# Thermodynamic Presynthetic Considerations for Ring-Opening Polymerization

Peter Olsén, Karin Odelius, and Ann-Christine Albertsson*

Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

S *Supporting Information*

ABSTRACT: The need for polymers for high-end applications, coupled with the desire to mimic nature's macromolecular machinery fuels the development of innovative synthetic strategies every year. The recently acquired macromolecular-synthetic tools increase the precision and enable the synthesis of polymers with high control and low dispersity. However, regardless of the specificity, the polymerization behavior is highly dependent on the monomeric structure. This is particularly true for the ring-opening polymerization of lactones, in which the ring size and degree of substitution highly influence

the polymer formation properties. In other words, there are two important factors to contemplate when considering the particular polymerization behavior of a specific monomer: catalytic specificity and thermodynamic equilibrium behavior. This perspective focuses on the latter and undertakes a holistic approach among the different lactones with regard to the equilibrium thermodynamic polymerization behavior and its relation to polymer synthesis. This is summarized in a monomeric overview diagram that acts as a presynthetic directional cursor for synthesizing highly specific macromolecules; the means by which monomer equilibrium conversion relates to starting temperature, concentration, ring size, degree of substitution, and its implications for polymerization behavior are discussed. These discussions emphasize the importance of considering not only the catalytic system but also the monomer size and structure relations to thermodynamic equilibrium behavior. The thermodynamic equilibrium behavior relation with a monomer structure offers an additional layer of complexity to our molecular toolbox and, if it is harnessed accordingly, enables a powerful route to both monomer formation and intentional macromolecular design.
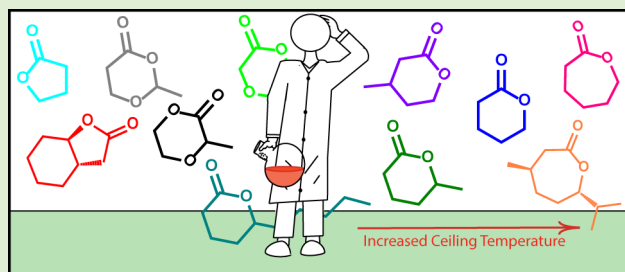
■ INTRODUCTION

A long-sought dream within the polymer community is to acquire the ability to create materials that mimic nature's control and refinement. Within this, the struggle is to synthesize not only polymers with perfect control over the monomeric sequence and supramolecular assembly behavior, but also materials with predetermined mechanical and degradation properties. To achieve this, it is important to keep in mind that all polymers in nature are not perfect. When the demand is for very selective processes, such as species-specific enzymes, the correct assembly behavior and exact monomeric sequence plays a key role. Although in terms of mechanical performance and selective degradation behavior, dispersity and disruption of the monomeric sequence are critical factors.

A perfect example of selective degradation behavior can be seen in the buildup of the plant cell wall, constituted mainly of three different polymeric components: cellulose, lignin, and hemicellulose. These polymeric components have very different dispersity, hydrophobicity, crystallinity, hydrolyzable groups and, thus, degradation behavior, ordered in a fashion that meets the "desired application". Although, natural polymers are not suited for all applications; hence, there is a need for the ability to create these types of materials synthetically.

In this sense, synthetic aliphatic polyesters are perfect candidates; they encompass numerous different polymer types with different degradation modes and degradation products and hence are suited for a wide range of applications.[1−4] In addition, their synthesis is possible with an array of different polymerization methodologies and catalytic systems.[5−8] There are many ways to synthesize degradable polymers, though the different synthetic strategies can be summarized as either stepwise or through chain growth.

The synthesis of degradable aliphatic polyesters through stepwise polymerization started to appear in the scientific literature in the late 1920s in work by Carothers et al.[9] Stepwise polymerization enables the synthesis of a wide range of degradable polymers whose properties are easily tailored by varying the starting mixture.[10−12] The inherent mechanistic features require high conversion and long reaction times to reach high molecular weight, leading to highly dispersed polymers. In addition, the relation with long reaction times and high molecular weight severely hampers the industrial applicability, in which the amount of material per unit time is important.

In this respect, chain growth polymerization offers an advantage by enabling high control over both the polymer structure and rate of polymerization. The most commonly applied chain growth methodology toward aliphatic polymers include ring-opening polymerization (ROP) of a heterocyclic monomer—e.g., lactone or ketene acetal. The employed catalytic system dictates both the rate of polymerization and control over the macromolecular structure, thus making it possible to achieve more refined macromolecular architectures, such as star-shaped,[13−15] branched,[16,17] as well as statistical[18,19] and block copolymers.[20−22]

Depending on the catalytic system, different degrees of activation with either the monomer or propagating chain end are obtained.[23,24] An example of this is the difference in ROP behavior between ε-caprolactone (εCL) and L-lactide (LLA). Cationic ROP with diphenyl phosphate (DPP) proceeds with good control at a moderate rate in the case of εCL, whereas poor control is seen for LLA. Whereas, the reversed trend is observed for the anionic catalyst, 1,8-diazabicycloundec-7-ene (DBU).[25−27] Hence, the mode of activation, both monomeric and chain-endwise, are crucial factors for archiving good ROP behavior of the selected monomer. Although, independent of the degree of symbiosis with the catalytic system, the structure of the monomer has a large impact on the polymerization behavior, e.g., some monomers achieve high conversion at high temperatures, whereas others struggle to obtain merely moderate conversion at ambient temperatures. In other words, there are two crucial aspects to consider when examining the polymerization behavior of a specific monomer, what catalytic system yields the best control, i.e., dispersity and rate of polymerization, and how the monomeric structure influences the polymerization equilibrium behavior.

We have a long history in the synthesis of degradable polymers through both stepwise and chain growth polymerization with a large emphasis on the whole lifecycle perspective of the material.[28−30] The initial focus was placed on condensation polymerization of esters and anhydrides,[31,32] followed by more elaborate construction of clearly defined polymers through ROP of different heterocyclic monomers under different catalytic systems.[33−35] This has yielded a solid understanding of the difference in polymerization behavior of a wide range of monomers and understanding of the dominating monomeric factors that govern its equilibrium polymerization behavior.

Even though the influence of the monomeric structure on polymerization equilibrium is independent of class of heterocycle, in light of clarity, this Perspective will only focus on ROP of lactones. The main question raised and addressed is how the difference in concentration, size, and degree of substitution will affect the equilibrium polymerization behavior of the lactone. Our aim is to develop a presynthetic protocol for ROP of lactones that facilitates the intentional design of both monomeric and polymeric structure and attributes. This is taken from the vantage point of the practical polymer chemist and emphasizes how temperature and concentration can be used to tailor the macromolecular structure and utilized to obtain the desired monomer. The motivation is that this will provide a logical division among the different monomers, not only as a matter of size but also depending on the thermodynamic equilibrium polymerization behavior.

■ THERMODYNAMICS OF EQUILIBRIUM CHAIN GROWTH POLYMERIZATION

Fundamentally, a chemical reaction can be viewed from the change in Gibbs free energy upon transformation (eq E-1): if $\Delta G < 0$, the reaction is favored, whereas if $\Delta G > 0$, the reaction is disfavored, and the same is of course true for polymers. The magnitude of ΔG will entail not how fast the reaction will occur but rather the lowest energy state. Depending on the catalytic system, different routes through the transition states are realized, although this will not change the fundamental features of the system.

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (E\text{-}1)$$

The polymerization equilibrium behavior between lactones of different sizes can be visualized in the magnitude of Gibbs free energy of polymerization (ΔG_p) at 25 °C (Figure 1 and eq
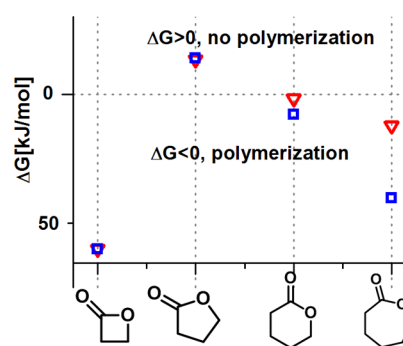
Figure 1. Difference in ΔG as a function of ring-size at normal pressure and at 25 °C; blue squares[36] and red triangles[37] represent different extracted values from the literature.

E-1). The topic concerning the thermodynamics of chain growth polymerization has been covered numerous times in the scientific literature, but the practical consequence of substitution is often overlooked and is usually only summarized to reduce the polymerization ability of the monomer.[38−40]

The thermodynamic description of equilibrium polymerization started to appear in the scientific literature in the late 1940s, as an observatory response to the peculiar copolymerization behavior between sulfur dioxide and olefins. Herein, Snow and Frey observed that as the reaction temperature increased, the rate of polymerization decreased, eventually, dependent on the type of olefin, reaching a temperature were no reaction occurred, this temperature was coined as the "ceiling temperature".[41] The fundamental thermodynamic description behind this was explained by Dainton and Irvin, who concluded that this phenomenon was independent of the catalytic system but dependent on the monomer concentration,[42−44] leading to the development of the more familiar Dainton's equation, eq E-2. Dainton's equation states that at the equilibrium point, i.e., when $\Delta G_p = 0$, there is a critical temperature, referred to as the ceiling temperature (T_c) or floor temperature (T_f), depending on the thermodynamic features of the polymerization. At this point, no conversion of monomer to polymer is obtained.

$$T = \frac{\Delta H_p}{\Delta S_p + R\,\ln([M])_{eq}} \qquad (E\text{-}2)$$

The Ceiling Temperature, T_c. Historically, the existence of T_c was described from the basis of a physical aggregation

Table 1. Thermodynamic Polymerization Properties between Different γ-Lactones

Monomeric structure	Abbreviation	State Transition[*]	Setup	ΔH_p [kJmol^{-1}]	ΔS_p [JK^{-1}mol^{-1}]	T_c [°C]	T_{eq} [°C]	Ref.
	γBL	l-c	Bulk (~ 13 M)	-5.7	-19.3	22	-46	52
	γBL	s-s	1 M	-5.7	-39.9	-131	-149	52
	T6L	l-c	Bulk (~ 6 M)	-23.5[a]	-65	89	55	53
	T6L	s-s	1 M	-23.5[a]	-80	21	1	53

[*]For detailed description see Supporting Information Table S-1.

process, e.g., the freezing point of a liquid to a solid, in which the solid was analogous to the polymer, the liquid was analogous to the monomer, and the freezing point was denoted as the ceiling temperature.[38,42] Despite the colorful analogy, more recent understanding regards the T_c phenomenon as a second-order transition.[45,46]

The current IUPAC definition of T_c is as follows: "T_c is the temperature at or above which the concentration of monomer in equilibrium with its polymer becomes essentially equal to the initial monomer concentration".[47] The T_c value of the system is highly dependent on the starting monomer concentration. Because most monomers have very different molecular weights and densities, they will have very different bulk concentrations. In light of this, it is advised that the equilibrium polymerization experiments be conducted at a concentration of 1 M, expressed as ΔS_p^0.[38,48] Although, it is possible to relate change in concentration solely as a change in ΔS_p. This makes it possible to extrapolate the equilibrium features of the polymerization at different concentrations, something commonly seen in the scientific literature (see Supporting Information [**SE-1**]). Of course, this assumes that the strain of the ring is independent of the concentration and solvent, which is not completely true. In fact, depending on the monomer, there will be different interactions with the surrounding solvent, as a function of both solvent polarity and concentration. This in turn will influence the strain of the ring as well as the entropy of polymerization that will impact the equilibrium monomer conversion. Although, at this point, research that systematically addresses these questions is lacking, and in light of clarity we are obliged to adhere to the assumption that the strain of the ring is independent of both the solvent and concentration.

$$\ln\left(\frac{n_m}{n_0}\right) = \frac{\Delta H_p}{R \cdot T} - \frac{\Delta S_p}{R}$$
(E-3)

From a practical polymer synthetic mindset, the magnitude of T_c is trivial without understanding how this will influence the

equilibrium monomer conversion. Fortunately, it is possible to express Dainton's equation as a function of equilibrium molar fraction and conversion rather than equilibrium monomer concentration (see Supporting Information [SE-2]), meaning we are able to explore other equilibrium conversion temperatures. The anticipated conversion of the monomer is dependent on the intrinsic thermodynamic equilibrium features of the polymerization, ΔH_p and ΔS_p, as a function of temperature. For example, synthetically, it may be interesting to know the equilibrium temperature (T_{eq}) when the conversion of monomer to polymer is 50% complete; hence, when $n_m = n_p$, this makes it possible to express eq E-3 as eq E-4.

$$\ln\left(\frac{\frac{1}{2}n_0}{n_0}\right) = \frac{\Delta H_p}{R \cdot T_{eq}} - \frac{\Delta S_p}{R} \rightarrow T_{eq} = \frac{\Delta H_p}{\Delta S_p + R \cdot \ln\left(\frac{1}{2}\right)}$$
(E-4)

Ring-Size and Thermodynamic Polymerization Behavior. Depending on the ring size and degree of substitution, the lactone monomers can exhibit very different polymerization behaviors. This has its origin in the thermodynamic equilibrium polymerization features of the ring; for smaller lactone rings, 4−7-membered, the polymerization is disfavored by an increase in temperature in contrast to many of the larger rings. In other words, the difference in ring size has a fundamental effect on both the sign and magnitude of ΔH_p and ΔS_p.[37] The total strain of a monomer is dependent on three different factors: angle, conformation, and repulsion strain.[49] Smaller lactone monomers are sufficiently strained to drive the monomer toward polymer formation, obviously in connection with a proper catalyst, indicated by a negative ΔH_p, followed by an increased order of the system, indicative of a negative ΔS_p. When the magnitude of the "increased order of the system," $T\Delta S_p$, upon polymerization outweighs the ring strain, ΔH_p, the temperature reached is T_c; this is opposed to larger rings, with more than 9 atoms in the ring, which exhibit the inverse temperature relation.[50]

■ DIFFERENCE IN POLYMERIZATION BEHAVIOR OF LACTONES

There has been a tremendous amount of work regarding the ROP of lactones in terms of both application and synthesis. However, compared with the development of new catalytic systems, scarce results cover the underlying thermodynamic equilibrium polymerization behavior of the monomer investigated. In addition, the kinetic data that are presented are not sufficient to pinpoint whether the polymerization reaches its equilibrium monomer conversion. If low equilibrium conversion is observed, it is often attributed to the low strain of the monomer. The strain of the monomer does not entail anything without knowledge of the entropic change upon polymerization. Hence, even more vital is the strain of the monomer relation to the increased order of the system upon polymerization.

γ-Lactones. The *γ*-lactones are a unconventional class of monomers, because most members' thermodynamic equilibrium polymerization features hinder them from being converted into homopolymers at normal polymerization temperatures (Table 1). The exception is if the polymerizations are not conducted at 20 000 bar,[51] which enables alteration of the thermodynamic features of the system, hence permitting polymerization or, more specific to this case, oligomerization. The traditional view on the T_c for $γ$BL is a value below absolute zero; of course, this value should not be considered an absolute truth but rather a relative value of the monomers' propensity to polymerize. In fact, resent results cast doubt on this low value. Inspiring work by Chen et al. showed that it was possible to actually obtain homopolymerization of $γ$BL at a concentration of 10 M in THF when conducting the polymerization at −40 °C.[52] However, whether this is due to the difference in solvent polarity to the monomer or an inherent thermodynamic feature of the monomer remains elusive.

There are other reports on the homopolymerization of specific diastereomers of a cyclohexane-substituted $γ$-butyrolactone. The orientation of the specific diasteromer exerts sufficient strain on the ring to enable polymerization, with T_c (bulk) = 89 °C and T_{eq} (bulk) = 55 °C (Table 1).[53] If we approximate the polymerization behavior at 1 M concentration, a very different polymerization behavior arises at standard concentration, i.e., T_c (1 M) = 21 °C and T_{eq} (1 M) = 1 °C (see Table 1 and Figure 2).
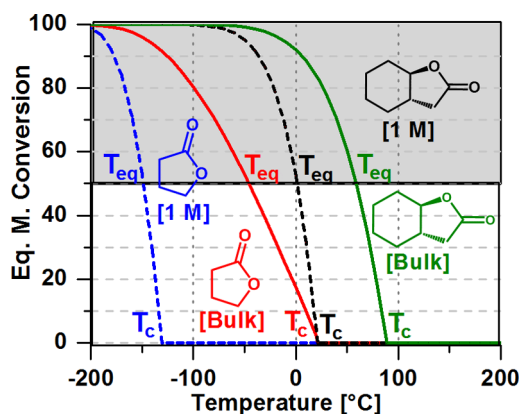
Figure 2. Change in equilibrium monomer conversion as a function of temperature during the polymerization of T6 L and $γ$BL.

Fortunately, even though there are few reports on homopolymers from $γ$-lactones, they are not excluded as monomers in the synthesis of polymers at conventional polymerization temperatures. The solution is to use the $γ$-lactones as comonomers with a monomer with a high T_c.[54−57] It is important to consider that above the temperature of T_c, there is not a conclusively dead system.[58−61] There will be a constant interchange between the kinetic and thermodynamic regimes of polymerization, meaning that there will be the formation of ring-opened monomers, even though it is thermodynamically forbidden.[63−66] This enables a very versatile route for obtaining functional polylactones by using this class of compounds as comonomers.[62−64]

δ-Lactones. *δ*-Lactones encompass numerous different monomers that cover many different applications. The inherent thermodynamic equilibrium polymerization behavior of this class of monomers—or, more specifically, the substituted and heteroatomic $δ$-lactones—is often highlighted for their low to moderate conversions at conventional polymerization conditions. The first known ROP of these monomers was reported in the early 1930s, for which Carothers et al. described the transformation of $δ$-valerolactone to a waxy solid. In the same report, he also investigated the polymerization behavior of a substituted six-membered lactone, $α$-propyl-$δ$-valerolactone, for one month at 80 °C, and no signs of increased viscosity were observed.[65] There were no concluding remarks on the nature of this behavior, which is probably due to the insufficient knowledge of the equilibrium polymerization behavior of different monomers in that era of science. By contrast, the answer is currently fairly straightforward and is related to the means by which the substituent affects the enthalpy and entropy of polymerization. The extent of this effect is still unclear, as is the identity of the most influencing contribution, enthalpy or entropy. The next section aims to clarify these questions by a deeper investigation of how the addition of a substituent or heteroatom will translate into a difference in polymerization behavior.

Substituted *δ*-Lactones. Several reports have shown that the equilibrium monomer conversion of substituted $δ$-lactones decreases with the addition of a larger substituent at the same polymerization temperature. More precisely, under polymerization conditions of 1 M concentration in toluene of different substituted $δ$-valerolactones, a decrease in equilibrium conversion with increasing size of the substituent was observed. In addition, when the polymerizations were performed in bulk, the equilibrium conversion increased.[66] The different substituted $δ$-valerolactones were derived from $α$,$β$-unsaturated $δ$-valerolactone through Michael addition with a thiol and displayed a highly versatile route from a monomer diversification perspective. However, the addition of a substituent at the $β$-position severely reduces the equilibrium monomer conversion, even though continued work regarding this monomer and others are still reported in the literature.[67−69] These results are directly related to the work by Matsuo et al. in the late 1990s, which observed the same trend regarding cyclic six-membered carbonates substituted on the 2-position.[70] In summation, when aiming for a specific monomeric structure, it is important to carefully presynthetically consider the influence of the substituent on the equilibrium polymerization behavior.

There are reports that more closely investigate the equilibrium behavior of the respected substituted $δ$-lactones (Table 2). In the literature, it is often regarded that a reduction of equilibrium monomer conversion is due to a decrease in the

Table 2. Thermodynamic Properties between Different Substituted δ-Lactones

| Monomeric structure	Abbreviation	State Transition[*]	Setup	ΔH_p [kJmol^{-1}]	ΔS_p [JK^{-1}mol^{-1}]	T_c [°C]	T_{eq} [°C]	Ref.
	δVL	l-c′	Bulk (~ 10 M)	-12.2	-9.5	1018	530	36
	δVL	s-s	1 M	-12.2	-28.6	155	83	36
	δCL	l-c	Bulk (~ 8.7 M)	-13.8	-23.2	322	204	36
	δCL	s-s	1 M	-13.8	-41.3	62	21	36
	βMeδVL	l-c	Bulk (~ 8.7 M)	-14.3	-28.5	228	144	71
	βMeδVL	s-s	1 M	-14.3	-46.5	34	0	71
	δDL	l-c	Bulk (~ 5.6 M)	-20	-48.2	141	97	72
	δDL	s-s	1 M	-20	-62.5	46	19	72

[*]For details, see Supporting Information Table S-1.

strain of the ring in relation to the unsubstituted analogues. In Table 2, we can clearly observe that this statement is far from true. As the length of the substituent at the δ-position is increased from 0 to 1 to 5 (δVL, δCL, δDL), the strain of the ring is also increased. The trend is as follows: increases from δVL = −12.2 kJ/mol to δCL = −13.8 kJ/mol to δVL = −20 kJ/mol (Table 2). Interestingly, the strain of the ring seems to be only marginally affected by its position on the ring (comparing δCL and βMeδVL; Table 2). This means that the difference in equilibrium polymerization behavior is more closely related to the substituent influence on the relation of ΔS_p with ΔH_p.

The increased order of the system upon polymerization will finally outweigh the ring strain, making the transition from monomer to polymer thermodynamically disfavored. For different substituted δ-lactones at standard polymerization conditions of 1 M, the longer the substituent, the greater the ΔS_p^0 value: δDL = −62.5 J/mol*K, δCL = −41.3 J/mol*K, and δVL = −28.6 J/mol*K (Table 2). This behavior is in close

relation to the Thorpe−Ingold effect, in which the increased degree of substitution leads to increased rate of cyclization.[73,74] In the same way, as the length or number of substitutions increases, the relational value between ΔH_p and ΔS_p decreases, thus reducing the equilibrium monomer conversion. However, the degree is strongly related to the starting concentration of the monomer upon polymerization.

When performing ring-closing reactions, it is advisable to perform the reaction in a dilute system if possible; one suggested reason for this is that this will reduce the probability of dimerization of the difunctional reactant, additionally making perfect sense from the perspective of equilibrium polymerization. As we increasingly dilute the system, the disorder of the system increases, giving the entropic contribution in relation to enthalpically larger values from bulk to 1 M, e.g., (δVL, bulk) = 9.5 J/mol*K and (δVL, 1 M) = 28.6 J/mol*K (Table 2), thus favoring ring closure. This is seen for the homopolymerization of εDL, in which a change in polymerization concentration at
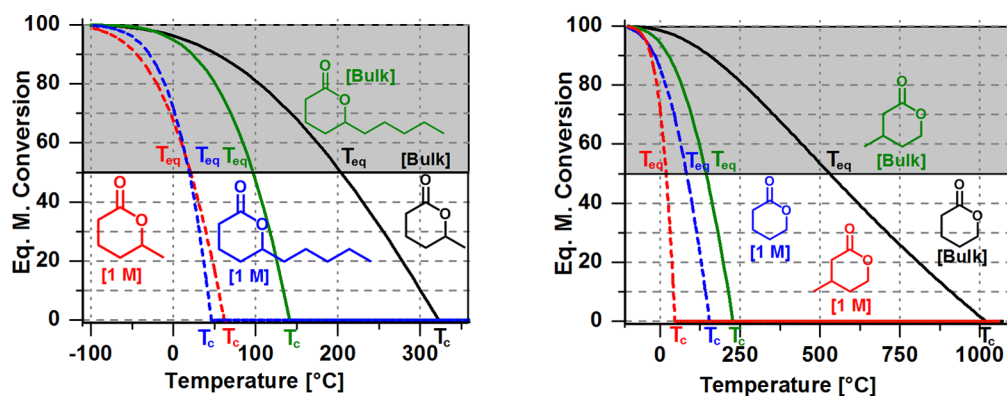
Figure 3. Depiction of how the equilibrium monomer conversion is affected for of δDL, δCL, βMe-δVL, and δVL, through change in temperature and concentration during polymerization.

**Table 3. Thermodynamic Properties between Different Ether-δ-lactones**

Monomeric structure	Abbreviation	State Transition[*]	Setup	ΔH_p [kJmol^{-1}]	ΔS_p [JK^{-1}mol^{-1}]	T_c [°C]	T_{eq} [°C]	Ref.
	PDX	l-c′	Bulk (~ 12 M)	-15.7	-28.9	271	180	[78]
	PDX	s-s	1 M	-15.7	-49.7	43	30	[78]
	αMe-PDX	l-c	Bulk (~ 10 M)	-9.9	-20.1	216	108	[82]
	αMe-PDX	s-s	1 M	-9.9	-41	-32	-62	[82]
	MDO	l-c	Bulk (~ 10 M)	-10.9	-29.6	95	35	[83]
	MDO	s-s	1 M	-10.9	-41	-57	-79	[83]

[*]For a detailed description, see Supporting Information Table S-1.

ambient conditions form 1.5 to 3.5 M resulted in equilibrium monomer conversions of 6 and 80%, respectively.[75]

Under the assumption that the ring strain is independent of the concentration, it is possible to use the thermodynamic equilibrium polymerization features, i.e., ΔS_p and ΔH_p, to predict the equilibrium monomer conversion as a function of temperature (Figure 3).[76] An increase in concentration leads to a wider temperature range below T_c and hence a larger temperature range that favors polymerization. In addition, the smaller the substituent, e.g., δVL and δDL, the more pronounced this effect. This is due to the smaller molecule and higher density enabling a higher concentration in the bulk state, making it possible to reach a higher concentration, resulting in a further reduction of ΔS_p. In addition, Figure 3
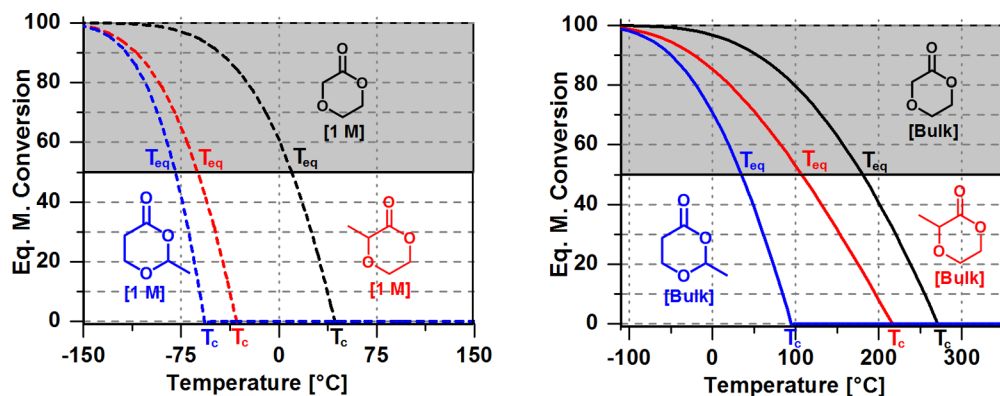
Figure 4. How the equilibrium monomer conversion is affected for MDO, αMe-PDX, and PXO through change in temperature and concentration during polymerization: bulk (left) and 1 M (right).

clearly visualizes how the larger substituent significantly reduces the temperature range for polymer formation; this is exemplified in the difference in T_c of the monomers, where T_c (βMeδVL, 1 M) = 34 °C, T_c (δDL,1 M) = 46 °C, T_c (δCL,1 M) = 62 °C, and T_c (δVL,1 M) = 155 °C. The longer the substituent is—and, hence, the larger the size of the monomer—the lower the concentration in bulk and, thus, the reduction in T_c.

Ether-δ-lactones. The ether-δ-lactones are cyclic monomers that, in addition to the lactone group, also consist of an ether structure in the ring. The presence of an ether group in the ring implies certain properties of the polymers, e.g., increased hydrophilicity and flexibility. Among these monomers, particular interest has been placed on p-dioxanone (PDX) as a monomer for biomedical applications, mainly because of the aforementioned properties.[77] The reversible nature of PDX has been extensively studied by several different groups with different catalytic systems, ranging from enzymes to transition metals.[78−80] In addition, the PDX monomer offers a perfect example of the importance of the aggregation state transformation during polymerization (poly(PDX) is a semicrystalline polymer), meaning that when the polymerization is conducted under T_m [T_m(poly(PDX)) = 110 °C], there will be an extra driving force that increases the monomer conversion.[78,79] This effect is the same for all semicrystalline polymers but mostly relevant when the monomer has a moderately high T_{eq} as is the case for T_{eq} (Bulk, PDX) = 180 °C.

The strain of the ring among ether-δ-lactones seems to be more or less in the same magnitude as the δ-lactones (Tables 2 and 3). Although, their relation with the addition of a substituent is reversed, e.g., when comparing δVL (ΔH_p= −12.2 kJ/mol) and βMeδVL (ΔH_p= −13.8 kJ/mol) (Table 3), with PDX (ΔH_p= −15.7 kJ/mol) and αMe-PDX (ΔH_p= −9.9 kJ/mol). One possible explanation is that the added substituent of αMe-PDX reduces the strain of the ring by placing the ether bond at a more preferable angle. This same logic would also explain the reversed strain-substituent relation of the substituted δ-lactones.[81] In this case, the bond angles of the unsubstituted δ-lactones are already at a somewhat preferred angle, meaning that the addition of a substituent implies more strain on the ring.

Although the difference in ΔH_p and ΔS_p between the ether-δ-lactones and δ-lactones are at the same magnitude, they have very different T_c values (Tables 2 and 3). The large difference in T_c is due to the small change in the relation of ΔH_p and ΔS_p

between the ether-δ-lactones and δ-lactones. In general, there is a larger ΔS_p value for the ether-δ-lactones compared with the δ-lactones, which is believed to originate from the increased flexibility of the ether group in the ring. At the bulk concentration, the ΔS_p value is similar to that of the δ-lactones. The equality in bulk is due to the higher density of ether-δ-lactones that enable higher concentration, thus reducing the entropic contribution. In summation, the strain trend of the ether-δ-lactones is different from that of the δ-lactones with the substituent, resulting in a relatively larger ΔS_p value, which consequently increases the equilibrium monomer conversion.

An approximation of the equilibrium monomer conversion of the ether-δ-lactones with temperature reveals the effect of the higher entropic contribution of the ether-δ-lactones in relation to the δ-lactones (Figures 3 and 4) resulting in an overall lower equilibrium monomer conversion. In other words, the addition of a heteroatom in the lactone ring of the δ-lactones results in monomers with an intermediate thermodynamic polymerization equilibrium behavior whose polymerization properties lie on the borderline between γ and δ-lactones.

ε-Lactones. The thermodynamic equilibrium polymerization behavior of the ε-lactones has not received an equal amount of attention as the δ-lactones. This is because the reversible nature of the monomers is not as easily recognized, meaning that most ε-lactones reach high conversion at standard polymerization concentrations and temperatures. Examples of the clear difference can be seen when comparing PDX with the ε-lactone counterpart, 1,5-dioxepan-2-one (DXO).[33,84] DXO readily polymerizes to high conversion both in dilute systems[85,86] and at high temperatures,[87] whereas these factors have a large impact on the equilibrium polymerization behavior of PDX.[78−80] Likewise, the same trend is seen when comparing the polymerization behavior of δDL with T_c (bulk) = 141 °C,[72,75] to ε-decalactone (εDL) that reaches high conversion (>90%), even at 150 °C.[88,89] Interestingly, an outlier in the ε-lactone family is 2,3-dihydro-5H-1,4-benzodioxepin-5-one (2,3-DHB), an α,β-benzene fused DXO that shows an clearly detectable equilibrium monomer conversion, as well as reformation of the monomer with lowered concentration.[90]

When comparing the difference in polymerization behavior between the ether-δ-lactones and δ-lactones and their ε-lactone counterparts—more specifically, the equilibrium polymerization behavior of PDX and δDL to DXO and εDL, respectively—a clear trend arises. The equilibrium polymerization features of the ε-lactones, DXO and εDL, enables high conversion at conventional reaction temperatures, making it

Table 4. Thermodynamic Polymerization Behavior between Different ε-Lactones

Monomeric structure	Abbreviation	State Transition	Setup	ΔH_p [kJmol^{-1}]	ΔS_p [JK^{-1}mol^{-1}]	T_c [°C]	T_{eq} [°C]	Ref.
	εCL	l-c′	Bulk (~ 8.7 M)	-28.8	-35.9	530	419	[37]
	εCL	s-s	1 M	-28.8	-53.9	261	210	[37]
	βMe-ε-iPr-εCL	l-c	Bulk (~ 5.6 M)	-18.6	-18.7	718	485	[91]
	βMe-ε-iPr-εCL	s-s	1 M	-18.6	-33,1	289	205	[91]

straightforward to synthesize, e.g., diblocks,[92−94] triblocks,[95] and stars,[87,96] etc., in contrast to the δ-lactones, in which sequential addition at moderate equilibrium conversion leads to unspecified block structures. The difference is that thermal equilibrium behavior is also reflected in their difference in thermal degradation properties; specifically, δDL has a thermal degradation onset approximately 200 °C below that of εDL.[88,97] Thermal degradation can occur through many different mechanisms; however, the low T_c of δDL would favor ring-closing unzipping of the chain under increased temperatures. There are additional examples of highly substituted ε-lactones that reach high conversions under demanding synthetic circumstances such as high temperature and low concentration, underlining the pronounced difference to the δ-lactone.[98,99]

The high conversion at moderate reaction temperatures makes it difficult to recognize the reversible behavior of ε-lactones, additionally and obviously making this knowledge less important when looking for specific material properties, such as adhesives and elastic thermosets.[100,101] Luckily, there are some reports regarding the thermodynamic polymerization features of the ε-lactones, namely, ε-caprolactone and a highly substituted ε-lactone, βMe-ε-iPr-εCL. There are examples of the high equilibrium monomer conversion of ε-lactone with bulky substituents.[102−104] The underlying cause of this is the high strain of the ε-lactones' seven-membered motif (Table 4). More precisely, the strain of εCL (ΔH_p = −28.8 kJ/mol) is more than 2 times higher than that of the δ-lactone analogue, δVL (ΔH_p = −12.2 kJ/mol) (Table 3), though the polymerization of εCL is accompanied by a relatively larger entropic increase: ΔS_p (εCL, 1 M) = −53.9 J/mol, ΔS_p(δVL, 1 M) = −28.6 J/mol. Again, it is more relevant to look at the ratio between ΔS_p and ΔH_p rather than their respective parts because both factors will influence the equilibrium polymerization behavior.

The high strain of the ε-lactones is reflected in the equilibrium monomer conversion with temperature (Figure

5). Even at 1 M concentration, both βMe-ε-iPr-εCL and εCL have a high T_c value (289 and 261 °C, respectively; Table 4).
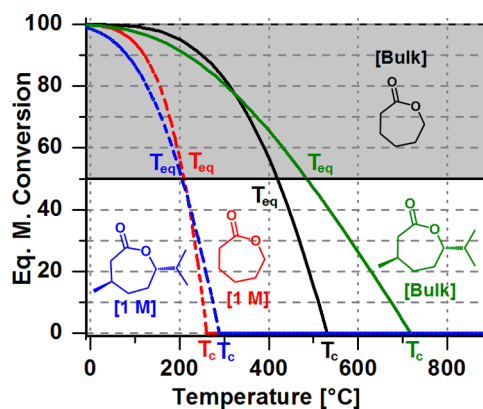
Figure 5. How the equilibrium monomer conversion is affected for βMe-ε-iPr-εCL and εCL through change in temperature and concentration.

The validity of the theoretical values at bulk conditions are questionable, and other reactions at elevated temperatures can occur; e.g., during thermal degradation of εCL, larger rings have been observed.[105] In the same way, at the high T_c value for β-propiolactone at 1115 °C, it is very improbable without favoring other ring-structures such as the more stable 12-membered ring prior to disintegration of the chemical bonds or combustion of the polymer.[36] Hence, it is important to remember that a high T_c value is merely a theoretical construction indicative of the equilibrium conversion behavior of the monomer to polymer but does not entail equilibrium between different-sized rings or thermal degradation. Nevertheless, this value still indicates whether the monomer transition polymer is favored or disfavored in terms of the thermodynamics of polymerization.
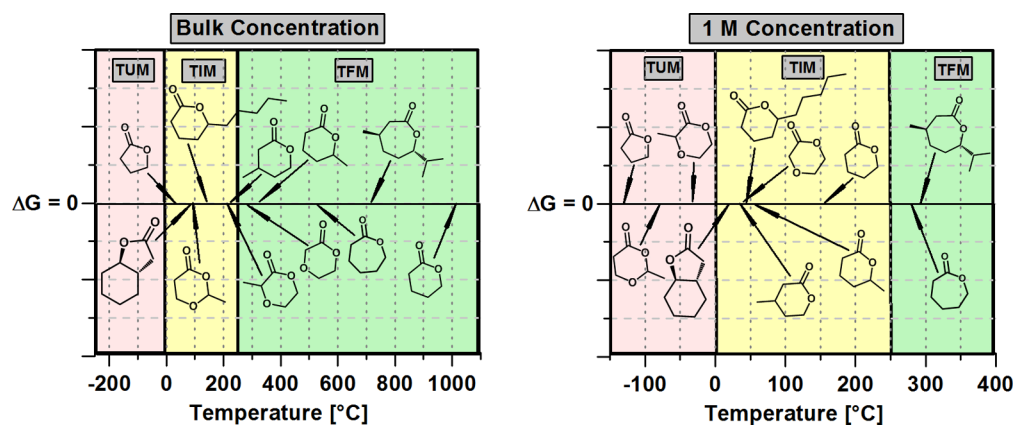
Figure 6. A division among the different monomers that reflects their thermodynamic behavior; the divisions are based upon a T_c interval in which the monomer is one of the following: Thermodynamic **U**n-favored **M**onomers (**TUM**), $T_c \leq 0$ °C; Thermodynamic **I**ntermediate **M**onomers (**TIM**), 0 °C $\leq T_c \leq 250$ °C or Thermodynamic **F**avored **M**onomers (**TFM**), $T_c \geq 250$ °C, and how this relates to change in concentration: bulk (left) and 1 M (right).

■ CONCLUSIONS AND FUTURE PERSPECTIVES

The ring size, addition of heteroatoms, and degree of substitution has a large influence on the thermodynamic equilibrium polymerization behavior of lactone. The strain of the ring should not be considered as the main factor that drives the monomer toward the polymer; in fact, it is found that a larger substituent inflicts larger strain on the ring even though the lactone suffers an overall decrease in equilibrium monomer conversion. This is due to the relative increase in entropy associated with a larger substituent. Hence, to fully characterize a lactone's propensity to undergo ROP, both of these factors must be considered. In light of this, we propose another way of looking at the different monomers, not as a matter of size but solely from the thermodynamic equilibrium polymerization behavior. The ceiling temperature (T_c) is the highest temperature at which it is possible to form a polymer with high molecular weight. T_c encompasses both the enthalpy and entropy of polymer formation and is independent of the catalytic system employed but dependent on concentration (Figure 5). Hence, a preselected T_c value will act as an independent way to describe each monomer's relation. The proposed intervals are as follows: Thermodynamic **U**n-Favored **M**onomers (**TUM**), $T_c \leq 0$ °C; Thermodynamic **I**ntermediate **M**onomers (**TIM**), 0 °C $\leq T_c \leq 250$ °C; Thermodynamic **F**avored **M**onomers (**TFM**), $T_c > 250$ °C. The division is made from the perspective of practical synthesis and how it translates into different synthetic behaviors. It is important to consider that this interval does not emphasize that the polymerization is conducted at this temperature but rather that the polymerization, if near to full conversion is desired, should be performed far below the T_c value of the monomer.

The **TFMs** are in many ways the ideal monomers for polymer synthesis, in which the monomeric state may be referred to only as an intermediate to the polymeric. This does not entail how fast this reaction will occur but rather what is the most favored state. In fact, many δ-lactones exhibit higher rates of polymerization than ε-lactones, though the latter has a higher T_c value.[14,26,106] This emphasizes that polymerization behavior, e.g., the rate of polymerization, dispersity control, is a different entity than the thermodynamic behavior of the polymerization. The **TFMs** are ideal when aiming at more refined macromolecular structures, such as sequential block copolymers, under the prerequisite that the catalyst employed has a low

degree of side reactions. Additionally, this class of monomers tolerates extensive monomeric alteration and still maintains a high equilibrium monomer conversion.

For **TIMs**, the polymer to monomer equilibrium is easily altered by temperature and concentration. At times, this may be considered as a drawback; but, when harnessed, it provides a powerful methodology for monomer synthesis[107−109] and control over the macromolecular structure.[110,111] Key factors to contemplate with regard to **TIM** involve the equilibrium conversion of the specific monomer at this temperature and concentration, that is, if the desired macromolecule is in the form of pure block copolymers or as a sequential tapered polymer.

TUMs as a monomeric species are highly unfavored with regard to the transition into the polymeric state, although this does not render this class useless in the synthesis of polymers. The ability to transition is possible when used as a commoner together with a **TIM** or **TFM**. It is important to note that the position of a monomer on the T_c scale is very dependent on the concentration of the system. Hence, a monomer that resides in the **TIM** area at bulk conditions may fall in the **TUM** area when diluted (Figure 6). The practical consequence of this is that the condition employed for both monomer formation and polymer formation must be considered carefully. In addition, new routes must be provided for polymer recycling.

The developed classification is meant to provide a clear and concise way to describe the equilibrium polymerization behavior of different monomers in relation to each other. The different definitions would not only encompass the lactones but should be applicable to other cyclic monomers, e.g., carbonates, ethers, cycloalkenes, and thiolactones. The preconceived polymerization behaviors of the monomer underline the importance of thoroughly contemplating the synthesis prior to commencing, providing ways to precisely control the conversion of the monomer (concentration or temperature) for tailoring the macromolecular structure— tapered, block, etc.—and the effect of adding different substituents. Our ambition is that this Perspective will provide an overview of important aspects to contemplate prior to commencing polymerization, emphasizing the importance of the underlying thermodynamic features of the monomer. In other words, the catalytic system employed will affect only the transition state of the monomer, but the intrinsic thermody-

namic features of the monomer will affect the entire polymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.5b01698.

> Explanations and equations used for calculating the equilibrium monomer conversion; recalculations of the equilibrium thermodynamic polymerization behavior of the monomers where appropriate data could be extracted from the literature (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: aila@polymer.kth.se; Tel. +46-8-790 82 74; Fax: +46-8-20 84 77.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Chiellini, E.; Solaro, R. *Adv. Mater.* **1996**, *8*, 305.
(2) Gross, R. A.; Kalra, B. *Science* **2002**, *297*, 803.
(3) Albertsson, A.-C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466.
(4) Vert, M. *Biomacromolecules* **2005**, *6*, 538.
(5) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147.
(6) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813.
(7) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalt. Trans.* **2010**, *39*, 8363.
(8) Mespouille, L.; Coulembier, O.; Kawalec, M.; Dove, A. P.; Dubois, P. *Prog. Polym. Sci.* **2014**, *39*, 1144.
(9) Carothers, W. H.; Arvin, J. A. *J. Am. Chem. Soc.* **1929**, *51*, 2560.
(10) Carothers, W. H. *J. Am. Chem. Soc.* **1929**, *51*, 2548.
(11) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(12) Kobayashi, S.; Makino, A. *Chem. Rev.* **2009**, *109*, 5288.
(13) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 319.
(14) Odelius, K.; Albertsson, A.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1249.
(15) Shaver, M. P.; Cameron, D. J. a. *Biomacromolecules* **2010**, *11*, 3673.
(16) Tian, D.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1994**, *27*, 4134.
(17) Trollsås, M.; Löwenhielm, P.; Lee, V.; Möller, M.; Miller, R.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 9062.
(18) Vanhoorne, P.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1992**, *25*, 37.
(19) Keul, H.; Schmidt, P.; Robertz, B.; Höcker, H. *Macromol. Symp.* **1995**, *95*, 243.
(20) Bates, F. S.; Hillmyer, M. a.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science* **2012**, *336*, 434.
(21) Hillmyer, M. A.; Tolman, W. B. *Acc. Chem. Res.* **2014**, *47*, 2390.
(22) Brannigan, R. P.; Walder, A.; Dove, A. P. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2279.
(23) Delcroix, D.; Couffin, A.; Susperregui, N.; Navarro, C.; Maron, L.; Martin-Vaca, B.; Bourissou, D. *Polym. Chem.* **2011**, *2*, 2249.
(24) Dove, A. P. *ACS Macro Lett.* **2012**, *1*, 1409.
(25) Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. a.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574.
(26) Makiguchi, K.; Satoh, T.; Kakuchi, T. *Macromolecules* **2011**, *44*, 1999.
(27) Makiguchi, K.; Kikuchi, S.; Yanai, K.; Ogasawara, Y.; Sato, S.; Satoh, T.; Kakuchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1047.
(28) Albertsson, A.-C.; Ljungquist, O. *Acta Polym.* **1988**, *39*, 95.
(29) Albertsson, A.-C.; Karlsson, S. *Acta Polym.* **1995**, *46*, 114.
(30) Undin, J.; Finne-Wistrand, A.; Albertsson, A.-C. *Biomacromolecules* **2014**, *15*, 2800.
(31) Albertsson, A.-C.; Ljungquist, O. *J. Macromol. Sci., Chem.* **1986**, *23* (3), 411.
(32) Albertsson, A.-C.; Lundmark, S. *Br. Polym. J.* **1990**, *23*, 205.
(33) Mathisen, T.; Albertsson, A.-C. *Macromolecules* **1989**, *22*, 3838.
(34) Albertsson, A.-C.; Sjöling, M. *J. Macromol. Sci., Part A: Pure Appl.Chem.* **1992**, *29*, 43.
(35) Albertsson, A.-C.; Löfgren, A.; Sjöling, M. *Makromol. Chem., Macromol. Symp.* **1993**, *73*, 127.
(36) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.
(37) Duda, A.; Kowalski, A. *Handbook of Ring-Opening Polymerization* **2009**, 1−51.
(38) Dainton, F.; Ivin, K. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(39) Dainton, F. S.; Devlin, T. R. E.; Small, P. A. *Trans. Faraday Soc.* **1955**, *51*, 1710.
(40) Höcker, H.; Keul, H. *Adv. Mater.* **1994**, *6*, 21.
(41) Snow, R. D.; Frey, F. E. *J. Am. Chem. Soc.* **1943**, *65*, 2417.
(42) Dainton, F. S.; Ivin, K. J. *Nature* **1948**, *162*, 705.
(43) Dainton, F. S.; Ivin, K. J. *Proc. R. Soc. London, Ser. A* **1952**, *212*, 96.
(44) Dainton, F. S.; Ivin, K. J. *Proc. R. Soc. London, Ser. A* **1952**, *212*, 207.
(45) Wheeler, J. C.; Kennedy, S. J.; Pfeuty, P. *Phys. Rev. Lett.* **1980**, *45*, 1748.
(46) Greer, S. C. *J. Phys. Chem. B* **1998**, *102*, 5413.
(47) Penczek, S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1665.
(48) Duda, A.; Kowalski, A.; Libiszowski, J.; Penczek, S. *Macromol. Symp.* **2005**, *224*, 71.
(49) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(50) Duda, A.; Kowalski, A.; Penczek, S.; Uyama, H.; Kobayashi, S. *Macromolecules* **2002**, *35*, 4266.
(51) Korte, F.; Glet, W. *J. Polym. Sci., Part B: Polym. Lett.* **1966**, *4*, 685.
(52) Hong, M.; Chen, E. Y.-X. *Nat. Chem.* **2016**, *8*, 42.
(53) Haba, O.; Itabashi, H. *Polym. J.* **2014**, *46*, 89.
(54) Nakayama, A.; Kawasaki, N.; Arvanitoyannis, I.; Aiba, S.; Yamamoto, N. *J. Environ. Polym. Degrad.* **1996**, *4*, 205.
(55) Lee, C.; Urakawa, R.; Kimura, Y. *Macromol. Chem. Phys.* **1997**, *198*, 1109.
(56) Ubaghs, L.; Waringo, M.; Keul, H.; Höcker, H. *Macromolecules* **2004**, *37*, 6755.
(57) Bhaw-Luximon, A.; Jhurry, D.; Motala-timol, S.; Lochee, Y. *Macromol. Symp.* **2005**, *231*, 60.
(58) Nakayama, A.; Kawasaki, N.; Aiba, S.; Maeda, Y.; Arvanitoyannis, I.; Yamamoto, N. *Polymer* **1998**, *39*, 1213.
(59) Duda, A.; Biela, T.; Libiszowski, J.; et al. *Polym. Degrad. Stab.* **1998**, *59*, 215.
(60) Nobes, G.; Kazlauskas, R.; Marchessault, R. *Macromolecules* **1996**, *29*, 4829.
(61) Duda, A.; Penczek, S.; Dubois, P.; Mecerreyes, D.; Jérôme, R. *Macromol. Chem. Phys.* **1996**, *197*, 1273.
(62) Deng, X.; Yao, J.; Yuan, M. *Eur. Polym. J.* **2000**, *36*, 2739.
(63) Olsén, P.; Undin, J.; Odelius, K.; Albertsson, A.-C. *Polym. Chem.* **2014**, *5*, 3847.

(64) Hong, M.; Chen, E. Y. X. *Macromolecules* **2014**, *47*, 3614.

(65) Carothers, W. H.; Dorough, G. L.; van Natta, F. J. *J. Am. Chem. Soc.* **1932**, *54*, 761.

(66) Kim, H.; Olsson, J. V.; Hedrick, J. L.; Waymouth, R. M. *ACS Macro Lett.* **2012**, *1*, 845.

(67) Chen, D.; Chang, C.-C.; Cooper, B.; Silvers, A.; Emrick, T.; Hayward, R. C. *Biomacromolecules* **2015**, *16*, 3329.

(68) Hao, J.; Kos, P.; Zhou, K.; Miller, J. B.; Xue, L.; Yan, Y.; Xiong, H.; Elkassih, S.; Siegwart, D. J. *J. Am. Chem. Soc.* **2015**, *137*, 9206.

(69) Li, X.; Li, H.; Zhao, Y.; Tang, X.; Ma, S.; Gong, B.; Li, M. *Polym. Chem.* **2015**, *6*, 6452.

(70) Matsuo, J.; Aoki, K.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 4432.

(71) Xiong, M.; Schneiderman, D. K.; Bates, F. S.; Hillmyer, M. A.; Zhang, K. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 8357.

(72) Martello, M. T.; Burns, A.; Hillmyer, M. *ACS Macro Lett.* **2012**, *1*, 131.

(73) Wheeler, O. H.; de Rodriguez, E. E. G. *J. Org. Chem.* **1964**, *29*, 1227.

(74) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735.

(75) Zhao, J.; Hadjichristidis, N. *Polym. Chem.* **2015**, *6*, 2659.

(76) Ivin, K. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2137.

(77) Yang, K.-K.; Wang, X.-L.; Wang, Y.-Z. *J. Macromol. Sci., Polym. Rev.* **2002**, *42*, 373.

(78) Nishida, H.; Yamashita, M.; Endo, T.; Tokiwa, Y. *Macromolecules* **2000**, *33*, 6982.

(79) Raquez, J.; Degée, P.; Narayan, R.; Dubois, P. *Macromolecules* **2001**, *34*, 8419.

(80) Dong, F. X.; Xu, C.; Tong, X. Z.; Wang, X. L.; Song, F.; Wang, Y. Z. *J. Mol. Catal. B: Enzym.* **2013**, *96*, 40.

(81) De Lio, A. M.; Durfey, B. L.; Gilbert, T. M. *J. Org. Chem.* **2015**, *80*, 10234.

(82) Lochee, Y.; Jhurry, D.; Bhaw-Luximon, A.; Kalangos, A. *Polym. Int.* **2010**, *59*, 1310.

(83) Neitzel, A. E.; Petersen, M. A.; Kokkoli, E.; Hillmyer, M. A. *ACS Macro Lett.* **2014**, *3*, 1156.

(84) Mathisen, T.; Masus, K.; Albertsson, A. *Macromolecules* **1989**, *22*, 3842.

(85) Löfgren, A.; Albertsson, A.-C.; Dubois, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1994**, *27*, 5556.

(86) Stridsberg, K.; Albertsson, A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1774.

(87) Ryner, M.; Valdre, A.; Albertsson, A.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2049.

(88) Olsén, P.; Borke, T.; Odelius, K.; Albertsson, A.-C. *Biomacromolecules* **2013**, *14*, 2883.

(89) Lin, J.; Chen, W.; Shen, Z.; Ling, J. *Macromolecules* **2013**, *46*, 7769.

(90) MacDonald, J.; Shaver, M. P. *Polym. Chem.* **2016**, *7*, 553.

(91) Zhang, D.; Hillmyer, M. a; Tolman, W. B. *Biomacromolecules* **2005**, *6*, 2091.

(92) Glavas, L.; Olsén, P.; Odelius, K.; Albertsson, A.-C. *Biomacromolecules* **2013**, *14*, 4150.

(93) Makiguchi, K.; Asakura, C.; Yanai, K.; Satoh, T.; Kakuchi, T. *Macromol. Symp.* **2015**, *349*, 74.

(94) Glavas, L.; Odelius, K.; Albertsson, A.-C. *Polym. Adv. Technol.* **2015**, *26*, 880.

(95) Arias, V.; Olsén, P.; Odelius, K.; Höglund, A.; Albertsson, A.-C. *Polym. Chem.* **2015**, *6*, 3271.

(96) Saito, T.; Aizawa, Y.; Tajima, K.; Isono, T.; Satoh, T. *Polym. Chem.* **2015**, *6*, 4374.

(97) Tang, D.; Macosko, C. W.; Hillmyer, M. A. *Polym. Chem.* **2014**, *5*, 3231.

(98) Lowe, J. R.; Martello, M. T.; Tolman, W. B.; Hillmyer, M. A. *Polym. Chem.* **2011**, *2*, 702.

(99) Holmberg, A. L.; Reno, K. H.; Wool, R. P.; Epps, T. H., III *Soft Matter* **2014**, *10*, 7405.

(100) Yang, J.; Lee, S.; Choi, W. J.; Seo, H.; Kim, P.; Kim, G.-J.; Kim, Y.; Shin, J. *Biomacromolecules* **2015**, *16*, 246.

(101) Ding, K.; John, A.; Shin, J.; Lee, Y.; Quinn, T.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2015**, *18*, 2537.

(102) Lecomte, P.; Riva, R.; Schmeits, S.; Rieger, J.; Van Butsele, K.; Jérôme, C.; Jérôme, R. *Macromol. Symp.* **2006**, *240*, 157.

(103) Winkler, M.; Raupp, Y. S.; Kohl, L. A. M.; Wagner, H. E.; Meier, M. A. R. *Macromolecules* **2014**, *47*, 2842.

(104) Wilson, J. a.; Hopkins, S. a.; Wright, P. M.; Dove, A. P. *Biomacromolecules* **2015**, *16*, 3191.

(105) Abe, H.; Takahashi, N.; Kim, K. J.; Mochizuki, M.; Doi, Y. *Biomacromolecules* **2004**, *5*, 1480.

(106) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. a; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 4556.

(107) Keul, H.; Müller, A.; Höcker, H. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 289.

(108) Endo, T.; Kakimoto, K.; Ochiai, B.; Nagai, D. *Macromolecules* **2005**, *38*, 8177.

(109) Olsén, P.; Odelius, K.; Albertsson, A.-C. *Macromolecules* **2014**, *47*, 6189.

(110) Kühling, S.; Keul, H.; Höcker, H. *Makromol. Chem.* **1990**, *191*, 1611.

(111) Olsén, P.; Odelius, K.; Keul, H.; Albertsson, A.-C. *Macromolecules* **2015**, *48*, 1703.