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Perspective

Improving the Accuracy of Ceiling Temperature Measurements: Best Practices and Common Pitfalls

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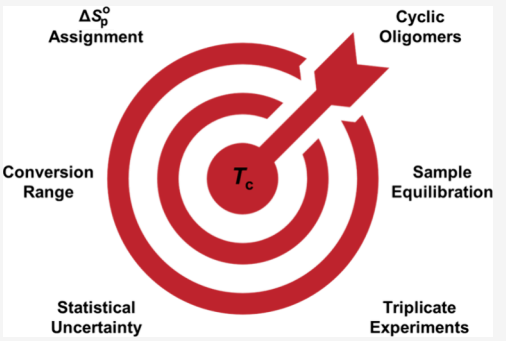
ABSTRACT: The investigation of low ceiling temperature (T_c) monomers is an active area of research in the field of polymer science to address modern challenges in waste and recycling. Many commendable contributions have been made to this field; however, a thorough survey of the literature has revealed common oversights in the calculations of the changes in enthalpy (ΔH_p) and entropy (ΔS_p) upon polymerization as well as T_c. This Perspective aims to clarify how to avoid these pitfalls, accurately calculate these values, and outline best practices for experimentally measuring these key thermodynamic parameters. In an era where researchers are increasingly reliant on the quality of data, especially for endeavors in machine learning and artificial intelligence, it is important to establish a unified approach for making these calculations to optimize precision and accuracy.



INTRODUCTION

The growing plastic waste problem has become a significant environmental concern, with vast amounts of plastic accumulating in landfills and oceans.[1] Of the plastic waste that is successfully recycled, most undergoes mechanical recycling and is converted into lower-quality materials.[2] To address this issue, chemical recycling to monomer (CRM) has emerged as a promising solution.[3−13] This approach involves breaking down the polymers in plastic waste into their constituent monomers. Upon recovery, these monomers can then be repolymerized to regenerate the plastic with no loss in material properties, thus contributing to a circular economy.

Monomers that are well-suited for CRM have a low ceiling temperature (T_c). The ceiling temperature is a key parameter that indicates the tendency of a polymer to revert to its monomeric form. T_c is determined by both the changes in enthalpy (ΔH_p) and entropy (ΔS_p) upon polymerization, as described by the Gibbs free energy equation: $\Delta G_p = \Delta H_p - T\Delta S_p$.[14] The position of the monomer−polymer equilibrium can be influenced by changing the temperature of the system, provided ΔH_p is not zero. Generally, a low T_c is considered to be any value below 200 °C for bulk conditions.[15] Many examples of low T_c monomers are cyclic in structure and undergo reversible ring-opening polymerization. However, there is also growing interest in low T_c vinyl monomers that can undergo reversible addition polymerization under suitable conditions.[16−19]

Precise knowledge of the experimental conditions under which the T_c is measured is essential for optimizing applications of CRM, as variations in concentration, solvent, pressure, and polymer microstructure can significantly affect the T_c values obtained. Additionally, in an era where data quality is increasingly critical for endeavors in machine learning and artificial intelligence,[20] it is important to establish a unified approach for making these calculations to optimize precision and reliability between reports. Accurate data on T_c, ΔH_p, and ΔS_p is crucial for developing predictive models and improving the design of recyclable polymers. A standardized method ensures consistency and comparability across studies, enhancing the robustness of data-driven insights.

The discussion of polymerization thermodynamics applies to both the solid and liquid phase states. However, this Perspective focuses on systems where the monomer and polymer are in the liquid state (bulk or in solution), as these are the most commonly reported systems in the literature. A consideration of systems in which the polymer precipitates upon formation was excluded, as this introduces additional thermodynamic effects, namely, crystallization energies and inhomogeneities, beyond the scope of this Perspective. When the polymerization does not involve a phase change, crystallization energies are not relevant. However, crystallization energies must be accounted for when the polymerization involves a phase change.[21]

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CEILING TEMPERATURE

First reported by Snow and Frey in 1943,[22] the T_c of a monomer is defined as the temperature at which the rates of polymerization and depolymerization reactions are equal, such that the system is at equilibrium. In 1948, Dainton and Ivin quantitatively described the thermodynamics of ceiling temperature, providing a foundational understanding of this phenomenon.[23] In principle, all polymerization reactions have an equilibrium between monomer and polymer that can be described using the equation for the Gibbs free energy of polymerization ($\Delta G_p = \Delta H_p - T\Delta S_p$). The T_c of a monomer is the temperature at which the rates of polymerization and depolymerization are equal, corresponding to $\Delta G_p = 0$. With simple rearrangement, the ceiling temperature can be expressed as $T_c = \Delta H_p/\Delta S_p$, which is commonly referred to as the Dainton equation. For most polymerizations, ΔH_p is negative (exothermic polymerization reaction) and ΔS_p is also negative (loss of translational freedom when individual monomers are entrained in a polymer chain). When both of these parameters are negative and the temperature of the system is decreased below the T_c, polymerization is favored. When the temperature of the system is increased above the T_c, depolymerization to monomer is favored. Thus, there is an upper bound (or "ceiling") to the temperature at which polymerization can occur. It is important to note that there is no definitive set of reference conditions for polymerization, as precise conditions (including monomer concentration, solvent, pressure, and structure of the formed polymer) can vary. Thus, these parameters should always be reported when quoting or discussing a T_c value for it to have any real thermodynamic meaning.[24]

T_c has been measured for various categories of monomers, including lactones,[25−41] thiolactones,[42−55] carbonates,[56−61] cyclic acetals,[62] aldehydes,[63−65] and others.[66−73] Table 1 reports a number of monomers that have been developed for their low T_c behavior. From a practical perspective, plastics made from low T_c monomers can be easier to recycle, as less energy and lower temperatures are needed to break down the polymers. Depolymerization of well-defined polymers back to monomers in the absence of side reactions is necessary for an efficient recycling processes.[74] Improving the ease of recycling is crucial for developing effective and environmentally friendly recycling technologies.

One of the goals when targeting low T_c monomers is to minimize the magnitude of ΔH_p, as this allows for a viable equilibrium that can shift between monomer and polymer as a function of temperature. This is frequently achieved by using 5- or 6-membered rings to minimize strain in cyclic monomer designs, while addition polymerizations leverage olefin substitution to increase steric strain between repeating units in the resulting polymer chain. For example, the monomer γ-butyrolactone (**γ-BL**) has a small ΔH_p of −5.4 kJ/mol and a low T_c (1 M) of −136 °C (Table 1, entry 2). In comparison, α-methylstyrene (**α-MS**) has a much more exothermic polymerization with ΔH_p = −29.1 kJ/mol and a much higher T_c (1 M) of 8 °C (Table 1, entry 4).

For monomers where the T_c is higher than the desired recycling temperature, techniques such as distillation and dilution can be used to either continuously remove monomer from the polymer system or dilute the monomer within it. This shifts the equilibrium toward the depolymerized state, thereby improving the feasibility and practicality of a chemically recyclable system. For example, the polymer made from 1,3-dioxolane (**DXL**) can be distilled to facilitate depolymerization.[62] Additionally, methyl methacrylate (**MMA**) has a T_c (1 M) of 164 °C (Table 1, entry 5).[75] However, by diluting the system to low concentrations (5 mM), researchers have recently demonstrated the complete depolymerization of **MMA** at 120 °C.[17] Some monomers, however, have very low ceiling temperatures. The utility of these very low T_c monomers can be enhanced by capping the chain ends to kinetically trap the polymer until a chemical trigger is introduced. For example, phthalaldehyde (**PHA**) has a T_c (1 M) of −35 °C (Table 1, entry 6) which requires polymerization at very low temperatures but can rapidly depolymerize when triggered under ambient conditions, even from the solid state.[63] However, for other applications where a more robust material is needed, a system with a less extreme ceiling temperature would be necessary.

Although lowering the magnitude of ΔH_p is a common synthetic target, this is not the only consideration when designing a monomer for CRM. The balance of the ratio of $\Delta H_p/\Delta S_p$ is crucial, as focusing solely on ΔH_p does not provide a complete picture. Two monomers could have the same T_c but different values of ΔH_p and ΔS_p, which affect the system's sensitivity to temperature changes. In Figure 1, a contour plot illustrates what we have defined as the conversion window (W_{90}) as a function of ΔH_p and ΔS_p°. W_{90} represents the temperature range (ΔT) required to go from 0 to 90% conversion, calculated for an initial monomer concentration, $[M]_0$, of 1 M. W_{90} quantifies the temperature sensitivity of the system: a smaller W_{90} value indicates that the monomer is (de)polymerized within a narrower temperature range. Each contour on the plot represents a constant value of W_{90}, and the color gradient between contours highlights the variation in W_{90}

Table 1. Thermodynamic Parameters for Various Monomers[a,b]

Entry	Monomer	ΔH_p (kJ/mol)	ΔS_p° (J/mol·K)	T_c (1 M) (°C)	W_{90} (°C)
1	Me_2-DTN[68]	-15.1	-45.6	58	98
2	γ-BL[37]	-5.4	-39.6	-136	44
3	DXL[62]	-20.2	-69.3[a]	19[a]	63
4	α-MS[81]	-29.1	-103.8	8	44
5	MMA[75]	-54.0	-123.4	164	59
6	PHA[63]	-36.5	-151.0	-35	27
7	N^{ene}-PenTL[46]	-9.4	-28.1	61	136

[a]Values for $[M]_{ss}$ = 1.0 M. [b]Entry 3 row: Values of ΔS_p° and T_c (1 M) have been corrected from the originally reported data due to an incorrect assignment of ΔS_p° in the original publication. W_{90} is the temperature difference required to achieve 90% conversion from an initial conversion of 0% at $[M]_0$ = 1 M.

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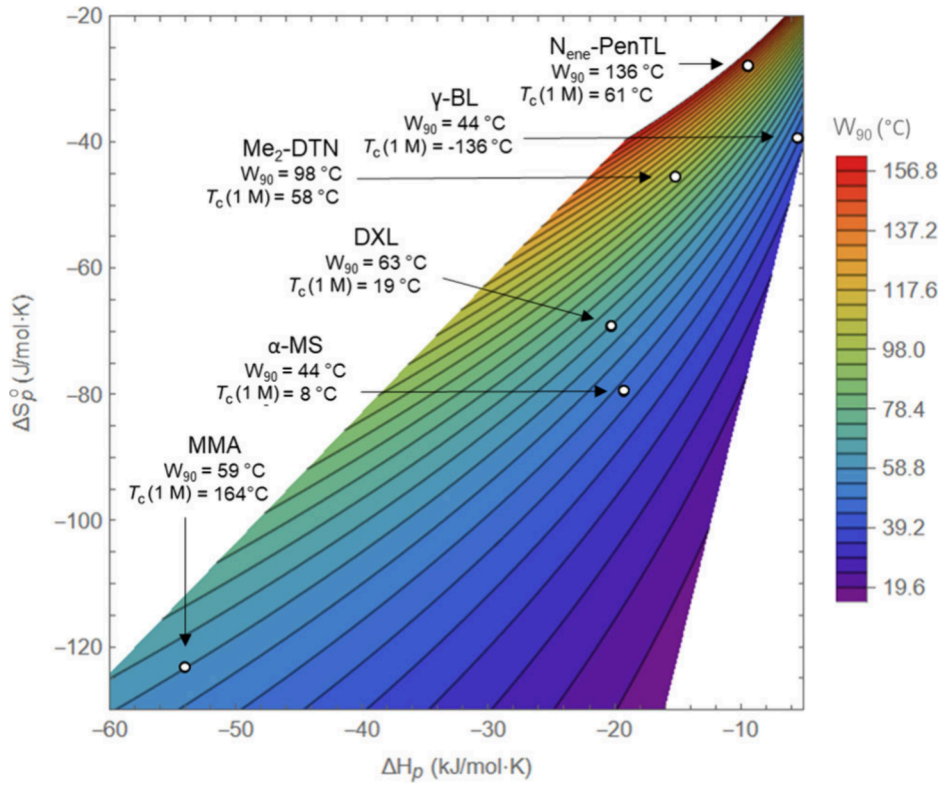

Figure 1. Heatmap illustrating polymerization sensitivity. Generated from combinations of ΔH_p and ΔS_p^o that yield T_c (1 M) values between −150 and 200 °C. Contours represent constant W_{90} values. The color gradient represents variations in W_{90}, with warmer colors representing larger values and cooler colors representing smaller values. Computed for $[M]_0$ = 1 M.

across the plot, with warmer colors representing larger values of W_{90} and cooler colors representing smaller values. The process used to generate Figure 1 is described in detail in the section on the sensitivity of polymerization in the SI. While a low T_c monomer is desirable, it is also important for the equilibrium to be sensitive to temperature. This sensitivity ensures that the energy required for conversion is minimized, reducing the operational requirements during the manufacturing and recycling process. An ideal monomer for CRM would exhibit a narrow temperature range in which it can be fully polymerized and depolymerized.

For example, **Me_2-DTN** and **N^{ene}-PenTL** have similar values of T_c (1 M), 58 and 61 °C, respectively (Table 1, entries 1 and 7). These two monomers have significantly different values of ΔH_p and ΔS_p^o, but the ratio of ΔH_p to ΔS_p^o is similar for both monomers, which is why they have comparable T_c (1 M) values. However, because these monomers have different values of ΔH_p and ΔS_p^o, they have different conversion windows. Specifically, **Me_2-DTN** has a W_{90} of 98 °C, which is narrower than that of **N^{ene}-PenTL**, which is 136 °C. This narrower window suggests that the polymer of **Me_2-DTN** can be more readily converted back to monomer with less energy input, provided a suitable mechanistic pathway for depolymerization exists. However, rigorous technoeconomic analysis and life cycle assessment are needed to make more definitive conclusions on comparisons between recycling processes.

FACTORS THAT AFFECT CEILING TEMPERATURE

T_c is not a single intrinsic value but rather varies with experimental conditions including monomer concentration, solvent, pressure, and polymer microstructure. The effect of monomer concentration will be discussed in later sections. Solvent choice can significantly impact the T_c by altering the free energies of the monomer and polymer, which affects the equilibrium monomer concentration and ceiling temperature.[76] The nature of the solvent also influences the volume fraction and interactions between the polymer and solvent, both of which can affect T_c.[16]

Additionally, using a solvent closer to the theta solvent condition can reduce chain coiling, resulting in longer backbone bonds, a lower enthalpy of polymerization, and consequently lower ceiling temperatures.[77] It is typically assumed that polymerizations occur under atmospheric pressure unless otherwise specified. Although pressure is frequently not an experimental factor, the Clausius−Clapeyron equation shows that higher pressures will favor polymerizations with negative ΔV_p (volume change of polymerization), which is the most observed case.[78]

THERMODYNAMIC DERIVATION OF THE DAINTON EQUATION

The thermodynamic derivation of the Dainton equation begins with the expression for free energy under nonstandard conditions (eq 1). (The standard concentration is defined by IUPAC as 1 M concentration, although this is not feasible for every monomer system.[79]) At equilibrium, ΔG_p = 0, and according to the law of mass action, the reaction quotient (Q) equals the equilibrium constant (K_{eq}). These conditions lead to the modified equation shown in eq 2.

$$\Delta G_p = \Delta G_p^o + RT \ln(Q) \quad (1)$$

$$0 = \Delta G_p^o + RT \ln(K_{eq}) \quad (2)$$

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Equation 3 describes the equilibrium of a monomer unit (M) and a propagating polymer chain (M_n), leading to the formation of a polymer chain (M_{n+1}) governed by K_{eq}. When expressing the equilibrium constant, under the assumption that $[M_n] \approx [M_{n+1}]$, the value of K_{eq} can be approximated as $[M]_{eq}^{-1}$. This approximation assumes that the addition of a single monomer unit to a propagating chain does not significantly change the concentration of the polymer. Furthermore, it assumes that the overall polymer concentration is negligibly small relative to the monomer concentration. In principle, monomer activities should be used instead of concentration, since ΔS_p° can vary from experimental conditions. However, measuring the concentration is significantly more practical than measuring the activity and is commonly viewed to be a suitable approximation.

$$M + M_n \overset{K_{eq}}{\rightleftharpoons} M_{n+1} \tag{3}$$

By substituting $\Delta G_p^\circ = \Delta H_p^\circ - T\Delta S_p^\circ$ into eq 2 and using the approximation $K_{eq} = [M]_{eq}^{-1}$, eq 2 can be rewritten as eq 4. Rearranging eq 4 to solve for $R\ \ln([M]_{eq})$ yields eq 5. Assuming the change in enthalpy upon polymerization to be independent of temperature and initial monomer concentration, ΔH_p° can be replaced by ΔH_p.

$$0 = RT\ \ln([M]_{eq}) - \Delta H_p^\circ + T\Delta S_p^\circ \tag{4}$$

$$R\ \ln([M]_{eq}) = \frac{\Delta H_p}{T} - \Delta S_p^\circ \tag{5}$$

It is important to note that in eq 5 the entropy term (ΔS_p°) represents the standard state change in entropy upon polymerization at 1 M. Here, the standard state monomer concentration is defined as $[M]_{ss}$ = 1.0 M. However, some researchers omit this standard symbol when presenting the Dainton equation, potentially causing confusion about whether the entropy term represents the standard change in entropy upon polymerization, as highlighted by Liu et al.[15] Therefore, it is recommended to explicitly include the standard symbol when using eq 5, as this denotes that the entropy term in this equation refers specifically to the standard state of 1 M, *regardless of the initial monomer concentration used in the experiment*.

A kinetic derivation of the Dainton equation can also be derived from the perspective of relative rates, which has recently been detailed by Liu et al.[15]

MOLE FRACTION VERSION OF THE DAINTON EQUATION

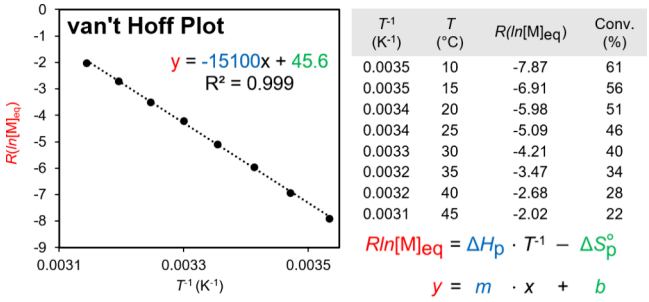
Although less commonly used, the Dainton equation can also be expressed as a function of the equilibrium mole fraction (n_m/n_0) rather than the equilibrium monomer concentration. In the mole fraction version of the equation (eq 6), n_m is the moles of monomer at equilibrium and n_0 is the starting moles of monomer. However, the mole fraction version of the equation has been known to pose confusion among researchers and lead to an incorrect determination of ceiling temperatures. A detailed derivation of the mole fraction version of the Dainton equation is available in the SI (eq SE 8). The important point to highlight is that the entropy term in this mole fraction version of the equation represents ΔS_p *at the initial monomer concentration*, not ΔS_p°.

$$R\ \ln\left(\frac{n_m}{n_0}\right) = \frac{\Delta H_p}{T} - \Delta S_p \tag{6}$$

Throughout the remainder of this Perspective, the more commonly used version of the equation, expressed in terms of $[M]_{eq}$ (eq 5), will be utilized.

FITTING EXPERIMENTAL NMR DATA TO THE DAINTON EQUATION

There are various techniques that can be used to measure T_c, including spectroscopy, calorimetry, and kinetic studies. Most researchers use NMR to measure the equilibrium monomer concentration ($[M]_{eq}$) at different temperatures (T). This can be achieved through individual batch experiments quenched at the desired temperature or through in situ measurement with variable-temperature NMR (VT-NMR). The data from these experiments is then plotted with T^{-1} on the x-axis and $R\ln([M]_{eq})$ on the y-axis. The data is then fit to the Dainton equation (eq 5), where ΔH_p is calculated as $\Delta H_p = m$ and ΔS_p° is calculated as $\Delta S_p^\circ = -b$, where m and b represent the slope and y-intercept, respectively (Figure 2). As previously discussed, the entropy term in eq 5 represents ΔS_p°. Thus, the y-intercept of the van't Hoff plot corresponds to ΔS_p°, regardless of the initial monomer concentration ($[M]_0$). Using these values, the ceiling temperature at 1 M is calculated as T_c (1 M) = $\Delta H_p/\Delta S_p^\circ$.



T^{-1} (K^{-1})	T (°C)	$R(ln[M]_{eq})$	Conv. (%)
0.0035	10	-7.87	61
0.0035	15	-6.91	56
0.0034	20	-5.98	51
0.0034	25	-5.09	46
0.0033	30	-4.21	40
0.0032	35	-3.47	34
0.0032	40	-2.68	28
0.0031	45	-2.02	22

Figure 2. Example van't Hoff plot of the **Me_2-DTN** monomer at $[M]_0$ = 1 M, where the slope corresponds to ΔH_p and the y-intercept corresponds to ΔS_p°.

While the conventional practice is to report T_c at either 1 M or under bulk conditions,[80] it is essential that any reporting of T_c includes all relevant experimental conditions ($[M]_0$, solvent medium, pressure, and polymer microstructure) under which it was measured. To calculate ΔS_p for bulk conditions (or any concentration), ΔS_p° can be extrapolated using eq 7, as introduced by Dainton and Ivin.[23] A common typographical error in the literature is the omission of the factor of R in eq 7, which leads to errors in both the change in entropy upon polymerization and the ceiling temperature.

$$\Delta S_p = \Delta S_p^\circ + R\ \ln([M]_0) \tag{7}$$

$[M]_{EQ}$ IS INDEPENDENT OF $[M]_0$

At first, it may seem counterintuitive that the y-intercept of data fitted to eq 5 represents ΔS_p°, regardless of the initial monomer concentration ($[M]_0$). This result is based on the idea that $[M]_{eq}$ thermodynamically determined is independent of $[M]_0$. McCormick's classical work on the low T_c monomer ***α*-MS**, published in 1957, demonstrates this concept.[81] Data

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from McCormick's experiments show that polymerizations with different initial monomer concentrations ($[M]_0$) equilibrate to approximately the same $[M]_{eq}$ at a given temperature. Figure 3 illustrates this with example data points where different initial concentrations ($[M]_0$ = 0.77, 1.54, and 2.30 M) all equilibrate to approximately 0.7 M at 0 °C.

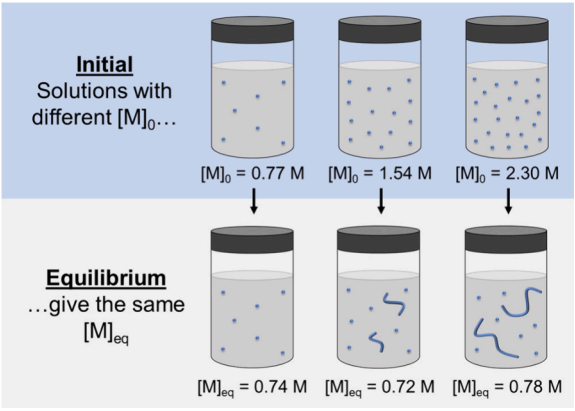

Figure 3. Equilibrium monomer concentration of ***α*-MS** polymerization. Data from ref 81 reproduced with permission from Wiley. Schematic representation of polymerizations with different $[M]_0$ reaching approximately the same $[M]_{eq}$ at the same temperature (0 °C).

Furthermore, when all of the data points from McCormick's various experiments at different $[M]_0$, ranging from 0.75 to 7.6 M, are plotted on a van't Hoff plot, they are colinear and share an identical slope (ΔH_p) and *y*-intercept (ΔS_p^o) (Figure 4).

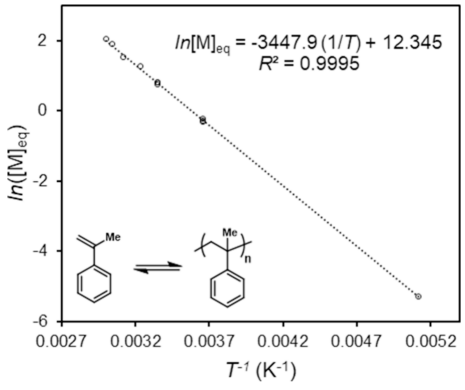

Figure 4. van't Hoff plot of ***α*-MS** polymerization. Adapted using data from ref 81 with permission from Wiley.

Each data point on a van't Hoff plot represents the system at equilibrium, where the rates of the forward and backward reactions are equal, which is the definition of the T_c. Thus, the $[M]_{eq}$ at any given temperature corresponds to the $[M]_0$ for which that temperature is the T_c. Since each value of $[M]_0$ only has one T_c value (assuming that the pressure, microstructure, and solvent are constant), the van't Hoff plot will be consistent for any value of $[M]_0$, with the *y*-intercept always representing ΔS_p^o. This can be explained more intuitively by eq 5, which shows that $[M]_{eq}$ is a function of T, ΔH_p, and ΔS_p^o. Therefore, $[M]_0$ cannot affect $[M]_{eq}$, since T, ΔH_p, and ΔS_p^o do not depend on $[M]_0$.

Another way to explain this phenomenon is that the *x*-intercept of the van't Hoff plot represents the temperature at which $[M]_{eq}$ = 1 M. Since each point on the plot corresponds to an equilibrium state, the *x*-intercept also represents the T_c (1 M), where $[M]_0$ = 1 M. This further illustrates why the van't Hoff plot should remain consistent, regardless of the initial monomer concentration used in the experiment.

ERROR IN ASSIGNING THE STANDARD CHANGE IN ENTROPY UPON POLYMERIZATION (ΔS_p^o)

A common error that has been observed in the literature is the incorrect assignment of ΔS_p^o from the van't Hoff plot. This mistake occurs when researchers misinterpret the *y*-intercept as representing the entropy of polymerization at the initial monomer concentration and incorrectly calculate it as $\Delta S_p = -Rb$. Equation 7 is then used to calculate ΔS_p^o as $\Delta S_p^o = S_p - R\ln([M]_0)$. In other words, this misinterpretation of the *y*-intercept leads to an unnecessary adjustment of ΔS_p^o *away* from an initially correct value. It is worth noting that if $[M]_0 < 1$, then this error will result in a T_c (1 M) value higher than the correct T_c (1 M). Conversely, if $[M]_0 > 1$, then this incorrect method of calculating T_c (1 M) will result in a value lower than the correct T_c (1 M).

MODEL SYSTEM

To demonstrate how an incorrect assignment of ΔS_p^o impacts the calculated thermodynamic values, the anionic ring-opening polymerization of dimethyl dithianone (**Me_2-DTN**) is used as a case study (Figure 5). This system will also be used in

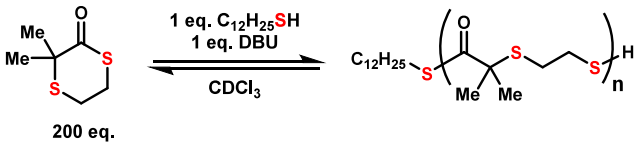

Figure 5. Polymerization of the **Me_2-DTN** monomer.

subsequent sections to illustrate how even when ΔS_p^o is correctly assigned, various sources of experimental error can still lead to challenges in correctly calculating the change in entropy upon polymerization and ceiling temperature. Additionally, this model system will be employed to evaluate different assumptions made in the van't Hoff analysis, highlighting when these assumptions hold true and when they break down. For all VT-NMR experiments using this monomer, the sample was equilibrated at each temperature following a specified timeline (detailed in Section 7 of the SI). However, equilibration time is system-specific and depends on various factors including monomer structure, temperature, solvent, and concentration.

For an experiment conducted at $[M]_0$ = 2.0 M, the correct ΔS_p^o is calculated as −47.5 J/mol·K and the T_c (1 M) is 68 °C (Table 2, entry 1). When the entropy of polymerization is incorrectly assigned (i.e., to ΔS_p instead of ΔS_p^o) using the same data, the ΔS_p^o is calculated to be −53.2 J/mol·K and the T_c (1 M) is 31 °C (Table 2, entry 2). This is a 5.7 J/mol·K difference in ΔS_p^o and a 37 °C gap in T_c (1 M). The correct calculation yields values for ΔS_p^o and T_c (1 M) that are notably closer to the values observed during experiments performed at a standard 1 M concentration (Table 2, entry 3). This example illustrates that incorrectly assigning ΔS_p^o results in relatively modest errors in both ΔS_p^o and T_c (1 M). These errors likely do not impact the overall conclusions or recyclability of a monomer miscalculated in the literature; however, they do lead

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Table 2. Comparison of Thermodynamic Parameters with Correct and Incorrect Entropy Assignments[a]

Entry	$[M]_0$ (M)	Entropy Assignment	ΔH_p (kJ/mol)	ΔS_p^o (J/mol·K)	T_c (1 M) (°C)
1	2.0	Correct	−16.2 (±0.1)	−47.5 (±0.5)	68 (±5)
2	2.0	Incorrect	−16.2 (±0.1)	−53.2 (±0.5)	31 (±4)
3	1.0	-	−15.1 (±0.2)	−45.6 (±0.5)	58 (±5)

[a]Comparison of ΔH_p, ΔS_p^o, and T_c (1 M) calculated from $[M]_0$ = 2 M polymerization data using the correct and incorrect assignments of ΔS_p^o.

Table 3. Thermodynamic Parameters at Different $[M]_0$[a]

$[M]_0$	0.75 M	1.0 M	1.5 M	2.0 M
ΔH_p (kJ/mol)	−15.5 (±0.6)	−15.1 (±0.2)	−15.9 (±0.07)	−16.2 (±0.1)
ΔS_p^o (J/mol·K)	−47.2 (±2.0)	−45.6 (±0.5)	−47.4 (±0.2)	−47.5 (±0.5)
T_c (1 M) (°C)	56 (±19)	58 (±5)	62 (±3)	68 (±5)

[a]Comparison of ΔH_p, ΔS_p^o, and T_c (1 M) calculated from polymerization data for $[M]_0$= 0.75, 1.0, 1.5, and 2.0 M experiments.

to challenges when directly comparing different monomer systems or using these values for computational models.

To determine if the **Me_2-DTN** system would equilibrate to the same $[M]_{eq}$ with different $[M]_0$ values and yield colinear van't Hoff plots, VT-NMR experiments were carried out with varying $[M]_0$ concentrations (0.75, 1.0, and 2.0 M). Table 3 and Figure 6 show notable variations in $[M]_{eq}$ across the different experiments. The data presented in Table 3 illustrate how seemingly small differences in ΔH_p and ΔS_p^o can impact the T_c (1 M). For this system specifically, the T_c (1 M) varies by 12 °C between the most dilute (0.75 M) and most concentrated (2.0 M) experiments.

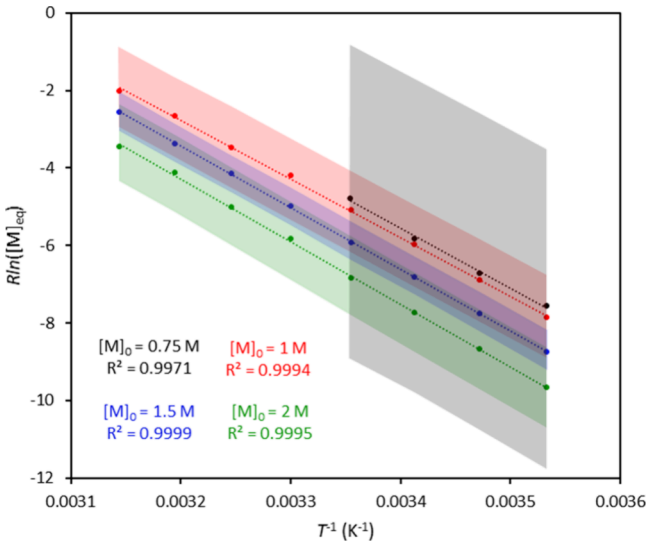

Figure 6. van't Hoff plot of $[M]_0$ = 0.75, 1.0, 1.5, and 2.0 M **Me_2-DTN** polymerizations in $CDCl_3$. Shaded regions represent the uncertainty in the regression fit, accounting for the standard error in both the slope and intercept.

IMPACT OF CYCLIC OLIGOMERS ON THERMODYNAMIC CALCULATIONS

For the polymerizations of **Me_2-DTN** with various initial monomer concentrations, the observed variations in $[M]_{eq}$ are hypothesized to originate from the formation of cyclic oligomers, which are favored under more dilute conditions. To our knowledge, the impact of cyclic oligomer formation on thermodynamic calculations has not yet been addressed in the literature.

The formation of cyclic oligomers is a commonly observed phenomenon in ring-opening polymerizations, especially at lower concentrations. This occurs when the chain end backbites, reacting with the polymer backbone to generate a stable, cyclic oligomer. This differs from the example of **α-MS**, which cannot form cyclic oligomers due to the absence of a backbiting mechanism, resulting in cleaner thermodynamic data.

In 1950, Jacobson and Stockmayer described the theory behind the equilibrium formation of cyclic polymer species from polycondensation systems,[82,83] which helped launch the field of topological polymers.[84,85] One important finding from this work was the existence of a critical cyclic concentration, which constitutes the maximum concentration of cyclic species that can form in a given system from ring−chain equilibration in combination with ring−ring and chain−chain equilibration. The fraction of cyclic species increases with decreasing initial monomer concentration until reaching this critical concentration, below which all polymer species are expected to be cyclic. Although recent work that considers end-to-end cyclization calls into question the nature of this critical cyclic concentration,[86] the Jacobson−Stockmayer theory continues to be the only model for describing the statistical formation of cyclic chains in equilibrium with linear chains. It is worth noting that ring-expansion polymerizations, which exclusively form cyclic polymers, are not subject to this theory because the topology is forced rather than being in equilibrium with linear chains.

Cyclic oligomers are not accounted for in the equilibrium expression (eq 3) used to derive the Dainton equation. As a result, their presence can lead to errors in the measurement of ceiling temperature as well as changes in enthalpy and entropy upon polymerization. However, accurately determining the extent of this impact is challenging because existing derivations, such as Dainton's, assume a system of exclusively linear species. Accounting for cyclic oligomers would require modifying the derivation to include their concentration, which would invalidate the approximation that $K_{eq} \approx [M]_{eq}^{-1}$ and significantly complicate the derivation. Given these challenges, the most practical approach is to conduct experiments under conditions that minimize or eliminate cyclic oligomer formation.

Figure 7 presents the analysis of monomer, polymer, and oligomer distribution using NMR and GPC. In this specific example, a $[M]_0$ = 1.5 M polymerization was quenched with trifluoroacetic acid (TFA) at 22 °C. The NMR results differentiate between monomer and the combined polymer +

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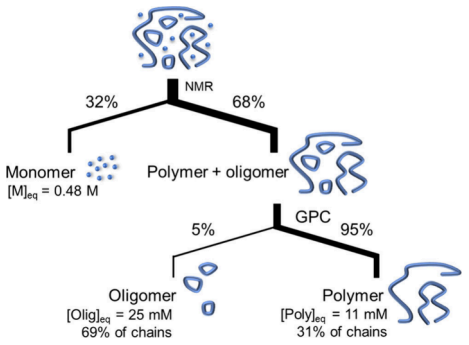

Figure 7. Analysis of monomer, polymer, and cyclic oligomer distribution using NMR and GPC for a $[M]_0$ = 1.5 M polymerization quenched at 22 °C.

cyclic oligomer fraction, revealing that 32% is monomer ($[M]_{eq}$ = 0.48 M) and 68% is polymer + cyclic oligomer. Subsequent GPC analysis further distinguishes the polymer from the oligomer within the combined fraction, showing that 5% of the consumed monomer ended up in cyclic oligomers and 95% ended up in polymers.

By mass, the primary product of the **Me_2-DTN** polymerization is the linear polymer. However, because the polymer has significantly higher molecular weight than the cyclic oligomer, there is a substantially higher number of cyclic oligomer chains (69%) compared to polymer chains (31%). This translates to a higher concentration of oligomers ($[Olig]_{eq}$ = 25 mM) relative to polymers ($[Poly]_{eq}$ = 11 mM). These estimates indicate that the quantity of cyclic oligomers formed during polymerizations is non-negligible. Moreover, Table 4 shows a trend where the percentage of chains that are cyclic oligomers decreases as $[M]_0$ increases.

Table 4. Equilibrium Concentrations of Monomer, Polymer, and Oligomer[a]

$[M]_0$	0.75 M	1.0 M	1.5 M	2.0 M
$[M]_{eq}$	0.51 M	0.46 M	0.48 M	0.49 M
$[Poly]_{eq}$	4.5 mM	6.7 mM	11 mM	16 mM
% chains (Poly)	20%	28%	31%	33%
$[Olig]_{eq}$	18 mM	18 mM	25 mM	32 mM
% chains (Olig)	80%	72%	69%	67%

[a]Monomer, polymer, and cyclic oligomer concentrations for $[M]_0$ = 0.75, 1.0, 1.5, and 2.0 M polymerizations quenched with TFA at 22 °C.

A cautionary note about the data in Table 4: due to the lack of baseline resolution between the polymer and cyclic oligomer peaks in the GPC analysis (Figure 8), the size of each peak cannot be accurately quantified. Consequently, the calculated values potentially contain a significant degree of error. For a detailed procedure and a sample calculation for the data in Table 4, see Section 5 of the SI.

SUITABLE CONVERSION RANGE

When using NMR to measure monomer conversions and concentrations, it is recommended to maintain monomer conversion within the 20−80% range. Outside this range, the data is prone to noise and nonlinearity, making it less reliable. At low degrees of polymerization, polymer proton resonances may be near the background noise level, leading to larger relative uncertainties in the measurement. Conversely, at high

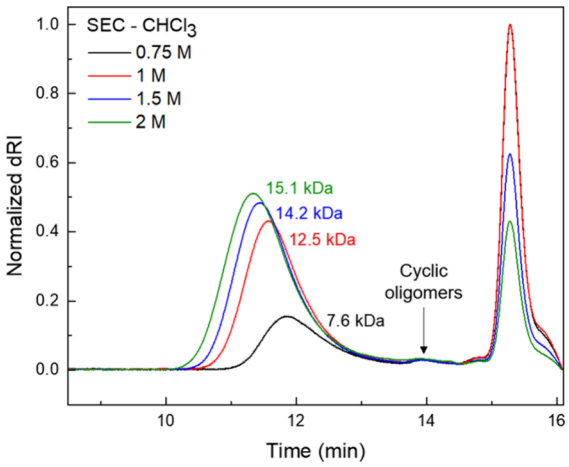

Figure 8. SEC in $CHCl_3$ of polymerizations with $[M]_0$ = 0.75, 1.0, 1.5, and 2.0 M, quenched with TFA at 22 °C.

conversions, monomer proton resonances approach the background noise level, again resulting in larger uncertainties. Additionally, chain-end effects become more pronounced at low conversion, which can cause short chains to exhibit different thermodynamic properties than longer chains, which can result in a nonlinear van't Hoff plot.

It is also recommended to encompass a broad range of conversions, which requires using a wide-enough temperature interval in the experimental setup. Some researchers use narrow temperature intervals and report data points where the conversion differs by only a few percentage points. However, this practice is discouraged, as the small difference in conversion may fall within the uncertainty of NMR measurements, potentially leading to inaccurate regression analysis. This issue becomes especially problematic when the conversion lies outside the preferred 20−80% range. Deviations outside this range are mainly attributed to chain-ends effects, which impacts the assumption that $[M_n] \approx [M_{n+1}]$, although a rigorous analysis of these phenomena has yet to be conducted.

To illustrate this point, a more dilute VT-NMR experiment of the **Me_2-DTN** polymerization at $[M]_0$ = 0.5 M was conducted. In this experiment, all the data falls below 20% conversion (Table 5). Despite the system being well-

Table 5. $[M]_0$ = 0.5 M Conversion Data[a]

Entry	T (K)	Conv.[b]
1	283	13.9%
2	288	7.7%
3	293	5.7%
4	298	3.1%
5	303	2.7%

[a]Conversion data for $[M]_0$ = 0.5 M polymerization of **Me_2-DTN** in $CDCl_3$. [b]Conversion determined by ^1H NMR in $CDCl_3$.

equilibrated, the conversion plotted against temperature reveals a nonlinear trend (Figure S7). Consequently, when this data is incorporated into a van't Hoff plot (Figure 9), it yields a notably low R^2 value of 0.89.

When using the nonlinear data obtained from the 0.5 M experiment to calculate ΔH_p, ΔS_p°, and T_c (1 M), there is a significant deviation from the values calculated from the 1.0 M experiment (Table 6), with percent differences of 72, 82, and

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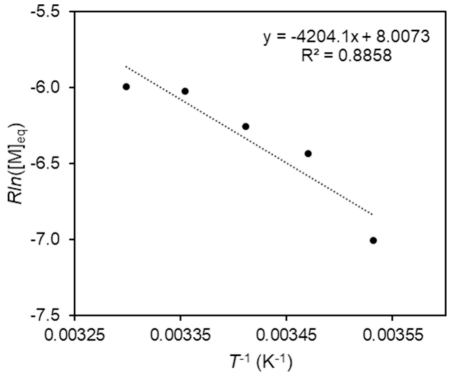

Figure 9. van't Hoff plot for $[M]_0$ = 0.5 M polymerization of **Me_2-DTN** in $CDCl_3$.

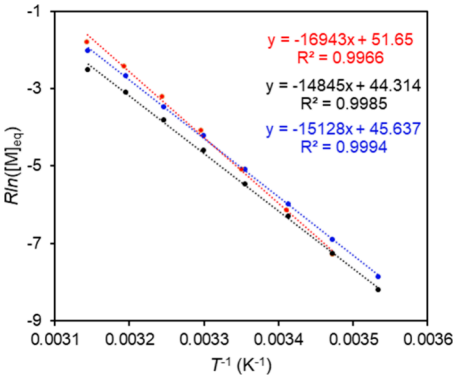

Figure 10. van't Hoff plot of triplicate experiments of **Me_2-DTN** polymerization at $[M]_0$ = 1 M in $CDCl_3$.

Table 6. Thermodynamic Parameters for $[M]_0$ = 0.5 and 1.0 M Polymerizations[a]

Entry	$[M]_0$ (M)	ΔH_p (kJ/mol)	ΔS_p^o (J/mol·K)	T_c (1 M) (°C)
1	1.0	−15.1 (±0.2)	−45.6 (±0.5)	58 (±5)
2	0.5	−4.2 (±0.9)	−8.0 (±3.0)	252 (±223)

[a]Thermodynamic parameters for $[M]_0$ = 0.5 and 1.0 M polymerizations of **Me_2-DTN** in $CDCl_3$. Entry 2 represents the $[M]_0$ = 0.5 M experiment, which exhibited low conversions (<20%).

Table 7. Triplicate $[M]_0$ = 1.0 M Polymerizations[a]

Entry	ΔH_p (kJ/mol)	ΔS_p^o (J/mol·K)	T_c (1 M) (°C)
1	−16.9	−51.6	55
2	−14.8	−44.3	62
3	−15.1	−45.6	58
Average	−15.6 (±0.7)	−47.2 (±2.2)	58 (±2.0)

[a]Thermodynamic parameters for triplicate $[M]_0$ = 1.0 M polymerizations of **Me_2-DTN** in $CDCl_3$.

334%, respectively. These differences arise from the large uncertainty in the 0.5 M data and the higher cyclic oligomer fraction in the experiment due to its low concentration. While dramatic, this example underscores the importance of using data in a suitable conversion range to obtain accurate thermodynamic calculations.

TRIPLICATE EXPERIMENTS AND STATISTICAL UNCERTAINTY IN EXPERIMENTAL DATA

A common practice in scientific experimentation is to conduct three separate experiments (in triplicate) under the same conditions and calculate the average. Surprisingly, triplicate experiments are not typically performed in NMR studies measuring the changes in enthalpy and entropy upon polymerization. In addition, most researchers do not report the standard error from the linear regression used to calculate ΔH_p (slope) and ΔS_p^o (intercept), which is readily available from common regression tools. Unfortunately, this leaves readers unaware of the statistical uncertainty associated with these reported values.

In light of this, conducting triplicate experiments and reporting the standard error from regression analysis is recommended. As highlighted by Liu et al., errors in experimental values of ΔH_p and ΔS_p^o propagate and can significantly influence T_c calculations.[87] As a case in point, triplicate VT-NMR experiments were conducted for the polymerization of **Me_2-DTN** at $[M]_0$ = 1 M. As shown in Figure 10 and Table 7, the standard errors in the average ΔH_p and ΔS_p^o are ±0.7 kJ/mol and ±2.2 J/mol·K, respectively.

CONCLUSIONS

This study underscores the importance of correct entropy assignments and precise experimental procedures in determining the thermodynamic properties of polymerizing systems. Through the polymerization of **Me_2-DTN**, it has been demonstrated how incorrect entropy calculations can lead to errors in the reported values of ceiling temperature. Additionally, the impact of cyclic oligomer formation on thermodynamic calculations was explored, revealing that oligomers can affect the accuracy of these measurements, though accounting for their formation remains a challenge. This Perspective also emphasizes the need for suitable conversion ranges and the use of triplicate experiments to reduce statistical uncertainty and ensure reliable data within the body of literature. Furthermore, when reporting T_c data, it is essential to provide the precise experimental conditions—including concentration, solvent, external pressure, and the structure of the formed polymer—for the data to have any real thermodynamic meaning.

The concepts discussed in this Perspective regarding T_c monomers also apply to floor temperature (T_f) monomers. In contrast to enthalpy-driven T_c monomers, the ring-opening polymerization of T_f monomers is entropy-driven. This occurs when the changes in both enthalpy and entropy upon polymerization are positive. As a result, polymerization is favored above the T_f and depolymerization is favored below the T_f. While far less common in the literature, there is growing interest in designing new monomers with T_f behavior to leverage triggered depolymerization at low temperatures.[88−90]

The study of polymerization thermodynamics, particularly focusing on low T_c monomers, is crucial to the development of chemically recyclable polymers, which has the potential to play a significant role in addressing the plastic waste crisis. By emphasizing the importance of a unified approach and best practices, this Perspective aims to enhance the accuracy and precision of these key thermodynamic parameters. The adoption of these methods is crucial for developing predictive models and designing recyclable polymers for a sustainable future.

Take-Home Messages for Improving the Accuracy and Precision of T_c Measurements.

- *Correct Assignment of* ΔS_p^o: When using the $[M]_{eq}$ version of the Dainton equation, ensure the *y*-intercept of the

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van't Hoff plot is correctly assigned as the standard entropy of polymerization at 1 M (ΔS_p°).

- *Identify the Presence of Cyclic Oligomers*: Cyclic oligomers can introduce errors in calculated thermodynamic values, as they are not accounted for in Dainton's derivation. When possible, experiments should be conducted under conditions that favor predominantly linear species.
- *Use Suitable Conversion Ranges*: Collecting data within a monomer conversion range of approximately 20−80% and across a broad range of temperatures is recommended to capture meaningful conversion differences while minimizing noise.
- *Ensure Equilibrium is Reached:* Allow the system sufficient time to equilibrate before collecting data; failure to do so may result in unreliable calculated thermodynamic values.
- *Conduct Triplicate Experiments*: Perform experiments in triplicate to enhance data reliability and minimize statistical uncertainty.
- *Report Statistical Uncertainty*: Report errors from regression analysis and triplicate experiments to convey the reliability of calculated thermodynamic values.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02526.

Experimental details and characterization data (PDF)

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The authors declare no competing financial interest.

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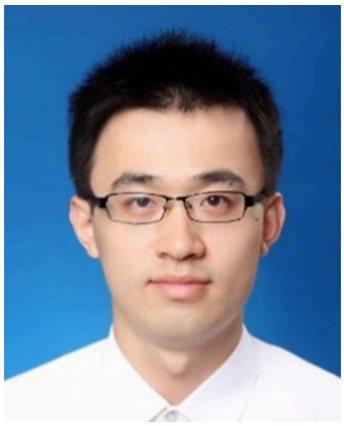

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