19 \text{ }^\circ\text{C}$, $T_m = 90 \text{ }^\circ\text{C}$, $X_c = 4 \%$.

PES₉₂-co-PCL₈: SEC (CHCl₃): $M_n = 87760 \text{ g}\cdot\text{mol}^{-1}$, $M_w = 146870 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D}_M = 1.67$. TGA (10 °C/min): $T_{d,5\%} = 262 \text{ }^\circ\text{C}$. DSC (5 °C/min): $T_g = -16 \text{ }^\circ\text{C}$, $T_m = 97 \text{ }^\circ\text{C}$, $X_c = 6.6 \%$.

6.3.3 Procedures for Chapter 4

6.3.3.1 Synthesis of Cyc(EF)_n

DOX (20 g, 68 mmol) was added in a two-neck round bottom flask equipped with a magnetic stirrer and condenser from one neck and a septum from the other. 300 mL dry chloroform was transferred *via* a cannula tube into the RBF. Fumaryl chloride (10.6 g, 68 mmol) diluted in 40 mL dry chloroform was added dropwise to the solution of DOX in dry chloroform at room temperature with magnetic stirring. After the addition, the reaction mixture was refluxed for 4 h at 70 °C and then cooled to room temperature. The solvent was removed on a rotary evaporator. The residue was extracted with hexane to remove dibutyltin dichloride (Bu₂SnCl₂) and purified by flashing through deactivated silica gel (treated with 1% triethylamine). cyc(EF)_n was obtained as a white solid with a 65% yield (6.3 g).

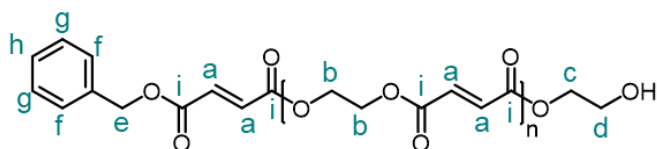


¹H NMR (400 MHz, CDCl₃, 298 K, ppm): δ = 6.96 – 6.80 (m, 2H^a, *trans*), 6.76 (s, 2H^a, *cis*), 4.55 (s, 4H^b, *cis*), 4.52 – 4.41 (m, 4H^b, *trans*); **¹³C NMR** (101 MHz, CDCl₃, 298K, ppm) δ = 164.59, 164.54, 164.40 (C^c), 134.34, 133.71, 133.65 (C^a) 63.21, 62.91, 62.68, 61.69 (C^b).

6.3.3.2 General Procedure for ROP of cyc(EF)_n

In an argon-filled glove box, cyc(EF)_n (2.1 g, 14 mmol), Ph₃Bi (12 mg, 0.028 mmol), benzyl alcohol (0.16 g, 1.4 mol or 16 mg, 0.14 mmol) and 4-methoxyphenol (105 mg, 5wt%) dissolved in anhydrous toluene (20 mL) in a reaction tube with a stopcock on the side arm. The reaction tube was removed from the glovebox, connected to the Schenk line and immersed in a pre-heated oil bath at 95 °C. Aliquots were taken under an argon blanket. The reaction was stopped by cooling down the medium in an ice bath after 4-8 h. For the purification, the crude polymer was dissolved

in chloroform and precipitated in cold methanol. The resulting polymer was filtrated and dried under vacuum for 24 h.

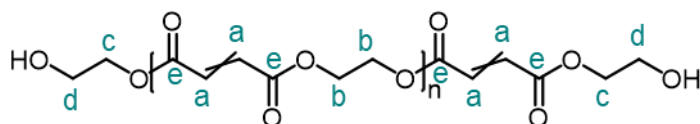


^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 7.40 – 7.31 (m, 5H, $\text{H}^{f,g,h}$), 6.89 (s, $2(n+1)\text{H}$, H^a), 5.23 (s, 2H, H^e) 4.47 (s, $4n\text{H}$, H^b), 4.38 – 4.31 (m, 2H, H^c), 3.95 – 3.84 (m, 2H, H^d);

^{13}C NMR (101 MHz, CDCl_3 , 298K, ppm): δ = 164.63 (C^e), 133.92 (C^a), 67.01 (C^c), 62.86 (C^b), 60.97 (C^d).

6.3.3.3 General Procedure for Polycondensation

Maleic acid (5 g, 0.043 mol, 1 eq.) is mixed with an excess of 1,2-ethanediol (2.9 g, 0.0473 mol, 1.1 eq.) and a catalyst (betaine or L-proline, 0.05 eq.) in a Schlenk flask equipped with a magnetic stirrer. The mixture is heated to 150 °C. After 2 h, a vacuum is applied, and the reaction continues until the increasing viscosity of the crude product prevents efficient stirring. The reaction is then terminated by cooling to room temperature. The crude polyester undergoes purification through an aqueous workup to remove the catalyst and unreacted monomers. First, the crude product is dissolved in 100 mL of chloroform, and the solution is extracted three times with a saturated sodium bicarbonate solution. The organic phase is filtered, and chloroform is removed using a rotary evaporator. The purified polyester is dried overnight under vacuum. Molecular weight and isomerisation degree are confirmed through ^1H NMR spectroscopy.



^1H NMR (400 MHz, CDCl_3 , 298 K, ppm): δ = 6.89 (s, $2(n+1)\text{H}$, H^a , *trans*), 6.30 (s, $2(n+1)\text{H}$, H^a , *cis*), 4.47 (s, $4n\text{H}$, H^b), 4.38 – 4.30 (m, 4H, H^c), 3.95 – 3.84 (m, 4H, H^d);

^{13}C NMR (101 MHz, CDCl_3 , 298K, ppm): δ = 164.63 (C^e), 133.92 (C^a , *trans*), 130.05 (C^a , *cis*), 67.01 (C^c), 62.86 (C^b), 60.97 (C^d).

6.3.3.4 General Procedure for Photocrosslinking

Ethylene fumarate oligomers (2 g, 0.014 mol alkene) and trimethylolpropane tris(3-mercapto propionate) (TMPMP, 1.85 g, 0.014 mol SH) at a stoichiometric thiol (SH) to alkene (C=C) ratio, and Irgacure 1173 (4 wt%) as a photoinitiator mixed in 50 chloroform (50 wt%) at room temperature until ethylene fumarate oligomers are well dissolved. Photocuring of materials is performed by depositing the resin in a pre-cut silicone mould, followed by curing with an OmniCure S1500 UV light source (370 nm) fitted with a fibre optic cable. Cured films are post-cured in an oven at 80 °C for 24 h.

6.4 References

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