

More than ring-strain: revisiting the definition of enthalpy in ring-opening polymerization†

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The thermodynamics of ring-opening polymerization (ROP) are central when predicting the chemical recyclability of aliphatic polyesters and polycarbonates. Conceptually, the enthalpy of polymerization, ΔH_p° , is widely understood as a measure of ring-strain for a given monomer. However, the ring-strain is commonly larger than ΔH_p° , generating the question of how the release of ring-strain energy during ring-opening transforms. In this work, we propose that ΔH_p° is the sum of the energy released by the ring-strain ($\Delta H_{\text{ring-strain}}^\circ$) and the energy absorbed by the polymer conformations ($\Delta H_{\text{conf}}^\circ$). Owing to the similar ring-strain, but vastly different ΔH_p° values, δ -valerolactone, δ -caprolactone, δ -octalactone, and δ -decalactone were used as model compounds to evaluate the energy cost of polymer conformational freedom. Polymer conformation, measured by ^{13}C NMR, DSC, and molecular dynamics, results are in good agreement with the hypothesis and can explain previous literature observations *i.e.* positive ΔH_p° for systems with ring-strain, substituent effects, and solvent effects, that are difficult to understand when only using the analogy of ring-strain and ΔH_p° . We believe that our results provide a deeper understanding of the underlying thermodynamics and their interpretation in ROP.

Introduction

Chemical recycling of plastics by converting polymers into monomers is widely investigated as an option for a circular materials economy.¹ Within this field, aliphatic polyesters are often highlighted as promising, due to the inherent chemical reversibility of ring-opening polymerization (ROP). ROP allows for the

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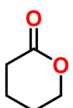
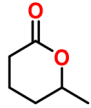
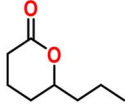
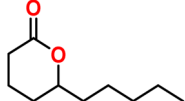
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synthesis of high molecular weight polymers with, for example, mechanical properties comparable to polyolefins whilst also possessing facile chemical recyclability.^{2,3} To assess the chemical recyclability of polyesters, the thermodynamics of ROP are commonly used as a benchmark.^{1,4-10} The thermodynamics describe the equilibrium monomer concentration, often represented as the enthalpy and entropy of polymerization at standard state conditions or ΔH_p° and ΔS_p° , respectively. As such, it is important that our understanding and thereby interpretation of the physical meaning of the definitions of ΔH_p° and ΔS_p° are clear. To support this for ROP and facilitate new monomer design through an extended perception of structure and recyclability relationships, this work revisits the conceptual understanding of ΔH_p° using δ -valerolactone (δ VL), δ -caprolactone (δ CL), δ -octalactone (δ OL), and δ -decalactone (δ DL) as model compounds.

Table 1 The experimental and calculated ring-strain, ΔH_p° , and ΔS_p° values for δ -valerolactone (δ VL), δ -caprolactone (δ CL), δ -octalactone (δ OL), and δ -decalactone (δ DL). Please note that ring-strain is released during polymerization and will thus be negative in sign

Monomer	Ring-strain (kJ mol ⁻¹)	ΔH_p° (kJ mol ⁻¹)	ΔS_p° (J mol ⁻¹ K ⁻¹)
δ VL 	39.7 ^g	-8.4 ^a	-14.7 ^a
	44.3 ^h	-10.5 ^d	-15.0 ^d
	46.0 ⁱ	-11.8 ^c	-29.6 ^c
	32.1 [*]	-12.2 ^b	-28.6 ^b
	36.2 ^{**}		
δ CL 	28.9 [*]	-13.1 ^c	-37.0 ^c
	30.3 ^{**}	-13.8 ^a	-41.2 ^a
		-19.3 ^e	-62.0 ^e
δ OL 	34.9 [*]	-18.5 ^e	-60.0 ^e
	32.6 ^{**}		
δ DL 	32.5 [*]	-17.1 ^f	-68.3 ^f
	33.6 ^{**}	-18.0 ^e	-57.0 ^e
		-20.0 ^b	-62.5 ^b

^a 30% (v/v) toluene in dichloromethane.²² ^b Recalculated by review.⁵ ^c Empirically determined in toluene (1 M).²³ ^d Calorimetry.²⁴ ^e Empirically determined in bulk.⁷ ^f Empirically determined in bulk.²⁵ ^g Ring-strain determined by bomb calorimetry.²⁶ ^h Calculated theoretically.²⁷ ⁱ Combustion calorimetry.²⁸ Rings strains were here calculated using molecular dynamics simulations of the ring structure compared to the strainless linear structure using the ^{*}MM3 or ^{**}CHARMM forcefield.



IUPAC defines ring-strain as the enhanced internal energy of a cyclic molecule, due to relatively unfavourable bond lengths, bond angles, or dihedral angles compared to a linear standard.¹¹ In ROP, ring-strain is generally considered an analogue of the enthalpy of polymerization among text books,^{12–14} review articles,^{5,6,15} and thermodynamic modelling work.^{16–20} However, there are two main issues with the assumption that enthalpy equals ring-strain. (i) First, substitutions on a ring generally lead to a lower ΔH_p° , despite having minimal effect on ring-strain energy (Table 1, with δ VL, δ CL, δ OL, and δ DL as examples). The decrease in ΔH_p° with ring substituents has been reported, discussed, and attributed to ring-strain for many monomers,^{5,8–10} without experimentally addressing changes in ring-strain and it is possible that any potential ring-strain alteration does not support the changes in ΔH_p° . It has for example been shown that substituents on the δ VL ring only marginally affect ring-strain.²¹ (ii) Secondly, the measured ring-strain is far larger than ΔH_p° , meaning that there must be other processes that absorb energy during ring-opening polymerization.

When trying to understand what this energy absorbing process could be, we notice a trend where systems with lower ΔH_p° values also have lower ΔS_p° , and when plotting values for ΔS_p° versus ΔH_p° from literature, Table 1, a linear trend ($R^2 = 0.92$) was evident (Fig. 1a). This indicates that the process that we are looking for is inherently tied to a simultaneous entropic process. In ROP, ΔS_p° consists of a loss of translational entropy during polymerization, as multiple monomers are consumed into a single polymer chain, and a gain in conformational entropy, as linear structures have more possible conformations than a ring structure.¹² The more negative ΔS the more ordered the system, the more positive the less ordered.

With this in mind, it is reasonable to assume that the loss in translational entropy is similar for the ring-opening polymerization of δ VL, δ CL, δ OL, and δ DL, as they follow the same mechanism. This means that a change in conformational entropy will be accompanied by an enthalpic term relating to the energy states of the new conformations that absorb part of the energy released by the release of ring-strain. The system's driving force will of course always be the minimization of ΔG_p° , and ΔG_p° decreases linearly with ΔH_p° (Fig. 1b).

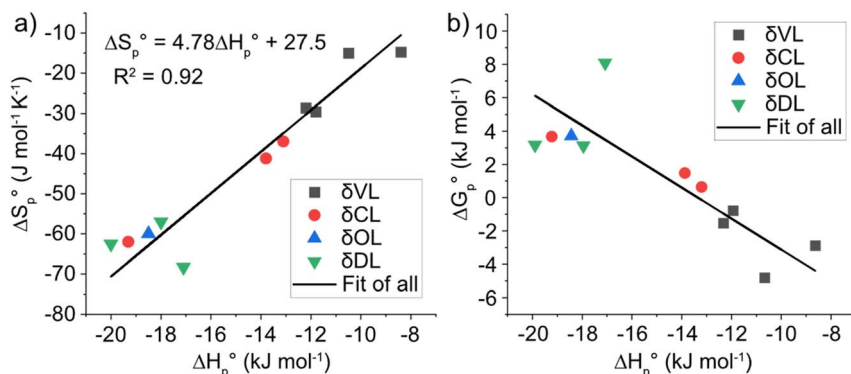


Fig. 1 (a) Plot of experimentally obtained ΔS_p° versus ΔH_p° values from literature, which can be found in Table 1 with data for δ VL,^{5,22–24} δ CL,^{7,22,23} δ OL,⁷ and δ DL.^{5,7,25} (b) Free energy of polymerization calculated at 373 K for the values in (a).



We hypothesize that the deviation in ring-strain ($\Delta H_{\text{ring-strain}}^{\circ}$) energy compared to the enthalpy of polymerization ($\Delta H_{\text{p}}^{\circ}$) relates to a second process, when the ring-strain energy is absorbed by the newly formed polymer to increase the entropy of the system in a process we denote as conformation enthalpy ($\Delta H_{\text{conf}}^{\circ}$). Polymer conformation is defined as the arrangement of bond orientations by means of *trans*, *-gauche*, and *+gauche* states, which determine the 3D spatial structure of the polymer. Entropically, the polymer will target to assume equal amounts of each of the three states, generating a random coil. However, *gauche* states are more energy expensive than *trans* states, meaning that depending on the temperature at which ROP is performed, there might not be sufficient energy to overcome the energy cost of *gauche* states, *trans* states will therefore not conform into *gauche* states, and the resulting polymer will be extended with long end-to-end distances. Thereby, at low temperatures, where little or no energy is absorbed by the polymer, a low $\Delta H_{\text{conf}}^{\circ}$ will be the result. $\Delta H_{\text{p}}^{\circ}$ is negative when $\Delta H_{\text{ring-strain}}^{\circ}$, the energy released (an inherently negative value as strain is released), is greater than $\Delta H_{\text{conf}}^{\circ}$, the energy absorbed (eqn (1)).

$$\Delta H_{\text{p}}^{\circ} = \Delta H_{\text{conf}}^{\circ} + \Delta H_{\text{ring-strain}}^{\circ} \quad (1)$$

Conceptually, our hypothesis can be described from the basis of two enthalpic processes, each of which is tied to an entropic process. First, the energy stored in a ring as ring-strain, drives the ring-opening, releasing ring-strain energy and this is accompanied by an entropic penalty due to the loss of translation (Fig. 2a, step 1). The monomer now attached at the chain end of the polymer attempts to obtain equal amounts of *trans*, *-gauche*, and *+gauche* states, to maximize entropy. However, this process is limited by the amount of energy that is available by means of temperature (Fig. 2a, step 2). We believe that ring-strain release and energy translation to polymer conformation, is a single process in practice, exemplified by $\Delta H_{\text{p}}^{\circ} < \Delta H_{\text{ring-strain}}^{\circ}$. The scenario in which a ring is opened to an all *trans* structure, releasing all heat, is improbable at any non-0 K temperature, yet for simplicity we will here consider $\Delta H_{\text{ring-strain}}^{\circ}$ and $\Delta H_{\text{conf}}^{\circ}$ as two separate processes. The energy difference for converting a *trans* state into a *gauche* state is lower for un- or less substituted polymers than polymers with larger substituents

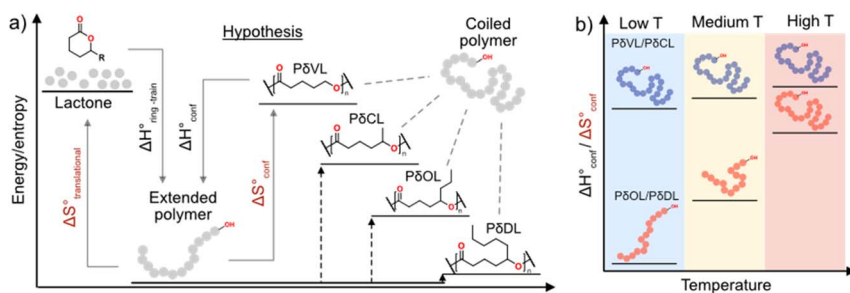


Fig. 2 (a) Schematic representation of the hypothesis consisting of an enthalpy driven ring-strain release step and an entropically driven polymer conformation changing step. (b) Schematic of the conversion of an extended polymer into a polymer coil due to the effect of temperature on $\Delta H_{\text{conf}}^{\circ}$ and $\Delta S_{\text{conf}}^{\circ}$ for P δ OL and P δ DL with larger substituents whilst un- and less-substituted P δ VL and P δ CL show little change in structure with temperature.



due to the additional steric effects that the substituents provide. Therefore, at low temperatures, the un- or less substituted polymers here exemplified as δ VL and δ CL will have more conformational freedom and a high (less negative) $\Delta S_{\text{conf}}^{\circ}$ value, however, more *gauche* states will be formed and thus a high (less negative) $\Delta H_{\text{conf}}^{\circ}$ will be a consequence. Polymers with larger substituents, exemplified here by lactones δ OL and δ DL, will not have sufficient energy to convert many *trans* states into *gauche* states and hence low $\Delta S_{\text{conf}}^{\circ}$ and $\Delta H_{\text{conf}}^{\circ}$ values are obtained. Consequently, the substituted polymers will show greater changes in $\Delta S_{\text{conf}}^{\circ}$ and $\Delta H_{\text{conf}}^{\circ}$ as temperature rises and *gauche* states become more attainable (Fig. 2b). It must be stressed that the coil formation for polymers, although driven by an entropic process, lowers the free energy of the system compared to an extended conformation.

Results and discussion

In ROP, the enthalpy of polymerization, $\Delta H_{\text{p}}^{\circ}$, has been considered equal to the ring-strain of the monomer for at least the past 40 years.^{5,6,12-15} Here we challenge this assumption since: (i) the ring-strain magnitude always exceeds the $\Delta H_{\text{p}}^{\circ}$ and (ii) monomers, such as δ VL, δ CL, δ OL, and δ DL, that have similar ring-strain values still display drastically different $\Delta H_{\text{p}}^{\circ}$ values. In this work, we hypothesize that part of the energy released by ring-strain, $\Delta H_{\text{ring-strain}}^{\circ}$, is transferred to attain energy expensive polymer conformations, a quantity we label $\Delta H_{\text{conf}}^{\circ}$.

If this holds true, then opening a single monomer should present a $\Delta H_{\text{p}}^{\circ}$ value similar to its ring-strain. In turn, as oligomers start forming, the measured $\Delta H_{\text{p}}^{\circ}$ should decrease until it levels off becoming equal to the determined enthalpy of polymerization and this occurs when all oligomers are the length of a polymer, which is considered to be around 20 repeating units.¹² To test this, ring-opening reactions of δ VL, δ CL, δ OL, and δ DL catalysed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with three equivalents of Et_3N co-catalyst in toluene containing 1, 0.2, 0.1, 0.07, 0.05, or 0.02 equivalents (respective theoretical DP = 1, 5, 10, 15, 20, and 50) of methanol as initiator were left until equilibrium was achieved and equilibrium concentrations were measured. To account for the competing polymerization and alcoholysis reactions, the following equation was derived to measure ΔH_{p} (eqn (2), see ESI† for full derivation of the equation).

$$R \ln \left(\frac{[\text{M}]_{\text{eq}} \left([\text{MeOH}]_{\text{eq}} + [\text{P}]_{\text{eq}} \right)}{[\text{P}]_{\text{eq}}} \right) = \frac{\Delta H_{\text{p}}}{T} - \Delta S_{\text{p}} \quad (2)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), M is lactone, MeOH is methanol, and P are the polymer/oligomer/monomer chains. Under these conditions the polymerization reaction conditions do not qualify as standard state due to the competitive reaction with methanol, which is why the thermodynamic terms are noted without the degree symbol. All equilibrium concentrations of M , P , and MeOH can be measured directly using ^1H NMR spectroscopy (Fig. 3) at different reaction temperatures to obtain a van't Hoff plot where the slope equals ΔH_{p} and the intercept equals ΔS_{p} (Fig. S1–S4†).

In all cases, the higher the ratio of monomer to methanol, the longer the polymer chains are, and the higher (less negative) the ΔH_{p} and ΔS_{p} (Fig. 4a and b respectively). This is a strong indication that opening a monomer releases more



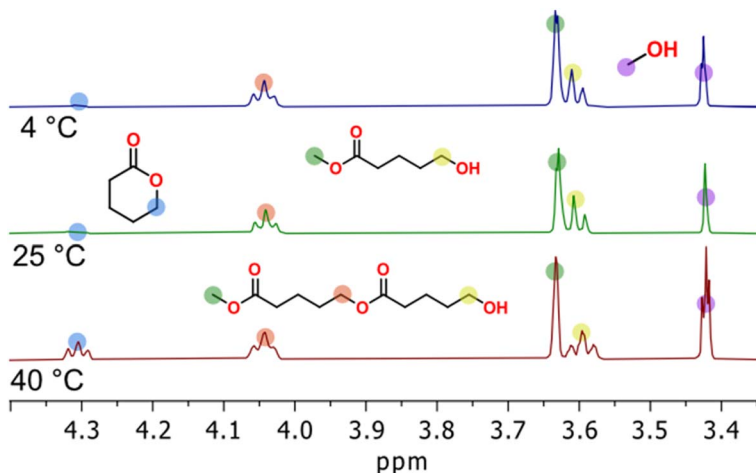


Fig. 3 ^1H NMR spectra (CDCl_3 , 400 MHz, 298 K) of the equilibrium states at different temperatures obtained during the polymerization of δVL with an equimolar amount of methanol at 2 M in toluene. Samples were quenched with acetic acid prior to analysis.

energy than incorporating a monomer into a polymer. The measured ΔH_p at equimolar methanol concentration for the substituted lactones is so low that it starts to approximate the calculated ring-strains and demonstrates that opening a single lactone releases all of the ring-strain energy (Fig. 4a). For δVL , even at an equimolar amount of methanol, polymers form and the measured ΔH_p is therefore substantially higher than its ring-strain (Fig. S5 †).²⁶ It is possible that because δCL , δOL , and δDL open to a secondary alcohol, as opposed to the primary alcohol generated when δVL is opened, their nucleophilicity is less competitive than methanol and methanolysis occurs more easily than polymerization. Without polymer, there are no energy absorbing polymer conformations. However, as the energy released by means of ΔH_p decreases, so does the ΔS_p in a linear fashion for all of the monomers, which strengthens the notion that polymers use part of the heat to increase conformational entropy (Fig. 4c).

To study polymer conformation, P δVL , P δCL , P δOL , and P δDL were synthesized to comparable molecular weights ($\sim 20 \text{ kg mol}^{-1}$) (Fig. S6–S9 †) and changes in conformational structure were analysed through ^{13}C NMR spectroscopy at

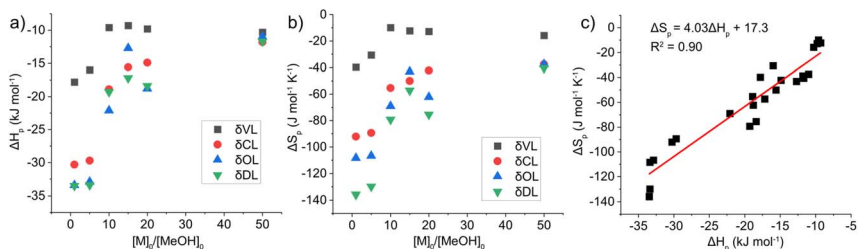


Fig. 4 Obtained (a) ΔH_p and (b) ΔS_p values for the polymerization of δVL , δCL , δOL , and δDL in the presence of varying methanol contents in toluene catalysed by $\text{TBD-Et}_3\text{N}$. (c) Plot of the obtained ΔS_p versus ΔH_p values.



different temperatures in toluene (Fig. S10–S13[†]). The terminal carbon of the repeating unit was chosen as a proxy to represent conformational changes, as this carbon should experience the greatest chemical shift when going from a *trans* to a *gauche* state. With increasing temperature, all polymers display a downfield shift towards higher ppm values, where compared to the signal at 25 °C, P δ DL and P δ OL show the greatest shift and P δ VL the smallest shift (a total shift of 0.116, 0.159, 0.273, and 0.270 ppm for P δ VL, P δ CL, P δ OL, and P δ DL respectively) (Fig. 5a). The magnitude of the difference in the shift between the model polymers is significant and not solely the effect of temperature on the spin relaxation,²⁹ as can be seen from the little difference in the magnitude of the shift with temperature for the methyl esters of δ VL, δ CL, δ OL, and δ DL (a total shift of 0.235, 0.201, 0.278, and 0.258 respectively) (Fig. S14–S18[†]). Due to their much smaller structure, the methyl esters of the lactones are less conformationally obstructed than their polymer variants and their low conformational energy thus serves as reference with regards to the conformational energy. These ¹³C NMR spectroscopy results are interpreted as changes in the polymer conformation dictated by entropy, enabled by the energy provided by increasing the temperature. The larger changes for P δ OL and P δ DL are a result of the higher energy difference between the *trans* and *gauche* states, meaning that at 25 °C only a few *gauche* states have yet been obtained. Differential scanning calorimetry (DSC) strengthens the ¹³C NMR results by showing that with increasing substitution length, more energy is absorbed per mol of repeating unit in the polymer as temperature increases (Fig. 5b), a trend that is irrespective of the heating rate (Fig. S19–S22[†]). The slope of the DSC curves represents the amount of additional energy that is absorbed by the polymer as the temperature increases, which can be seen as the energy penalty to satisfy entropically driven conformational changes. It should be noted that in polymers such changes are often not attributable to simple vibrational changes, but indeed linked to conformational motion.³⁰ This is further exemplified by the lower inclination of the more similar slopes obtained for the DSC traces of the methyl esters of δ VL, δ CL, δ OL, and δ DL (Fig. S23[†]). A steeper slope therefore represents more energy absorbed and greater polymeric conformational changes due to *trans* states being converted to *gauche* states. In terms of heat capacity, the difference between 0–120 °C was found to be 2.69–5.94, 4.44–7.38, 5.69–10.13, and 6.94–12.38 J mol⁻¹ K⁻¹ for P δ VL, P δ CL, P δ OL, and P δ DL respectively at

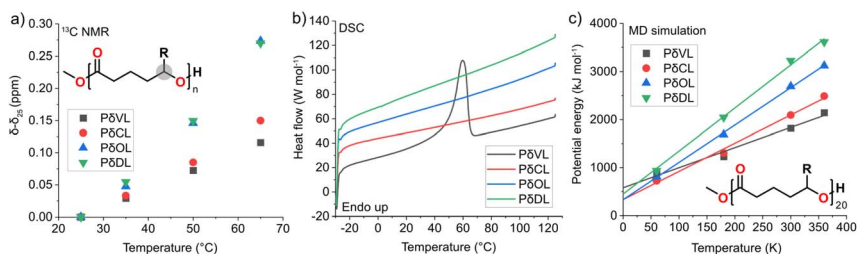


Fig. 5 Analysis of P δ VL, P δ CL, P δ OL, and P δ DL, evaluating (a) changes in chemical shift for the terminal methylene of the repeating unit with temperature derived from ¹³C NMR spectroscopy performed in toluene. (b) DSC (10 K min⁻¹, N₂) thermograms in bulk. (c) MD derived average potential energy over 10 ns simulation time using the MM2 forcefield in vacuum in the 60–360 K temperature range.



a heating rate of 10 K min^{-1} . Calculations of the average potential energy of a polymer chain consisting of 20 repeating units at different temperatures using the MM2 forcefield, which has been reported to be among the best for accurate energy calculations of conformers,^{31,32} further strengthen the ^{13}C NMR and DSC observations by showing that with increasing temperature the polymers with longer substituents absorb more energy (determined from slope in Fig. 5c). The presented results all indicate that P δ VL, and P δ CL to a lesser extent, are entropically more satisfied and have access to a comparatively large number of conformational states even at low temperatures and therefore do not experience great conformational changes as temperature increases. P δ OL and P δ DL, on the other hand, show much greater conformational changes; a result that indicates that these polymers are entropically unsatisfied, but lack the energy at low temperatures to increase the number of possible conformations.

To further study polymer conformation on an atomistic scale, we decided to study the conformation of oligomers with 5 repeating units of P δ VL, P δ CL, P δ OL, and P δ DL in toluene using MD. The statistical desire to obtain equal amounts of *trans* and *gauche* states, entropy, drives extended polymers to form coil-like conformations. However, the coil structure contains more *gauche* states, compared to the mostly *trans* states in an extended polymer, and hence increases the energy of the polymer (Fig. 6a). The amount of energy in the conformation will be heavily reliant on what is allowed by the monomer structure, where the unsubstituted P δ VL will coil up more easily than the sterically encumbered P δ DL. To test this and observe how polymer conformations change with temperature, the distance between the alcohol chain end and the second to last repeating unit in the polymer chain were extracted from the trajectory files of the MD simulation to serve as proxy for overall polymer conformation (Fig. 6b and S24–S27[†]). In agreement with ^{13}C NMR results, P δ VL and P δ CL showed little change in distance as temperature increased (Fig. 6c and S28[†]), whilst P δ OL and P δ DL presented more considerable changes in their distance distributions and increases in the alcohol to ester distance with an increase in temperature (Fig. 6d, 6e and S29[†]). This confirms that NMR indeed can be used as a proxy for conformational

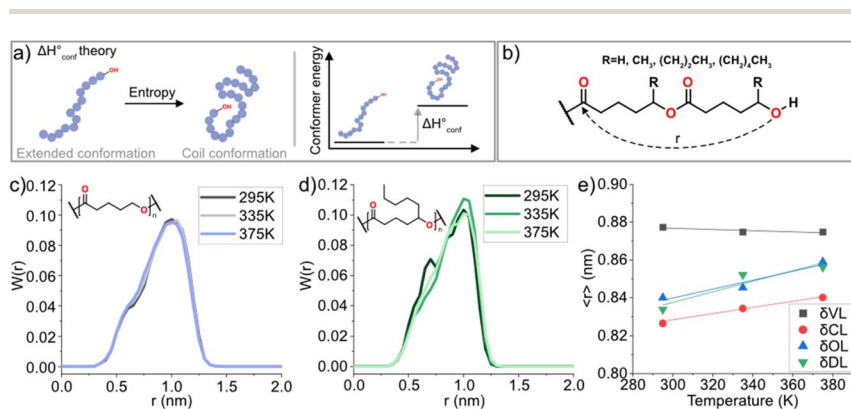


Fig. 6 Schematic representation of (a) the origins of $\Delta H_{\text{conf}}^{\circ}$ and (b) the intramolecular distance used as proxy for polymer conformation. Conformational probability density distribution for r at different temperatures for (c) P δ VL and (d) P δ DL. (e) Average distance r ($\langle r \rangle$) at different temperatures for polymers dissolved in toluene.



changes. Thereby, the DSC results and the observed MD changes, with regards to conformation, support that $\Delta H_{\text{conf}}^{\circ}$ is temperature dependent and that $\Delta S_{\text{conf}}^{\circ}$ is higher for δVL and δCL than for δOL and δDL as the prior pair show fewer conformational changes with rising temperature.

To better understand the atomistic origins of $\Delta H_{\text{p}}^{\circ}$ and why changing conformation affects polymerizability, we employed a recently developed molecular dynamics (MD) method used to calculate the thermodynamic polymerization parameters from collision frequencies.²³ By counting the intra- and intermolecular collisions, with a collision cut-off distance of 0.3 nm between the polymer chain-end either with itself or monomer units, $\Delta H_{\text{p}}^{\circ}$ and $\Delta S_{\text{p}}^{\circ}$ values for δVL , δCL , δOL , and δDL were obtained (Fig. 7a and b). In all cases, the obtained $\Delta S_{\text{p}}^{\circ}$ and $\Delta H_{\text{p}}^{\circ}$ are slightly lower and higher, respectively, than experimental values, however, the trend in $\Delta H_{\text{p}}^{\circ}$, where δVL is the lowest and δDL the highest, is in good agreement with experimental results.

An interesting part of calculating the thermodynamic parameters through MD, is the insight into all atomistic process that proceed, here studied by comparing the intra- and intermolecular collision frequencies recorded during the experiment. For δVL and δCL when the temperature is increased from 295 K to 375 K, they gain most of their $\Delta H_{\text{p}}^{\circ}$ from a sharp increase in intramolecular collisions (Fig. 7c), doubling in collision rate, with only a small decrease in intermolecular collisions (losing $\sim 5\%$) (Fig. 7d). On the other hand, δOL and δDL show a drastic drop $\sim 70\%$ in intermolecular collisions with increase in temperature from 295 K to 375 K (Fig. 7d), still with a significant increase in intramolecular collisions ($\sim 70\%$ more at 295 K than 375 K). In summary, the equilibrium monomer concentrations of δVL and δCL are higher at higher temperatures due to accelerated intramolecular reactions, whilst the equilibrium monomer concentrations of δOL and δDL are higher at higher temperatures due to the simultaneous acceleration of the intramolecular reaction and retardation of the monomer consuming intermolecular reaction. Hence, despite having a similar structure, the origin of the polymerizability of δVL and δCL is vastly different than that of δOL and δDL .

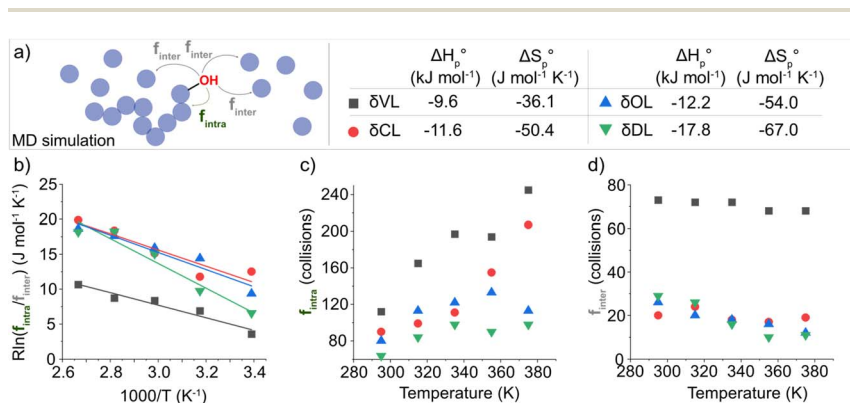


Fig. 7 (a) Schematic representation of the employed MD method for the calculation of thermodynamic parameters. (b) Modified van't Hoff plot used to calculate the thermodynamic parameters from MD results. (c) Intramolecular and (d) intermolecular collisions counted during the 50 ns simulation in the 295–375 K temperature range in toluene.



To attempt a complete calculation of ΔH_p° using the hypothesis described in eqn (1), MD derived average potential energies of polymers consisting of 19 repeating units or 20 repeating units, the lactones, the methyl ester of each lactone, and methanol were used to estimate $\Delta H_{\text{conf}}^\circ$, $\Delta H_{\text{ring-strain}}^\circ$, and ΔH_p° . It must be stressed that the following simulations and calculations are not optimized for this system and the resulting values should not be taken as literal values, but as an indication of the trend. Accurate parameterization is of high importance to obtain discreet values.^{31,33} The $\Delta H_{\text{conf}}^\circ$ was calculated at different temperatures by taking the difference in energy between a polymer of 20 and one of 19 repeating units (Fig. S30–S33†), and subtracting from this the potential energy of the respective methyl ester minus methanol (Fig. S34†). These equations should provide the energy of a single repeating unit in the polymer form and a linear unphysical reference state containing no end groups, respectively, meaning that the difference is due to conformation. In good agreement with experimental results, the calculated $\Delta H_{\text{conf}}^\circ$ shows a greater temperature dependence for δOL and δDL compared to δVL and δCL (Fig. 8a). As a result of the linear temperature dependence, at low temperatures the calculated $\Delta H_{\text{conf}}^\circ$ is higher for δVL and δCL than for δOL and δDL , but at higher temperatures (>1000 K), albeit irrelevant from a practical point of view, δOL and δDL surpass the $\Delta H_{\text{conf}}^\circ$ of δVL and δCL . With the calculation of ΔH_p° as the final goal, the $\Delta H_{\text{ring-strain}}^\circ$ at different temperatures was also calculated, which was performed by subtracting from the average potential energy of the lactone (Fig. S35†) that of the methyl ester minus methanol (Fig. S34†). These equations should provide the amount of energy that is stored in the ring *versus* the linear structure with the same number of atoms. From this, the $\Delta H_{\text{ring-strain}}^\circ$ could be estimated and the temperature dependence was found to be similar for all lactones at each given temperature (Fig. 8b). As a result of the equivalent ring-strain values at all temperature for all lactones, it is the $\Delta H_{\text{conf}}^\circ$ that determines the ΔH_p° , which was calculated by the addition of $\Delta H_{\text{conf}}^\circ$ and $\Delta H_{\text{ring-strain}}^\circ$ (Fig. 8c). The trend in the estimated ΔH_p° at room temperature is in good agreement with experimental results where δOL and δDL show lower values in the temperature range most commonly used for experiments (298–373 K) than δVL and δCL . It should be pointed out that ΔH_p° and ΔS_p° are known to be temperature dependent even when no phase changes occur.^{24,34} However, their variation within the experimental temperature window (usually $\sim 50^\circ\text{C}$) is small

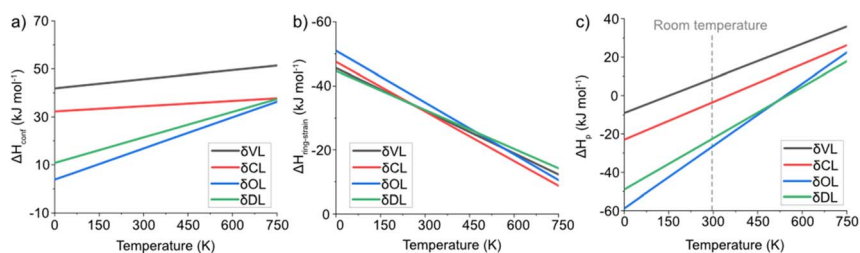


Fig. 8 (a) $\Delta H_{\text{conf}}^\circ$ and (b) $\Delta H_{\text{ring-strain}}^\circ$ calculated from the average potential energy derived from 10 ns MD simulations using the MM2 forcefield in vacuum in the 0–750 K temperature range. (c) ΔH_p° calculated from the addition of the $\Delta H_{\text{conf}}^\circ$ and $\Delta H_{\text{ring-strain}}^\circ$. Calculations were done using non-optimized forcefields and the values should only be taken as an indication of trend.



enough that they appear practically constant in equilibrium monomer concentration studies and deviations are more likely derived from experimental error.

To study if the hypothesis concerning $\Delta H_{\text{conf}}^{\circ}$ provided in this work supports previous work, a small review of examples of monomers with positive $\Delta H_{\text{p}}^{\circ}$, other variants of substituted δVL , and solvent effects on thermodynamics was performed. Most monomers used in ROP are driven by a release of ring-strain, leading to an overall negative $\Delta H_{\text{p}}^{\circ}$ and thus increasing the reaction temperature promotes the depolymerization reaction. However, there are cases where $\Delta H_{\text{p}}^{\circ}$ is positive, for example macrolactones such as pentadecanolid (PDL),³⁵ the recently published ketal-ester,³⁶ and ethylene carbonate.³⁷ Such examples simply defy the analogy of ring-strain and $\Delta H_{\text{p}}^{\circ}$. What is more intriguing, despite being widely cited as a strainless lactone within the ROP scientific community, PDL actually contains non-neglectable ring-strain experimentally measured to be $\sim 11 \text{ kJ mol}^{-1}$,³⁸ which is supported by the considerable ring-strain for other unsubstituted macrolactones of similar size,^{28,38,39} and cyclohexadecane (also 16 atoms in ring).⁴⁰ Additionally, albeit having a positive $\Delta H_{\text{p}}^{\circ}$, ethylene carbonate (entry 1, Table S1†) also has ring-strain. Following the hypothesis of this work, such systems can be described as having $\Delta H_{\text{conf}}^{\circ}$ as the dominant term. Hence, information about $\Delta H_{\text{conf}}^{\circ}$ demystifies the ROP process and explains thermodynamics by including the energy state of the polymer as an additional driving force of polymerization. Examples of this can already be found within literature, for example, di-substituting the α -position of δVL has shown to change $\Delta H_{\text{p}}^{\circ}$ and $\Delta S_{\text{p}}^{\circ}$ remarkably.¹⁰ The diethyl substituted variant of δVL , δVLEt_2 , displays $\Delta H_{\text{p}}^{\circ} = -27.9 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{p}}^{\circ} = -79.6 \text{ J mol}^{-1} \text{ K}^{-1}$, more than doubling both the enthalpy and entropy values of δVL despite having very similar ring-strain (entries 2–5, Table S1†). Changes in ring-strain for substituted δVL are small,²¹ which is supported by the lower than cyclohexane ring-strain energy for 1,1-dimethylcyclohexane.⁴¹ Therefore, changes in $\Delta H_{\text{p}}^{\circ}$ cannot be attributed to ring-strain for substituted δVL . Instead, going from the extended state of $\text{P}\delta\text{VLEt}_2$ to its coil state is very energy expensive, a cost which is simply too high to be supplemented by available thermal energy at the temperatures at which polymerization is performed, and as a result this polymer will absorb little energy released by the ring-strain, yielding low $\Delta H_{\text{conf}}^{\circ}$, and by extension low $\Delta H_{\text{p}}^{\circ}$ and low $\Delta S_{\text{p}}^{\circ}$ values as the polymer can only access a few conformational states and is entropically unsatisfied. Another clear example that demonstrates how one may change polymerizability through $\Delta H_{\text{conf}}^{\circ}$, are through the effect solvent has on the thermodynamics of polymerization in ROP.^{42–45} The polymerization of L-lactide, for instance, in DMSO provides $\Delta H_{\text{p}}^{\circ} = -8.9 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{p}}^{\circ} = -22 \text{ J mol}^{-1} \text{ K}^{-1}$, whilst in chlorobenzene as solvent $\Delta H_{\text{p}}^{\circ} = -21 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{p}}^{\circ} = -34 \text{ J mol}^{-1} \text{ K}^{-1}$, a result which has been attributed to the difference in energy of solvation of the polymer and monomer.⁴² The differences in $\Delta H_{\text{p}}^{\circ}$ between different solvents are thought to be mostly the result of changes in $\Delta H_{\text{conf}}^{\circ}$ as the internal non-equilibrium bond lengths and angles that make up $\Delta H_{\text{ring-strain}}^{\circ}$ are not altered in different solvents. Altogether, the hypothesis of this work provides both conceptual and mathematical support for observations made in literature, making it a powerful concept to understand the factors that govern the thermodynamics of ROP.



Conclusions

Our study explores and attempts to demystify why enthalpy of polymerization ΔH_p° does not equal its ring-strain ($\Delta H_{\text{ring-strain}}^\circ$). We hypothesise that part of the energy released by the $\Delta H_{\text{ring-strain}}^\circ$ is absorbed to attain polymeric conformations ($\Delta H_{\text{conf}}^\circ$) that are entropically favourable, but enthalpically expensive. This hypothesis was tested through the combined use of NMR spectroscopy, DSC and MD simulations. ^1H NMR spectroscopy equilibrium studies demonstrated that ring-opening with methanol releases more energy than adding a monomer unit to an existing polymer chain, contributing to the concept of energy absorption by the polymer. MD simulations revealed that δVL and δCL perform faster depolymerization reactions with no change to the intermolecular reaction rate as temperature rises, whilst δOL and δDL demonstrated a steep decrease in intermolecular reaction rate as temperature rises as a result of significant polymer conformational changes for $\text{P}\delta\text{OL}$ and $\text{P}\delta\text{DL}$ compared to $\text{P}\delta\text{VL}$. This was further supported by ^{13}C NMR, DSC, and MD potential energy calculations, which showed that polymers with larger substituents, $\text{P}\delta\text{OL}$ and $\text{P}\delta\text{DL}$, absorb more energy enabling alteration of their polymer conformation as temperature rises than unsubstituted $\text{P}\delta\text{VL}$. More importantly, the hypothesis fits observations in literature that are unexplainable when considering ΔH_p° as purely ring-strain driven and $\Delta H_{\text{conf}}^\circ$ thus provides new conceptual insights to polymer chemists focusing on the thermodynamics behind ROP.

Data availability

All raw unprocessed data and NMR spectra are available on KTH Zenodo (<https://doi.org/10.71775/kth.9qy5e-nea08>). The supplementary information file contains experimental methods and additional data for presented experiments.^{10,23,26–28,37,46–59}

Conflicts of interest

The authors have no conflict of interest to declare.

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