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Thermodynamics of Ring-Opening Polymerisation Informatics Collection (TROPIC): a database to enable polymer chemical recycling†

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The development of artificial intelligence and machine learning in chemistry is opening new avenues for data-driven discoveries. However, the application of such methodologies in polymer chemistry has been hampered due to the complex structure–properties relationship of polymers and the lack of (meta)data available. Recent efforts have been made to experimentally determine or computationally evaluate thermodynamic parameters associated with (de)polymerisation reactions, such as enthalpy and entropy of polymerisation, as well as ceiling temperature, to design polymers primed for chemical recycling. Here, we report TROPIC (Thermodynamics of Ring-Opening Polymerisation Informatics Collection), an open-source database harnessing experimental and computational thermodynamic parameters for ring-opening polymerisation (ROP) from the academic literature. TROPIC links thermodynamic parameters with the experimental conditions or the computation methodologies used to determine them, to allow further analysis. TROPIC can be accessed *via* an interactive website or application programming interface (API) and presents a first step towards facilitating the data-driven discovery of novel functional polymers.

Introduction

Since the pioneering work of Staudinger in the early 1920's, the beginning of this second century of polymerisation and depolymerisation chemistry is marked by the emergence of polymer informatics.[1] The advent of artificial intelligence (AI) and machine learning (ML)‡ approaches within chemical research is

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† Electronic supplementary information (ESI) available: A list of acronyms, a detailed schema description along with screenshots from the interactive website are provided in ESI. See DOI: https://doi.org/10.1039/d5fd00098j

‡ While being different, both terms are used interchangeably and ML will be used here.

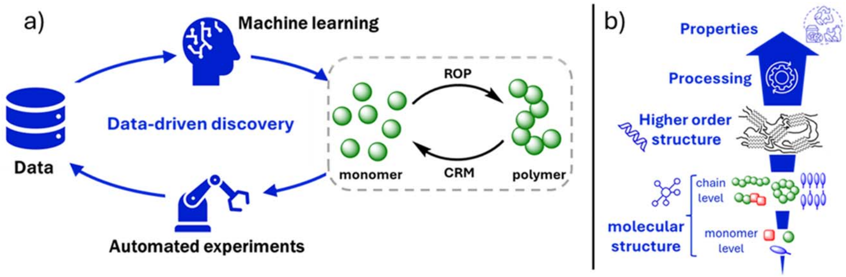


Fig. 1 (a) Data-driven discovery approach, and (b) monomer-to-materials relationship.

transforming this landscape, and continues to open new avenues towards data-driven discoveries (Fig. 1a).[2]

Within polymer chemistry, ML has established its utility in the prediction of intrinsic properties (*e.g.* glass transition temperature, T_g), guiding the creation of novel materials for specific use cases or end-of-life options.[3] Recent reviews have touched upon its multi-faceted applications, which include dielectric polymers for energy storage, polymers for fuel cells, polymers for battery electrolytes, membranes for gas–liquid mixture separation, conjugated conducting polymers, and for informing the design of sustainable polymers that are primed for chemical recycling. This latter point is particularly timely, and as this second century of polymer chemistry is emerging, the negative impacts of plastics on our planet and our health cannot be ignored and need to be remediated.[4] A task for which AI should be challenged!

Nevertheless, applications of these data-driven approaches often face challenges – many of which are tied to the complex nature of polymers and their macroscopic properties.[5] For instance, the observable properties of a polymeric material (*e.g.* its transparency) are not only governed by its molecular structure but also the specific processing steps taken during its synthesis (Fig. 1b). Moreover, the number of each monomeric species within the polymer chain (monomer level) and their arrangements at the molecular level (*i.e.* microstructure) will affect higher-order structure (*e.g.* crystallinity) and properties (*e.g.* thermal and mechanical). As a result, modelling the structure–property relationships that map the monomeric starting units to the final polymeric material is non-trivial, and remains one of the major bottlenecks to the application of AI, when compared to other branches of chemical science.[6]

Another critical aspect behind the slow uptake of AI within polymer chemistry is the lack of obvious (meta)data formats and standards from which databases can be constructed. Since the pioneering work of Adams and coworkers in the late 2000s to adapt the Chemical Markup Language (CML) to polymers (PML), there have been multiple initiatives to unify schemata within polymer informatics.[7] Recent endeavours include the "polyDAT" schema to characterise experimentally-synthesised polymers and the "CRIPT" data model that attempts to capture highly-granular data within a graph architecture.[6b,7,8] Another crucial contribution within polymer informatics has been the development of the "bigSMILES" line notation and "bigSMARTS" query language, which are intended to function analogously for polymers as their less 'big' counterparts do for small molecules.[6a,c] Such efforts within polymer informatics attempt to overcome some of the limitations hindering the widespread adoption of data-driven techniques, and are contributing to findable, accessible, interoperable, and reuseable (FAIR) polymer data.[9]

A commonality of data-driven methodologies is their reliance on input data, either experimentally- or computationally-generated, of adequate quality and quantity (Fig. 1a). Efforts have emerged to collate such information under a unified domain (*e.g.* PolyInfo, PolymerGenome) and facilitate further data-driven ventures within polymer science (*e.g.* dielectric constant).[10] While admirable, these platforms represent limited amounts of information, especially when compared to established informatics sources in adjacent scientific domains. For instance, the Protein Data Bank (PDB) contains more than 200 000 entries, which was necessary for the success of the AlphaFold protein-structure prediction platform.[11] This culminates in an urgent need for more (machine-readable) datasets, databases, or digital libraries to fuel and inspire data-driven insights within polymer chemistry.

In line with the most recent initiatives to design sustainable polymers,[3b,12] our team has garnered an interest in gathering and predicting the thermodynamic parameters of the ring-opening polymerisations (ROP) of polar cyclic monomers (PCM). The ultimate aim is the identification of monomers and specific structural characteristics that improve the recyclability of the resultant polymer (Fig. 1a) – a process commonly termed chemical recycling to monomer (CRM).[13]

ROP is a method of choice to afford well-defined polymers and co-polymers. A broad range of cyclic monomers, including cyclic ethers, esters, carbonates and amides, are known to undergo this process. Poly(lactic acid) or PLA, which is the flagship of bioplastics as being both bio-based and degradable, is industrially produced *via* lactide ROP with an annual worldwide production capacity of circa 900 kT.[14] ROP is an equilibrium between monomers and polymeric chains. The displacement of the equilibrium towards one side or the other (*i.e.* monomers or polymers side) is driven by both thermodynamic and kinetic parameters which can then be harnessed by experimental conditions.[15] Thermodynamically, the reaction is favoured when its Gibbs free energy is negative ($\Delta G_p < 0$). As detailed later, this expression can be uncoupled to evaluate monomer polymerisability in terms of the enthalpy, ΔH_p, entropy, ΔS_p, and ceiling temperature, T_c, of the polymerisation.[16]

Kinetically, for the polymerisation to be productive, the propagation rate (*i.e.* monomer addition to the growing polymeric chains) should be reasonable with the experimental conditions. In other terms, the energy activation required to grow polymers should be accessible and compatible with the experimental conditions. This can be aided by catalysts which help to reduce energy activation and enable equilibrium conditions to be reached more rapidly. Knowing both thermodynamic and kinetic parameters, experimental conditions can be adjusted to control the polymerisation equilibrium. For example, working in higher monomer concentrations and/or at low temperatures to favour the polymerisation of monomers with a low ceiling temperature (*e.g.* polymerisation of 5-membered γ-caprolactone).[17] Conversely, working in high polymer concentrations under reduced pressure in the presence of a catalyst can contribute to depolymerization and recovery of the monomers (*e.g.* chemical recycling of PLA to lactide).[18]

Thus, because of this polymerisation equilibrium and the potential tunability of the monomers, polymers obtained by ROP are potentially well-suited for chemical recycling. Whereas monomers that are thermodynamically easy to polymerise (*e.g.* with high ring strain, with high ceiling temperature) can lead to "too stable" polymers that are difficult to chemically depolymerise reversibly, monomers that are more challenging to polymerise (*e.g.* with lower ring strain, with lower ceiling temperature) can lead to polymers that are easier to turn back to their initial components. One of the key challenges is to identify monomers that can balance this equilibrium to allow CRM while leading to materials with useful properties.[13c] This quest has led to the design of so-called hybrid monomers, usually combining features of monomers with high and low ceiling temperatures (to some extent the ceiling temperature can be used as a surrogate of monomer polymerisability).[13c,16,19] However, predicting monomer thermodynamic polymerisability, and conversely polymer chemical recycling, remains challenging and currently relies on pre-synthetic chemist intuition.[20]

As the chemical space is too large to be experimentally investigated exhaustively, few computational studies and data-driven approaches to calculate and predict monomer thermodynamic parameters have been investigated. Early studies have focused on estimating monomer ring strain and understanding the difference in reactivity between lactones of various ring sizes, generally using a combination of molecular dynamics and DFT methods.[21] More recently, Ramprasad and co-workers have developed a first principle model to predict the enthalpy of ring-opening polymerisation for various cyclic monomers, including cyclic ether, ester, amide, and more. Combining these computed data with experimental data from the literature led to a dataset of circa 400 entries. This dataset was subsequently used to develop an ML model to predict ΔH_p with an accuracy of 8 kJ mol^{-1}.[22] Alternatively, Wohlert and co-workers recently demonstrated that a model considering the collision frequency between reactive groups in polymers and monomers can simultaneously provide ΔH_p and ΔS_p with low root mean squared error (RMSE) respective to experimental data for 8 lactones of different ring sizes and with different substituents.[23]

Considering the diversity and volume of both experimental and computational thermodynamic data for ROP which are scattered in the literature, and the lack of tools or platforms to harvest or access such data, we undertook the task of building a database dedicated to the thermodynamics of ring-opening polymerisations. After briefly reviewing common data sources for polymer chemistry, we present here TROPIC, a unique database gathering from literature both experimental and computational thermodynamic parameters for ROP of cyclic monomers, with the aim to support and enable data-driven discoveries for polymer chemical recycling.

Common sources of "polymer data"

Common sources of data for polymer chemistry include dedicated databases (*e.g.* PolyInfo), datasets and data repositories (*e.g.* Materials Data Facility), digital handbooks as well as specialised online platforms, such as Polymer Genome able to predict polymer properties, or Polymer Scholar able to extract some polymer properties from the literature. To the best of our knowledge, no database or online tools are available to harness machine-readable thermodynamic parameters (ΔH_p, ΔS_p, T_c) associated with the ROP of polar cyclic monomers. Below is a list of open sources providing machine-readable "polymer data".

Databases

• PoLyInfo (**https://polymer.nims.go.jp/**)[18b] is a large polymer database providing various polymer properties collected from the literature. It contains information on homopolymers, copolymers, blends and composite materials.

• Polymer Property Predictor and Database (PPPdb) (**https://pppdb.uchicago.edu/**)[24] includes a database of Chi (χ) values, T_g values and binary solution cloud points for polymers. It includes tools to generate Flory–Huggins phase diagrams, random phase approximation structure factors, and estimate binary solution cloud points.

• IUPAC Monomer database (**http://sql.polymatter.net/**)[25] is a machine-readable online database for rate coefficients in radical polymerisation. It includes Arrhenius parameters for a given reaction, key information on the experimental conditions, and information considering its validation by IUPAC benchmarks.

• Polymer Informatics 1 Million (PI1M)[26] is a benchmark database for polymer informatics. A generative model has been trained using data available from PolyInfo to generate a large open dataset of polymer data intended to fuel further data-driven discoveries in polymer chemistry.

• Block Copolymer Database (BCDB)[27] is an online platform gathering phase behaviour for block copolymers, including information on the experimental conditions. BCDB is accessible *via* the Community Resources for Innovation in Polymer Technology (CRIPT).

• CoPolymerisation DataBase (CoPolDB)[28] is a database of experimental kinetic parameters for radical copolymerisation including a graphical user interface. CoPolDB is a relational database which relates Monomer, Copolymer and Copolymerisation.

• Copolymer Descriptor Database (CopDDB)[29] is a database of descriptors calculated for radical polymerisation, such as activation barriers and reaction energies.

• NanoMine (**https://brinsonlab.pratt.duke.edu/research/mgp/Nanomine**)[30] is an online platform for materials genome prediction, offering data on polymer nanocomposites (polymers doped with nanoparticles) and tools for characterisation and analysis.

• MatWeb (**https://www.matweb.com/**) is a searchable database of material properties collecting data from data sheets of thermoplastic and thermoset polymers.

Data repositories and datasets

• Materials Data Facility (**https://materialsdatafacility.org/**)[31] (MDF) offers a data repository to host and search material datasets of published work.

• BOTTLE (**https://figshare.com/authors/Material_Characterization/16866117**)[32] Plastic Substrates Database includes characterisation data on polymer substrates from common commercial suppliers, such as size-exclusion chromatography (SEC), thermogravimetric analysis (TGA), differential scanning calorimetric (DSC) analysis, *etc…*

- Datasets from Khazana (**https://khazana.gatech.edu/dataset/**) is an online platform of computational datasets, along with tools allowing polymer data predictions.

Books and handbooks should not be overlooked, with some now available digitally, such as *The Wiley Database of Polymer Properties* initially built from *The Polymer Handbook*.[33] Useful thermodynamic parameters of polymerisation for selected PCM are also available from Chapter 1 of the *Handbook of Ring-Opening Polymerisation*.[15]

Online tools and platforms

- PolymerGenome (**https://www.polymergenome.org/**) is a polymer informatics tool to predict polymer properties using machine learning models. More than 20 properties can be predicted including thermal and mechanical properties.[10a]
- PolymerScholar (**https://polymerscholar.org/**) offers an online tool to search among polymer properties extracted from the literature using large language models.[34]
- PolyAGM[35] (Polymer Property Prediction based on Automatic Generation of Motifs) is an ML algorithm developed to predict properties of block copolymers, trained from experimental and literature data.
- Khazana (**https://khazana.gatech.edu/**) not only offers datasets as aforementioned but also tools to predict some polymer properties.

Methods

Data collection and curation

Data collection. Various properties of polymers can be extracted from the literature using large language models and have been made available *via* the Polymer Scholar online tool.[34] However, no relevant thermodynamic data such as enthalpy, entropy, or ceiling temperature are currently available on this platform.[36] Thus, data were manually extracted from the literature, starting from recent reviews and book chapters discussing general concepts such as thermodynamics of ring-opening polymerisation or polymer chemical recyclability.[15,20] Original works cited in these reviews, and studies citing these reviews, were then analysed. Only data published in peer-reviewed journals were considered. Further searches were carried out using scholarly literature search engines (*e.g.* Google Scholar, SciFinder) using keywords such as “ROP”, “ceiling temperature”, “polymerisation enthalpy”, “lactone” with different combinations and refinements. All documents contained within the database are referenced using their DOI, which allows fetching further metadata (*e.g.* author, year of publication, journal name, *etc.*) *via* the DataCite API. This metadata can be found adjacent to the respective results within the database (*vide infra* for screenshot of database). A combined list of these references can also be conveniently downloaded from the “references” page on the TROPIC website.

The decision to manually scrape ROP thermodynamic data was deliberate. This was largely due to the observation that, due to the interest in CRM only peaking in recent years,[37] the number of relevant articles represented a very small portion of polymer chemistry literature (and an even smaller portion of the entire published scientific corpus). Hence, a large language model for web scraping – even one pretrained for chemical information extraction[38] – would likely be overfit and lead to greater inaccuracies compared to a thorough manual search by a domain expert.

It is worth stating that despite the care taken to comprehensively scout the literature, the current data entries do not represent an exhaustive list of published thermodynamic data for ROP reactions. Rather, the database serves as a starting point from which individuals can easily append existing and future sources of information. The database contains template spreadsheets that contributors can complete and submit to facilitate this process. The provided information can then be rapidly verified and included within the database for immediate use.

Both experimental and computational studies providing relevant thermodynamic data – namely ΔH_p, ΔS_p, and T_c – for the ring-opening polymerisation (ROP) of polar cyclic monomers (PCM) leading to linear or cyclic homopolymers, were considered. The current dataset (referred to as PCM_v1) is restricted to a few classes of monomers, including lactones (L), cyclic carbonate (CC), lactams (Lm), S-containing lactone derivatives (referred to as S-L, including tL, tnL,dtL) and S-containing cyclic carbonate derivatives (referred to as S-CC, including CtC, CdtC, CtnC, CX and CtX) as depicted in Fig. 2. The term polar cyclic monomer is used to differentiate from monomers used for ring-opening metathesis polymerisation (ROMP), which contain a double bond, are typically non-polar (*e.g.* norbornene), and are not included in the TROPIC database as of now.

Data curation. Experimentally, enthalpy and entropy of polymerisation, as well as ceiling temperatures, are generally determined and reported using various experimental conditions (*e.g.* in solution or bulk monomer) with monomers and polymers in different states (liquid, in solution, *etc*… see details in the schema). This can lead to high heterogeneity of data for a given monomer, and some misleading comparisons, particularly for T_c.[16] In addition, T_c can have a high uncertainty due to the sensitivity to change with ΔH_p and ΔH_s and the experimental errors associated with their determination. Thus, as previously highlighted in the literature, having a single ceiling temperature (or a single set of ΔH_p and ΔS_p) for a given monomer can be misleading, due to the dependence on experimental conditions.[16,39] Therefore, as recommended by others, key elements of the experimental conditions used to determine ΔH_p, ΔS_p (and T_c) are included

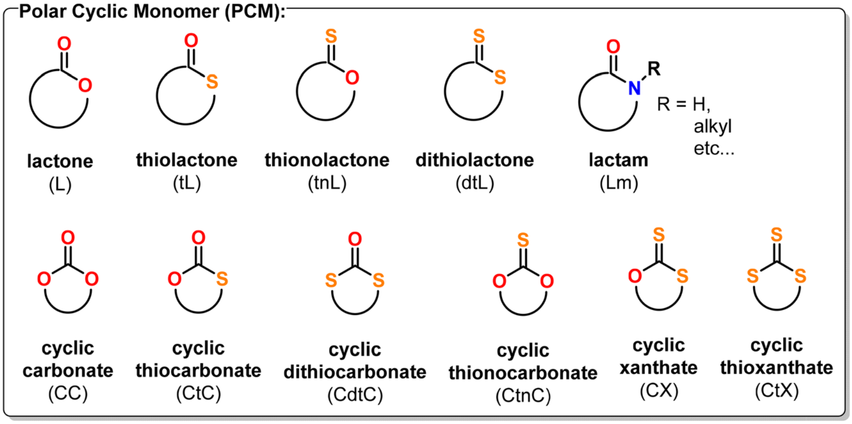


Fig. 2 Polar cyclic monomers (PCM) included in PCM_v1 dataset.

such as monomer initial concentration, medium of the reaction (*i.e.* solvent or bulk monomer), polymer microstructure. Unless stated otherwise, pressure is assumed to be atmospheric pressure. Enthalpy and entropy of polymerisation are associated with the monomer and polymer state, using the terminology recommend by IUPAC (see details in ESI†).[40] The ceiling temperature, when provided in the reference is included and specified as reported, along with the experimental conditions for its determination (*e.g.* bulk or in solution, along with the associated concentration, if specified).

To maximise data consistency and facilitate comparison, a ceiling temperature is recalculated using eqn (4) and the data reported in the literature, using the IUPAC recommended standard states, *i.e.* $[M]_{\mathrm{eq}} = 1$ M for polymerisation carried in solution, or $[M]_{\mathrm{eq}} = [M]_{\mathrm{bulk}}$ (bulk monomer concentration).[40] Such calculated ceiling temperatures are referred to as $T_{\mathrm{c}}(1\ \mathrm{M})^{\circ}$ and $T_{\mathrm{c}}(\mathrm{bulk})^{\circ}$, with "°" used to denote that the standard state has been considered (and ΔH_{p} assumed to be constant over the range of temperature investigated).

As recently discussed,[16] either a thermodynamic derivation or kinetic derivation of the Dainton equation leads to eqn (1) with:

- $[M]_{\mathrm{eq}}$: monomer concentration at equilibrium.
- $[M]_{\mathrm{SS}}$: standard state monomer concentration, *i.e.* bulk monomer concentration for polymerisation in neat monomer, or 1 M for polymerisation in solution.[40]
- ΔH_{p} and ΔS_{p}: enthalpy and entropy of polymerisation respectively, assumed to not change significantly over the range of temperature investigated.
- $\Delta S_{\mathrm{p}}^{\circ}$: standard state change of entropy.

Eqn (1) leads to eqn (3) which is used for Van't Hoff-type analysis and determination of the ceiling temperature by measuring $[M]_{\mathrm{eq}}$ at different temperatures.

$$\mathrm{Ln}\left(\frac{[M]_{\mathrm{eq}}}{[M]_{\mathrm{SS}}}\right) = \frac{\Delta H_{\mathrm{P}}}{RT} - \frac{\Delta S_{\mathrm{P}}}{R} \tag{1}$$

$$\mathrm{Ln}\left([M]_{\mathrm{eq}}\right) = \frac{\Delta H_{\mathrm{P}}}{RT} - \left(\frac{\Delta S_{\mathrm{P}} - R\cdot\mathrm{Ln}\left([M]_{\mathrm{SS}}\right)}{R}\right) \tag{2}$$

$$R\cdot\mathrm{Ln}\left([M]_{\mathrm{eq}}\right) = \frac{\Delta H_{\mathrm{P}}}{T} - \Delta S_{\mathrm{P}}^{\circ} \tag{3}$$

$$\text{Thus, } T_{\mathrm{c}} = \frac{\Delta H_{\mathrm{P}}}{\Delta S_{\mathrm{P}}^{\circ} + R\cdot\mathrm{Ln}\left([M]_{\mathrm{eq}}\right)} \tag{4}$$

Data quality

Despite manual collection and curation, some data may be incomplete (*e.g.* concentration not specified to calculate T_{c}) or require further verifications (*e.g.* wrong units). Such data will be flagged to alert the users, along with some comments. Three types of flags have been defined:

- Admin flag: missing information or lack of metadata for a reference, *e.g.* authors, journal name, *etc.*
- Info flag: experimental conditions or computational details are incomplete, *e.g.* bulk monomer concentration, unclear value of $[M]_{\mathrm{eq}}$ to calculate T_{c}, *etc.*

- Check flag: the data seem inconsistent with other values collected for the same monomer, in the same conditions or for the same (model) reactions.

Data schema

The database is composed of polymerisation documents, each corresponding to a thermodynamic result obtained from the literature (Fig. 3). The fields of the polymerisation document attempt to describe the details of the reaction that may allow its thermodynamic results to be reproduced. This includes the reactants, products, experimental conditions, computational parameters, and other relevant information. The only mandatory fields are a SMILES string for the monomer, the type of polymerisation (explained below), and a flag indicating whether the result is experimental or computational. The remaining fields are left optional. The schema of the polymerisation document attempts to capture all information that may be relevant, rather than act as a unifying descriptor which may be infeasible given the complexities underlying the polymerisations. A full description of the polymerisation schema is provided in Section S1 of the ESI.†

The schemas are defined as Pydantic models. These provide several benefits: (i) they can be easily documented alongside the schema definition, (ii) they are naturally serialisable in Javascript Object Notation (JSON) format which is used by both the database backend and Representational State Transfer Application Programming Interface (REST API), (iii) they provide powerful options for data validation through Python type hinting, meaning that all data are checked for

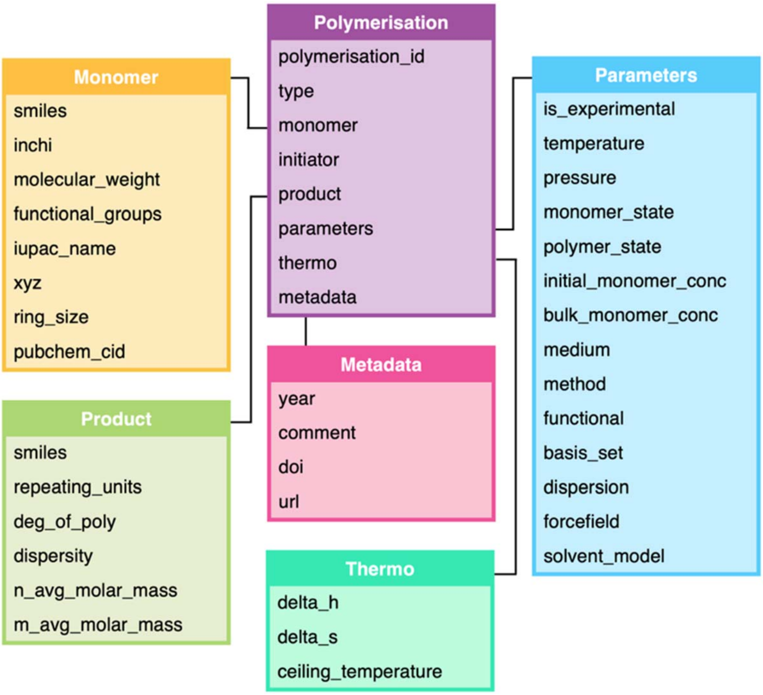


Fig. 3 The entity relationship diagram for the TROPIC database contains polymerisation records, with sub-fields for: monomer, product, parameters, thermo, and metadata.

validity (*e.g.* all fields have the expected types) before entering the database, (iv) they allow for dynamic computation of derived subfields (*e.g.* molecular weight), which minimises the quantity of information that must be entered manually and ensures that these fields are calculated using a common methodology, (v) finally, they allow for facile generation of a REST API based on tools built upon the Pydantic framework (see below).

Database backend and API

We have employed MongoDB as a database backend, due to its flexibility, scalability, and integration with the Python frameworks outlined above. MongoDB is a NoSQL database, meaning data collections do not have to conform to specific schemas. This provides an advantage when storing ROP data since the field is rapidly developing and there will likely be a need to update the type and format of data collected in the future. Any JSON object can be inserted into a MongoDB collection provided it is smaller than the document limit of 16 MB. This is not expected to be a limitation considering that the types of data collected in this work are low dimensional and do not include large numerical arrays – indeed the average document size was found to be 1.8 kB.

A RESTful application programming interface (API) was developed to facilitate programmatic access to the TROPIC database. This enables human and machine access in a structured manner. The API was implemented using FastAPI given its strong integration with Python's type hints and Pydantic's data validation. FastAPI conforms to OpenAPI specifications, allowing the automatic generation of a formal API schema that describes available endpoints, parameters, request bodies, response formats, and error codes. It also provides an automatically generated interface for exploring and testing API endpoints, allowing users to trial database queries alongside the API documentation. To interface with MongoDB, the API employs Beanie, an asynchronous object-document mapper for Python integrated with Pydantic. Each document stored in MongoDB corresponds to a Beanie model, which in turn is defined as a subclass of a Pydantic model. This dual-layered schema definition ensures consistency between the API interface and the underlying database structure and enables any modifications to the underlying schemas to be represented in the API with minimal changes.

User interface

The TROPIC website provides a portal to interact with the database through a graphical interface, enabling users to explore, filter, and analyse ring-opening polymerisation data. The front end was developed using Plotly Dash, a low-code Python framework designed for building interactive web applications. Dash integrates Plotly.js for rendering interactive graphics, React.js for responsive user interface components, and Flask as the underlying web server framework. The Dash Mantine Components library provides UI elements from the Mantine React library and was employed to design the interface. Interactive tables are rendered using the Dash AG Grid, which enables column filtering, row selection, and in-browser sorting. These tools collectively facilitate the creation of a rich, user-friendly front end with minimal reliance on JavaScript, thereby ensuring maintainability within a primarily Python-based development environment. All website interactions with the database are mediated *via* the REST API described in the previous section.

Reaction types and models

Experimental ring-opening polymerisation and computed model reactions have been classified into four categories.

ROP (experiment only): a ring-opening polymerisation (ROP) refers to experimental polymerisations of cyclic monomers leading to linear polymers, generally characterised by significant molar masses (M_n, M_w, degree of polymerisation higher than 20) and low dispersity ($Đ$). Reactions are typically carried out in solution or bulk, as specified in the medium class. In both cases, when reported, the polymer state and initial monomer concentration ($[M]_0$), either in solution or in bulk, will be included.

RCE (experiment only): a ring-chain equilibrium (RCE) considers the equilibrium between all rings (including monomers) and polymers as depicted in Fig. 4. As proposed by Olsén and co-workers, considering RCE rather than the traditional monomer–linear polymer equilibrium, can lead to identify polymers suitable for chemical recycling in mild conditions.[41]

ROR (computation or experiment): a ring-opening reaction (ROR) refers to the "simple" ring-opening of one or a few cyclic monomers by one (nucleophilic) initiator to afford the corresponding "open monomer", as depicted in Fig. 4. One or several monomers can be considered leading to short linear polymeric chain (slpc) with few n repeating units (generally $n < 5$). Different initiators have been considered such as methanol (MeOH), water (H_2O) and ethyl acetate (AcOMe). The latter case corresponds to an isodesmic reaction where the type of broken and formed bonds are the same (*i.e.* ester).[21b] The polymer thus features two identical ester end-groups, potentially avoiding any end-group effects (*e.g.* no OH end-groups potentially engaging in hydrogen bonds). For this model reaction, the type of initiator must be specified. ROR encompasses both experimental and computational data. Indeed, this linear model has generally been applied to computationally estimate the ring-strain and ring-opening energies of lactones.

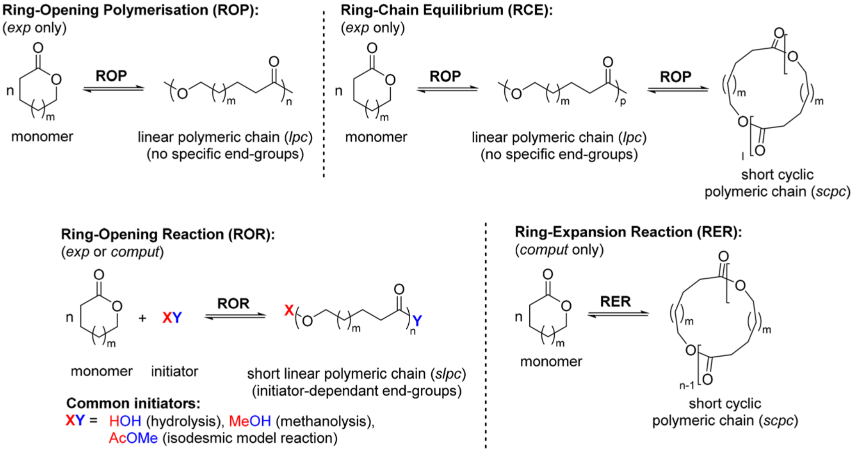


Fig. 4 The four different types of reactions: ROP, RCE, ROR and RER.

However, the simple methanolysis of lactones has also been recently proposed to provide some information on their polymerisability and will be included in TROPIC as a ROR.[42]

RER (computation only): a ring-expansion reaction (RER) consists of forming short cyclic polymeric chains (scpc) or "loops" of different sizes from the corresponding cyclic monomers (*e.g.* cyclic ester) as depicted in Fig. 4. This model reaction has been used for computational estimation of ΔH_p and ΔS_p. For this reaction model, no initiator needs to be specified.

Experimental methodologies to determine polymerisation thermodynamics

As previously reviewed,[16,20,43] experimental determination of polymerisation thermodynamics (ΔH_p, ΔG_p, ΔS_p) and thus ceiling temperature T_c, can be carried out *via* different methods, including Van't Hoff analysis and calorimetric analysis.[44]

In Van't Hoff-type analysis (the most common approach), ΔH_p and ΔS_p are determined from the monomer concentration at equilibrium for different temperatures.[45] Reactions are generally performed in bulk or solution, and concentrations are measured using ^{1}H NMR spectroscopy. Alternatively, DSC is a useful and small-scale technique to perform such analysis.[46]

Computational methodologies to estimate reaction thermodynamics

Different computational methodologies have been considered, including the use of (*ab initio*) molecular dynamics (MD), density functional theory (DFT), and a combination of both.

DFT: the use of DFT is commonly applied to ROR which compromises a limited number of atoms (<50) as only one or very few monomers and repeating units are considered. The energy differences between the reagents (*e.g.* monomer, initiator) and the product (*e.g.* slpc) are used to calculate thermodynamic parameters such as ΔH_p, ΔG_p, and ΔS_p. These results are generally compared with experimental values (ΔH_p, T_c) and show a similar trend which can help to rationalise observed reactivity (*e.g.* ring strain).[47] Such calculations are generally performed using hybrid functionals (*e.g.* B3LYP, M06), a double or triple zeta basis set, a dispersion correction (*e.g.* GD3BJ) as well as an implicit solvent model (*e.g.* cpcm, smd). Only the most stable conformer for both the monomer and the product is considered and is usually deduced from chemical knowledge or the crystal structures of related compounds.

MD-DFT: combined MD and DFT methods have been reported which use classical MD calculations to identify the most stable conformer (or a conformer ensemble) for both the monomer and the product, before using DFT calculations in conjunction with the ROR model (with few repeating units), to calculate the thermodynamic parameters as aforementioned.[21b] This approach can lead to values close to the experimental ones.[21b]

Other Methods: we also aim to capture a range of additional methods that have been employed to computationally assess the thermodynamics of ring-opening polymerisations. These include semi-empirical quantum mechanical methods such as GFNn-xTB and their descendants, along with emerging machine-learned interatomic potentials whether applied through structural optimisations or molecular dynamics.[48]

Results and discussion

Database design

TROPIC is a monomer-centric database gathering thermodynamics parameters (*e.g.* ΔH_p, ΔS_p, T_c) for ROP of polar cyclic monomers (*e.g.* lactones). Data are manually extracted from the academic literature and published datasets. Data obtained from both experimental and computational investigations have been collected.

To maximise data analysis and comparison, experimental conditions and computational models used to determine thermodynamic parameters are also reported. Thus, for a given monomer, all studies reporting relevant thermodynamic data are provided and associated with a reaction type. As detailed in the methods section and as depicted in Fig. 4, four types of reactions have been defined, namely ring-opening polymerisation (ROP), ring-opening reaction (ROR), ring-expansion reaction (RER) and ring-chain equilibrium (RCE). Whereas ROP and RCE refers to experimental (de)polymerisation reactions only, ROR and RER refer to model reactions generally used for computational investigation (few experimental ROR have been reported and included). The latter consider the opening of a discrete number of cyclic monomers (usually up to 5) to either a short linear polymeric chain (slpc, aka linear model) or a small cyclic polymeric chain (scpc, aka loop model). As investigations into the chemical recycling of polymer progress, new types of reactions may be added.

Thus, it is possible to refine search results, for example, per type of study (experimental *versus* computational), or experimental methods (Van't Hoff type analysis or calorimetric analysis) as detailed in the schema. Many other criteria can be used to refine data, including solvent and computational methods (*e.g.* DFT, AIMD).

Contents

As expected, experimental and computational thermodynamic data for ring-opening polymerisation of PCM were relatively scattered in the literature and not always easily discovered. Whereas some studies specifically focused on determining such data and were easily identified (*e.g.* effect of substituent position on lactone ring), works including discrete thermodynamic data as part of a bigger (experimental) study, were more difficult to locate (*e.g.* DFT calculations for enthalpy associated with lactone methanolysis). The current list of references included in the database is accessible *via* the "references" panel and can be exported in comma-separated values (CSV) format. This is a live component of the database and further references will be added as they are published or spotted by our team. However, to help with updates, we encourage authors of studies including relevant data to upload their data using the submission form or to contact us at polycatlab@gmail.com.

Our manual data extraction as detailed in the methods section led to the identification of 67 references covering over 200 unique polar cyclic monomers (Fig. 5(a,b)), for which computational and/or experimental data have been collected.[1c,15,16,19,21a,22,23,42,44c,45a,46,47b,49] This PCM_v1 dataset mainly compromises lactones (Fig. 5(b)) with ring sizes ranging from 4 to 16. The detailed content of TROPIC can be visualised *via* the "About" page which provides an overview

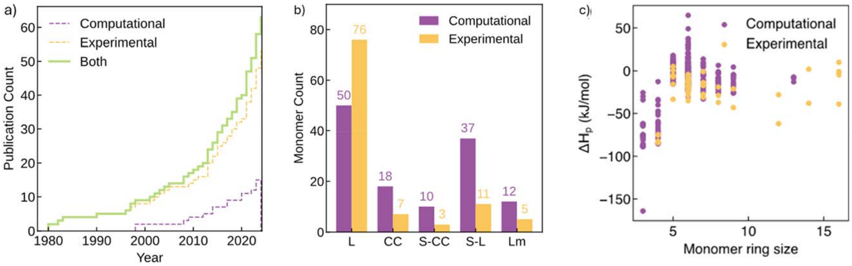


Fig. 5 Statistics of the polymerisation data in the PCM_v1 database (as per July 2025). (a) Histogram of collected publications as a function of year. (b) Number of monomers with selected functional groups (S-L = S-containing lactone derivatives, and S-CC = S-containing cyclic carbonate derivatives). (c) Comparison of computation and experiment for the enthalpy of polymerisation against monomer ring size.

including the number and type of monomers and type of data (experimental or theoretical), among others. Whereas experimental studies generally report both enthalpy (ΔH_p) and entropy (ΔS_p) of polymerisation, computational investigations are generally limited to reporting enthalpy change for a given reaction model (ΔH_p). Indeed, very few computational studies have focused on calculating entropy or free energy, which would be needed to estimate a theoretical ceiling temperature.

To extract similar data from the literature, Ramprasad and co-workers have investigated natural language processing data extraction techniques using ChemDataExtractor[38] and a BERT-based model.[22a] Overall, this approach led to collecting the data of 109 monomers, for which *ca.* 50 are included in PCM_v1 (different types of monomers such as cyclic ether are not covered in PCM_v1). Our manual approach, while tedious and time-consuming, led to a slightly larger dataset, not only including thermodynamic data such as enthalpy, entropy and ceiling temperature (when available) but also other key information such as reaction conditions (*e.g.* for experimental data) or type of model reaction (*e.g.* for computational data). The somewhat high granularity and diversity of collected data make automated data extraction difficult, hence the need for manual collection and curation (see Methods).

In addition to thermodynamic data for ROP being highly scattered in the literature, there are also some inconsistencies and variability in how these data are reported, leading to uncertainty and common pitfalls, as recently reviewed.[16] With our best efforts, and as much as possible with data provided in the literature, the thermodynamic data reported for a given monomer and a given (model) reaction include the methods (see schema details) and the conditions on how they have been determined, *i.e.* the monomer initial concentration ($[M]_0$), the polymer structure (see schema details) and the medium (*i.e.* solvent or bulk monomer). Pressure is also an important parameter that should be included, but unless stated otherwise is assumed to be atmospheric pressure.

As detailed in the methods section, a complete set of experimental data for a given monomer should include, along with the methods and the conditions, enthalpy of polymerisation ΔH_p, standard entropy of polymerisation ΔS_p° (*i.e.*

standard change of entropy assuming polymerisation is carried at 1 M), and the as reported ceiling temperature T_c, when available.

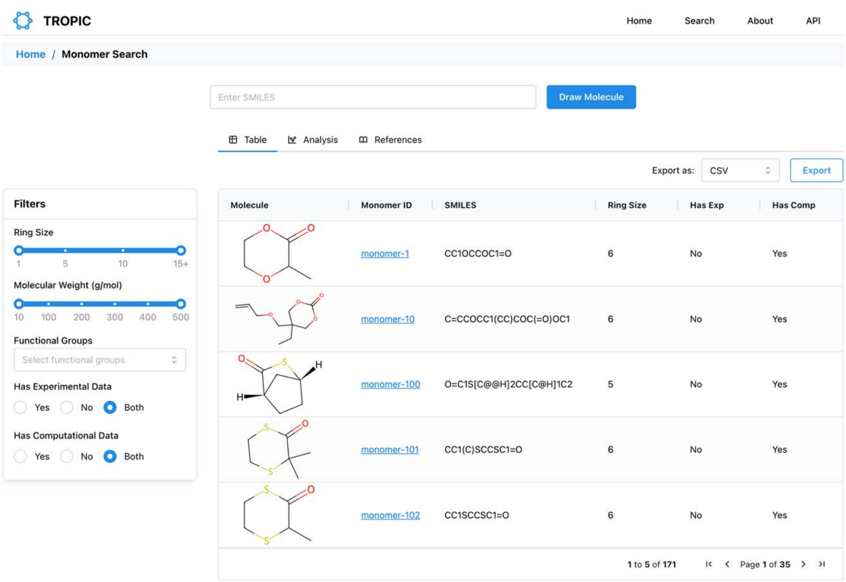
It should be noted that data in TROPIC are classified as "as reported", "validated" or "revised" indicating: (i) the data have simply been added using the values provided in the reference ("as reported"), or (ii) the reported values have been checked and added without modification ("validated") or (iii) the data from the reference have been modified, for example to take into account the effect of concentration. In the latter case, calculations and justifications for the modification are detailed as comments.

User interface, visualisation and analysis

The website is structured into several pages, each tailored to different modes of data exploration. ESI pages† are included to support transparency and usability. An About page outlines the scope and curation strategy of TROPIC. An API page offers instructions for using the REST API and the endpoints available.

Monomer search page. A central feature is the monomer search page, which allows users to query the database using monomer structures (*e.g. via* SMILES). Search results are returned in tabular format and can be filtered based on parameters such as ring size and functional groups (Fig. 6). Users can export the resulting datasets in machine-readable formats such as JSON or CSV, facilitating further external analysis or integration into modelling workflows, including machine learning.

The monomer search page also features an analysis panel that provides interactive plots for visualising trends across different studies, such as variations in ΔH_p or ceiling temperature as a function of ring size (Fig. 5(c)and 7). Additional analysis modes and filtering options will be integrated into future versions of the



Has Experimental Data
○ Yes ○ No ● Both

Has Computational Data
○ Yes ○ No ● Both

Export as: CSV

Molecule	Monomer ID	SMILES	Ring Size	Has Exp	Has Comp
	monomer-1	CC1OCCOC1=O	6	No	Yes
	monomer-10	C=CCOCC1(CC)COC(=O)OC1	6	No	Yes
	monomer-100	O=C1S[C@@H]2CC[C@H]1C2	5	No	Yes
	monomer-101	CC1(C)SCCSC1=O	6	No	Yes
	monomer-102	CC1SCCSC1=O	6	No	Yes

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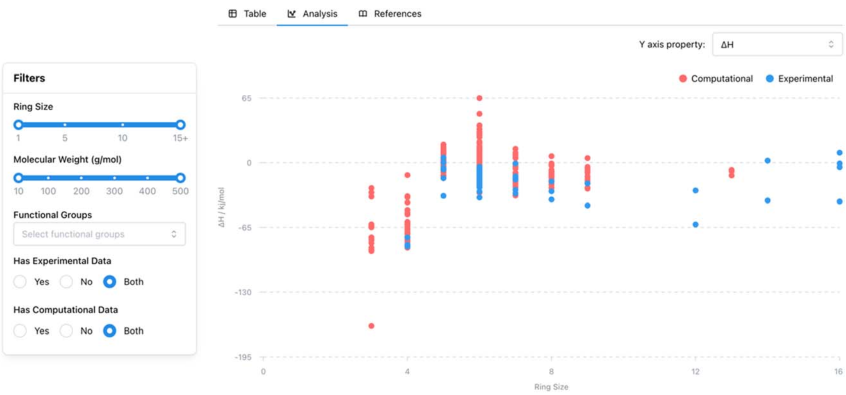
Fig. 6 Screenshot of the monomer search page, showcasing the filter options, results table, and export functionality.



Y axis property: ΔH

Has Experimental Data: ○ Yes ○ No ● Both

Has Computational Data: ○ Yes ○ No ● Both

Fig. 7 Screenshot of the analysis panel, showcasing the correlation of ΔH_p against ring size along with filtering options.

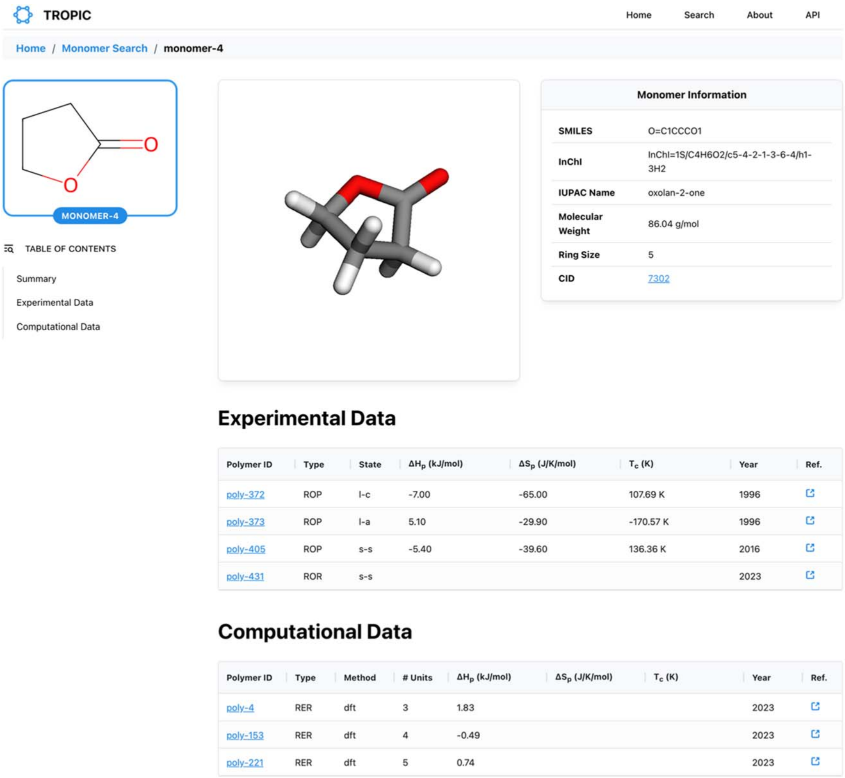
website. A references panel further details all the references associated with a given monomer, allowing users to quickly see authors, journals and year of publication (see Section S2 of the ESI†).

Monomer summary page. Another key component is the monomer summary page, which aggregates detailed information on a specific monomer (Fig. 8). This includes a visual rendering of the monomer structure, a summary of associated polymerisation reactions, and metadata on the conditions under which thermodynamic parameters were obtained. The summary page further provides hyperlinks to related databases such as PubChem and links to the publications of each related polymerisation. Further information can be obtained from PubChem such as the Cambridge Crystallographic Data Centre number.

REST API. The TROPIC REST API allows users to retrieve polymerisation data programmatically by constructing HTTP requests with query parameters that filter results according to relevant chemical or experimental descriptors. Two primary API endpoints are provided, one to search the full database of polymerisation documents, and the second to query data grouped by monomers. Each endpoint allows for filtering based on the fields present in the documents through query parameters such as monomer structure (*via* SMILES), polymerisation type, temperature, and flags for computational *vs.* experimental data. In addition, an endpoint for data submission is in development, allowing for the future incorporation of community-contributed data or automated ingestion pipelines, contingent on curation and quality control. The following example illustrates a simple GET request to retrieve experimental polymerisation entries for ROR-type reactions, with a monomer ring size of less than 10 atoms.

The full list of set of search filters is provided in the automatically generated online API documentation.

```
GET /polymerisations?type=ROR&monomer__ring_size__lt=10\
     &parameters__is_experimental=true
```



Monomer Information

SMILES	O=C1CCCO1
InChI	InChI=1S/C4H6O2/c5-4-2-1-3-6-4/h1-3H2
IUPAC Name	oxolan-2-one
Molecular Weight	86.04 g/mol
Ring Size	5
CID	7302

Experimental Data

Polymer ID	Type	State	ΔH_p (kJ/mol)	ΔS_p (J/K/mol)	T_c (K)	Year	Ref.
poly-372	ROP	l-c	-7.00	-65.00	107.69 K	1996	↗
poly-373	ROP	l-a	5.10	-29.90	-170.57 K	1996	↗
poly-405	ROP	s-s	-5.40	-39.60	136.36 K	2016	↗
poly-431	ROR	s-s				2023	↗

Computational Data

Polymer ID	Type	Method	# Units	ΔH_p (kJ/mol)	ΔS_p (J/K/mol)	T_c (K)	Year	Ref.
poly-4	RER	dft	3	1.83			2023	↗
poly-153	RER	dft	4	-0.49			2023	↗
poly-221	RER	dft	5	0.74			2023	↗

Fig. 8 Screenshot of the monomer summary page for the γ-butyrolactone monomer.

Conclusion and future work

TROPIC is an open-source database containing thermodynamics parameters such as enthalpy and entropy of polymerisation for ROP of polar cyclic monomers (*e.g.* lactone, cyclic carbonate). Data were manually extracted and curated from the literature, considering both experimental and computational studies. Each data point is associated with conditions of their determination, such as experimental methods (*e.g.* Van't Hoff or calorimetry) or computational approach (*i.e.* model reaction, DFT or AIMD). A system of flags has been designed to maximise data quality and consistency and to alert users on data which may be incomplete or containing data that needs to be checked.

The database is monomer-centric and thus can be queried *via* monomer structures (*e.g.* SMILES). Results for a given monomer provide an overview of the reaction(s) and model reactions(s) that have been investigated along with the parameters that were measured or calculated. By having conditions associated with the results, meaningful comparison between monomers can hopefully be carried out, for example by comparing the enthalpy of polymerisation *versus* ring size for polymerisation carried out in similar conditions (*e.g.* bulk). A visualisation tool has been provided allowing users to perform some analysis. Alternatively, users can export machine-readable data (*e.g.* resulting from a search) to perform further bespoke analysis or train ML models.

TROPIC is still burgeoning and under development. A data schema has been conceived but as data get collected and new studies are carried out, is likely to evolve to include recent progress in the field. As highlighted by others, uncertainty in the determination of ceiling temperature may need to be considered and added in the future. Currently limited to homopolymers, TROPIC could expand in the future to include copolymerisation, as well as other classes of monomers (*e.g.* relevant to ROMP).

Data availability

The software powering TROPIC is provided at **https://github.com/virtualatoms/tropic** and publicly accessible. The interactive website is available at **http://polytropic.org**.

Conflicts of interest

There are no conflicts to declare.

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During the preparation of this manuscript, the authors used Microsoft Copilot to create the figure in the graphical abstract. The requirements to use Microsoft Copilot were followed. The authors reviewed and cropped the figure as needed. The authors take full responsibility for the content of this figure.

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