

Nucleation–Elongation Polymerization under Imbalanced Stoichiometry

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Abstract: As a result of the helical structure of the polymeric product, the folding-driven polymerization of oligo(*m*-phenyleneethynylene) imines in solution should inherently show nucleation–elongation in chain growth. Here, we present evidence for this behavior based on results of polymerizations conducted under conditions of imbalanced stoichiometry. Because the polymerization proceeds via imine metathesis between a pair of bifunctional monomers of types A–A and B–B, the molar ratio of the polymerizing functional groups can be arbitrarily varied. Alternatively, stoichiometry can be controlled by the addition of a monofunctional oligomer. Similar results were obtained in both cases whereby the molecular weight distribution was significantly different from that expected for classical step-growth polymerizations. At equilibrium, high molecular weight polymers were observed to coexist with the monomer in excess. Thermodynamic equilibrium was established by showing that the same distribution was reached starting either from a monomer mixture or from high polymers to which one monomer was added. These results are in great contrast to the low molecular weight oligomers that were produced when the reaction was conducted by melt condensation of bifunctional aldehyde and amine monomers, a polymerization that apparently proceeds without the nucleation event. An equilibrium model that captures the features of nucleation–elongation under conditions of imbalanced stoichiometry qualitatively supports the monomer–polymer distribution observed experimentally.

Introduction

Polymerization reactions following a nucleation–elongation mechanism are ubiquitous in biological systems such as the self-assembling process of proteins into helical or tubular structures.¹ The main feature of these polymerizations involves a cooperative chain growth; that is, a critical size must be acquired by the growing chain before subsequent monomer addition becomes much more favored. The species at this critical size is the nucleus, and the events leading to its formation are nucleation. The occurrence of nucleation in protein polymerizations is believed to result from the helical structure adopted by these polymers (Figure 1). Each repeating unit within the helix is simultaneously in contact with multiple neighboring units; hence, a monomer added to a preexisting helix end is stabilized by its associations with multiple other repeating units from the same and neighboring turns of the helix. However, interactions with monomers from neighboring turns are absent when the first turn of the helix is assembled. The entropic cost of assembling the first turn is thus not compensated by an offsetting enthalpic gain; the result is an energetically less favored initiation event.

Despite its common presence in biological polymerizations, the nucleation–elongation mechanism is rarely exhibited by synthetic polymers.² The reason for this void is evident: most synthetic polymers are chain molecules composed of repeating

units that are simply joined end-to-end through covalent linkages, lacking any well-defined internal supramolecular structure. As reactivities of functional groups involved in covalent ligations are mostly chain-length independent,³ synthetic polymerizations are predominantly isodesmic processes (i.e., the chain propagates with an identical free energy change for each monomer addition regardless of the size of the growing species). Nevertheless, the ever-increasing understanding and rapid development in the area of supramolecular polymer chemistry has produced solution-stable helical conformations in a variety of synthetic structures.⁴ Accordingly, synthetic polymerizations exhibiting a nucleated chain growth can now be envisioned.

Previously, we demonstrated that the closed-system, reversible polymerization of *m*-phenyleneethynylene (*m*PE) starter sequences **1** and **2** in solution is driven by the folding energy of

- (2) Precedents of synthetic polymerizations with a nucleation process are limited. See: (a) Kern, W.; Jaacks, V. *J. Polym. Sci.* **1960**, *48*, 399–404. (b) Leese, L.; Baumber, M. V. *Polymer* **1965**, *6*, 269–286. In both of these reactions, crystallization of the polymeric products occurred. Nucleation has thus partially coincided with the formation of crystal nuclei. The supramolecular energy in these polymerizations was mostly derived from polymer crystallization. More recently, a cooperative chain growth has been reported in the supramolecular polymerization of certain urea derivatives through H-bond interactions: (c) Lortie, F.; Boileau, S.; Bouteiller, L. *Chem.-Eur. J.* **2003**, *9*, 3008–3014. In this case, the polarization of the urea units resulting from dimerization favors further H-bonding and chain elongation into polymers.
- (3) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953; Chapter 3. (b) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; Chapter 2.

(1) Oosawa, F.; Asakura, S. *Thermodynamics of the Polymerization of Protein*; Academic Press Inc.: New York, 1975.

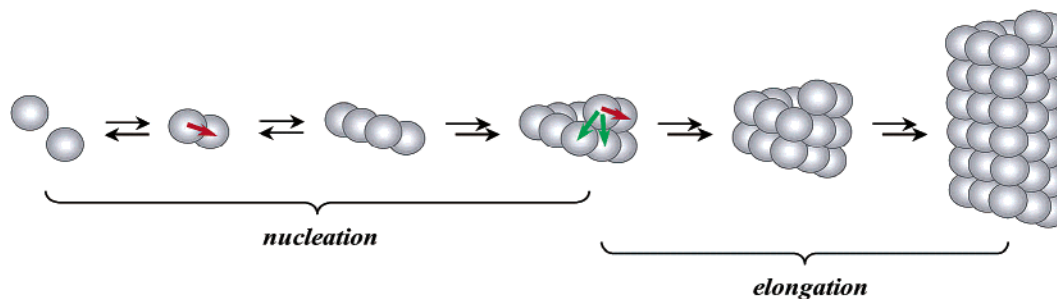


Figure 1. Representative schematic of nucleation and elongation stages of a protein polymerization generating a helical structure (the arrows represent the interactions among repeating units). Secondary interactions (green arrows), absent in the first turn of the helix, are the molecular origins of a less favorable nucleation event (i.e., the critical chain length) beyond which propagation becomes more favored.

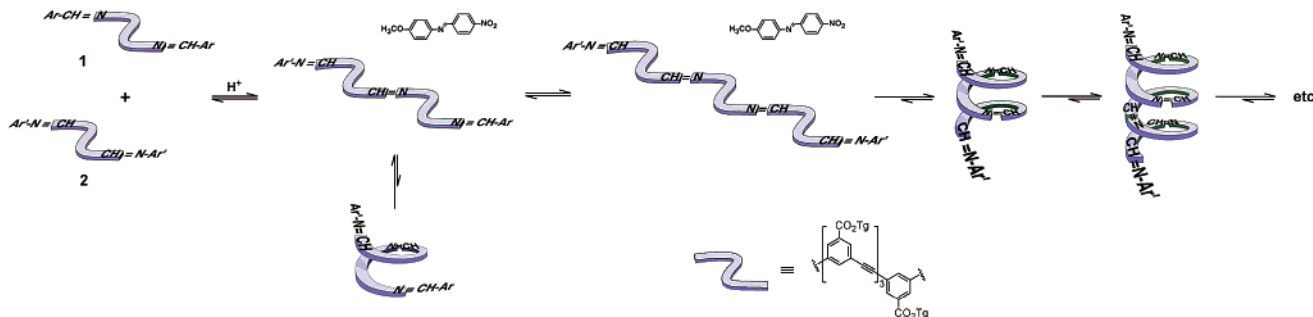
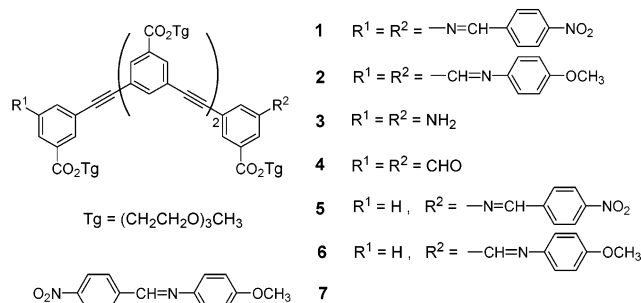


Figure 2. Schematic diagram of folding-driven polymerization of oligo(*m*-phenyleneethynylene) imines following a nucleation–elongation mechanism. At room temperature in acetonitrile, the helical conformation is stable for chains longer than ca. 10 *m*-phenyleneethynylene units.¹⁹

the resulting polymers (Figure 2).^{5,6} Considering the helical conformation adopted by the polymeric product,⁷ we suspected that this polymerization might follow the nucleation–elongation mechanism.⁸ As a result of the bifunctional A–A and B–B types of monomers that are employed in this reaction (i.e., **1** and **2**), the opportunity to study the nucleation–elongation polymerization under conditions of imbalanced stoichiometry emerged.⁹ Such investigations are of particular interest because it is imagined that a nucleation–elongation mechanism of growth should be fairly tolerant of mismatched functional-group stoichiometry.^{10,11} Like the exclusion of impurities in crystallization, we predicted that nucleated polymerizations run under conditions of imbalanced stoichiometry would still achieve high

molecular weight, doing so by excluding the excess monomer. The behavior would be in great contrast to isodesmic, step-growth polymerizations of bifunctional monomers, for which the molecular weight is very sensitive to the monomer stoichiometry.³ The following experiments were carried out to test this idea.



Results

The effect of stoichiometry on the metathesis polymerization of *m*PE oligomers was first investigated by systematically varying the relative ratio of starter sequences **1** and **2** under the same reaction conditions as those previously described.⁵ As the molar ratio of **1** and **2** ranged from 1:1 to 1:2, a decrease in the average molecular weight was observed at polymerization equilibrium (Figure 3 and Table 1, traces a–g). However, careful examination of the SEC traces revealed rather distinct size distributions from what would be expected from a conventional step-growth (i.e., isodesmic) polymerization under reversible

- (4) (a) Seebach, D.; Matthews, J. L. *Chem. Commun.* **1997**, 2015. (b) Gellman, S. H. *Acc. Chem. Res.* **1998**, *31*, 173. (c) Kirshenbaum, K.; Zuckermann, R. N.; Dill, K. A. *Curr. Opin. Struct. Biol.* **1999**, *9*, 530. (d) Barron, A. E. *Curr. Opin. Chem. Biol.* **1999**, *3*, 681. (e) Stigers, K. D.; Soth, M. J.; Nowick, J. S. *Curr. Opin. Chem. Biol.* **1999**, *3*, 714. (f) Archer, E. A.; Gong, H. G.; Krische, M. J. *Tetrahedron* **2001**, *57*, 1139. (g) Gong, B. *Chem.-Eur. J.* **2001**, *7*, 4336. (h) Cubberley M. S.; Iverson, B. L. *Curr. Opin. Chem. Biol.* **2001**, *5*, 650. (i) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (j) Schmuck, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2448.
- (5) (a) Zhao, D.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 9996–9997. (b) Zhao, D.; Moore, J. S. *Macromolecules* **2003**, *36*, 2712–2720.
- (6) For investigations at folding-driven syntheses of *m*PE imine oligomers, see: (a) Oh, K.; Jeong, K.-S.; Moore, J. S. *Nature* **2001**, *414*, 889–893. (b) Nishinaga, T.; Tanatani, A.; Oh, K.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 5934–5935. (c) Oh, K.; Jeong, K.-S.; Moore, J. S. *J. Org. Chem.* **2003**, *68*, 8397–8403.
- (7) Additional evidence for the helical structure of the polymers has recently been obtained. The Mark–Houwink coefficient α of ca. 1.6 indicates a highly elongated, rigid rod structure: Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953; Chapter 7.
- (8) Zhao, D.; Moore, J. S. *Org. Biomol. Chem.* **2003**, *1*, 3471–3491.
- (9) For biological systems, nucleation–elongation polymerization under imbalanced stoichiometry is not easily studied because the monomers (globular proteins) are typically self-complementary (i.e., A–B type) and the stoichiometry is thus intrinsically balanced.
- (10) A classical example of polymerization under imbalanced stoichiometry is interfacial polymerization: (a) Morgan, P. W.; Kwolek, S. L. *J. Chem. Educ.* **1959**, *36*, 182–184. (b) Morgan, P. W.; Kwolek, S. L. *J. Polym. Sci.* **1959**, *40*, 299–327.

- (11) A more recent example of polymerization under imbalanced stoichiometry: (a) Kimura, K.; Kohama, S.; Yamashita, Y. *Macromolecules* **2003**, *36*, 5043–5046. (b) Kimura, K.; Kohama, S.; Yamashita, Y. *Macromolecules* **2002**, *35*, 7545–7552. In this case, crystallization of the polymer product was responsible for driving the polymer growth by excluding the monofunctional monomer.

Scheme 1

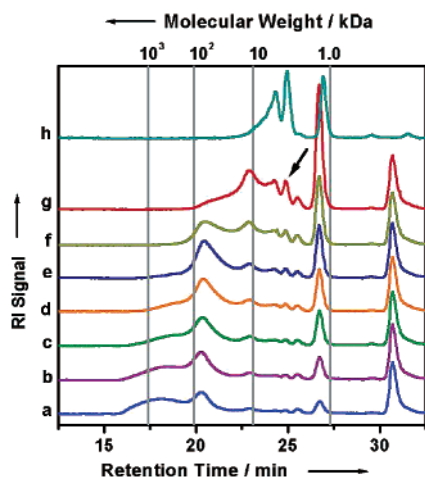
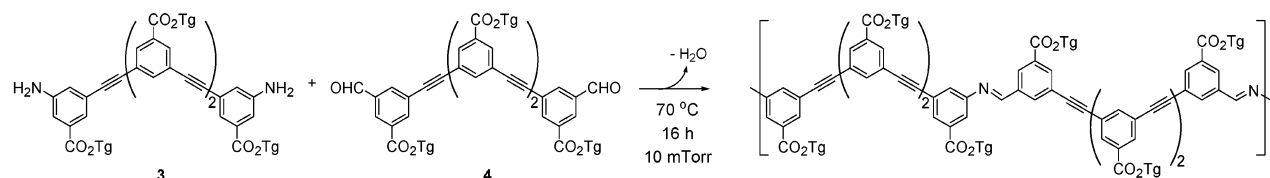


Figure 3. SEC traces of metathesis products equilibrated in the presence of 0.5 mM oxalic acid for 14 d at room temperature in CH_3CN , with the initial molar ratios of **1** and **2** at: (a) 1:1, (b) 10:11, (c) 5:6, (d) 4:5, (e) 3:4, (f) 2:3, (g) 1:2. The initial concentration of **1** was kept constant at 5 mM in all of the polymerizations. The reactions were quenched with Et_3N prior to SEC analysis (eluted by THF). Starter sequences **1** and **2** coeluted at ca. 27 min. The peak at ca. 31 min corresponds to byproduct **7**. The arrow in trace g indicates the peak corresponding to the trimer. Trace h is given by melt condensation of **3** and **4** at a molar ratio of 1:2 (Scheme 1). In this reaction, trimer is the major product.

conditions. Particularly, low molecular weight oligomers were not prevalent, even when one of the starter sequences was in large excess.¹² An unusual chain-length distribution was especially evident when the stoichiometry was far from balanced. For instance, in the reaction that gave rise to trace g (**1** and **2** at a molar ratio of 1:2), polymer products were present at equilibrium along with a substantial amount of monomer but relatively little dimer or trimer.¹³ The significance of this observation is best appreciated by comparing this distribution with that resulting from a polymerization run at the same monomer stoichiometry but under open-driven conditions of aldehyde and amine condensation in the melt (Scheme 1).¹⁴ Because the helical folding of *m*PE chains should not take place under these melt conditions,¹⁵ this polycondensation reaction is expected to behave more consistently with an isodesmic polymerization. According to the Flory distribution,³ an isodesmic polymerization with a monomer ratio of 0.5 should produce a set of low molecular weight oligomers even at a quantitative conversion of the quantity-limiting monomer.¹⁶ The product distribution from the condensation of **3** and **4** (trace h) is in

Table 1. Polymerization Conditions and Molecular Weight Data as a Function of Starter Sequence Stoichiometry

| SEC trace (Figure 3) | [1] ^a (mM) | [2] ^a (mM) | monomer molar ratio (1:2) | M_n^b (kDa) | M_w^b (kDa) | rel. excess monomer ^c | normalized monomer peak intensity ^d |
|----------------------|-----------------------|-----------------------|---------------------------|---------------|---------------|----------------------------------|--|
| a | 5.0 | 5.0 | 1:1 | 31 | 419 | 0.0 | 0.10 |
| b | 5.0 | 5.5 | 10:11 | 27 | 283 | 0.10 | 0.16 |
| c | 5.0 | 6.0 | 5:6 | 21 | 157 | 0.20 | 0.23 |
| d | 5.0 | 6.3 | 4:5 | 19 | 94 | 0.25 | 0.28 |
| e | 5.0 | 6.7 | 3:4 | 17 | 63 | 0.33 | 0.35 |
| f | 5.0 | 7.5 | 2:3 | 12 | 34 | 0.50 | 0.48 |

^a Initial monomer concentration. ^b The molecular weight data were obtained from integrating SEC traces between 15.5 and 26.1 min (i.e., monomer peak was excluded) and calibrated on the basis of polystyrene standards (the calibrated molecular weight of starter sequences **1** and **2** is ca. 1.5 kDa; the molecular weights of polymers were underestimated). ^c Calculated on the basis of $([2] - [1])/[1]$. ^d Integration of the monomer peak (ca. 27 min) in SEC traces normalized relative to the peak intensity of **2** at 5.0 mM concentration.

good agreement with this prediction,^{13,17} while the trace resulting from the metathesis polymerization of **1** and **2** in acetonitrile at room temperature (trace g) deviates significantly.

Further evidence indicating that the folding-driven polymerization was distinctly different from isodesmic behavior came from an analysis of monomer concentration at equilibrium. The monomer peaks (**1** and **2** coeluted at ca. 27 min) in traces a–g appeared to be disproportionately large, suggesting that the excess monomer was not effectively incorporated into oligomer or polymer. Quantitative analyses of integrated intensities of these peaks revealed that the equilibrium monomer concentrations in these reactions were nearly in direct proportion to the excess amounts of monomer originally present at the start of the polymerization (last two columns in Table 1). With excess monomer almost quantitatively excluded from polymers, it inevitably follows that the polymer portion of the product mixture (i.e., products excluding the unreacted monomer) has a higher average molecular weight than what is calculated on the basis of step-growth statistics.¹⁶ This is in contrast to an isodesmic polymerization wherein the product size distribution strictly follows statistical principles.³

A reasonable question that could be asked at this point is whether the recorded distributions are true equilibrium states or merely metastable products produced from slow redistribution kinetics.¹⁸ Although our previous investigations showed the allowed equilibration time to be sufficient for the polymerization

(12) Very similar distributions were obtained when **1** was in excess. SEC traces of these reactions are shown in the Supporting Information.

(13) Sequences containing an even number of repeating units are statistically suppressed under conditions of imbalanced stoichiometry relative to those having an odd number of repeating units.

(14) An open-driven system was chosen to obtain a reaction conversion comparable to that achieved in the metathesis polymerization in acetonitrile for a consistent comparison of the product distribution.

(15) Prest, P.-J.; Prince, R. B.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 1, 5933–5939.

(16) The average degree of polymerization of products from an isodesmic polymerization under imbalanced stoichiometry can be calculated using statistical methods. The number-average degrees of polymerization: $\langle dp \rangle_n = (1+r)/(1+r-2rp)$, and $\langle dp \rangle_n = 1 + 2/(2-p-rp)$ if monomers are not counted. These values tend to 3.0 and 5.0, respectively, when stoichiometry imbalance $r = 0.5$ and reaction conversion $p \rightarrow 1$.

(17) A nearly quantitative conversion in this melt polymerization was evidenced by the disappearance of resonance signals belonging to starter sequence **3** in the ¹H NMR spectrum of the product mixture.

(18) We note that for isodesmic polymerizations the product distribution should follow statistical predictions throughout the entire course of the reaction, both at equilibrium and at any point prior to that.

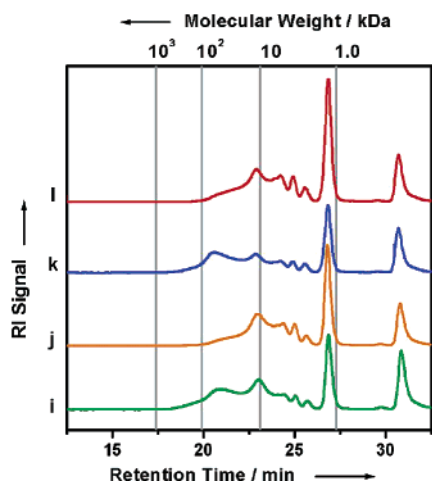


Figure 4. Upon equilibrating equimolar **1** and **2** at 5 mM in the presence of 0.5 mM oxalic acid for 14 d at room temperature in CH_3CN , **2** was added at 2.5 (j) or 5 mM (l). After the mixtures were equilibrated for another 14 d, the reactions were quenched and gave traces i and j. Metathesis polymerization products equilibrated for 14 d at room temperature in CH_3CN , starting with a mixture of **1**, **2**, and **6** at molar ratios of (k) 2:2:1 and (l) 1:1:1. The initial concentrations of **1** and **2** remained constant at 5 mM in (k) and (l).

to reach equilibrium,⁵ depolymerization experiments were performed to unambiguously confirm this point. In these experiments, polymers were first obtained by equilibrating stoichiometric equivalents of **1** and **2** for 14 days (the presence of high polymers was verified by examining an independent reaction run in parallel). Without quenching the reaction, the desired excess of starter sequence **2** was then added to the equilibrated high polymer mixture. At the end of another 14-day equilibration, the reaction was quenched and analyzed by SEC. The resulting distributions were nearly identical to those initiated from mixtures of starter sequences at corresponding molar ratios (traces i and j in Figure 4 as compared to traces f and g in Figure 3, respectively). These results confirmed the notion that the observed product distributions represented the thermodynamic equilibrium state, because consistent distributions were reached independently of the initial starting point.

Finally, it was demonstrated that similar polymer–monomer distributions could be achieved when the stoichiometric imbalance was induced by the presence of a monofunctional starter sequence. When **1** and **2** were copolymerized with either of the monofunctional sequences **5** or **6**, consistent distributions were observed at corresponding stoichiometries (Figure 4, traces k and l).

Discussion

The polymerization behavior of **1** and **2**, in particular, the low level of oligomers and large excess of unreacted monomer, under conditions of stoichiometric imbalance can be explained by the nucleation–elongation mechanism. In a closed-system isodesmic step-growth polymerization, all coupling reactions between different sized molecules take place with identical free energy changes. Consequently, the statistically most probable distribution dominates according to the ratio of functional groups. However, in a nucleated polymerization, species of subcritical lengths are relatively unstable. Consequently, given the same monomer stoichiometry, short oligomers represent less favorable species than longer, more stable polymers that coexist

with monomers. The system thus bifurcates into polymer and monomer with oligomer depleted.

For the current system, our previous studies indicated that the critical chain length for *m*PE oligomers to form a stable, helical conformation is approximately 10 *m*PE units.^{6,19} Accordingly, the immediate product from a single coupling reaction between **1** and **2** will possess eight *m*PE units and be unable to fold (Figure 5). Adding another starter sequence to this growing oligomer produces a molecule having 12 *m*PE units, which should be able to fold but only with marginal stability due to the limited chain length. Further extending the molecule will result in polymers with increasing folding stabilities. Under an imbalanced stoichiometry (e.g., a monomer ratio of 1:2), the enthalpy gained from the folding of long polymers drives the polymerization equilibrium to deviate from the statistically most favorable distribution, as such a distribution would include a set of short oligomers having no or diminutive folding stability. Rather, the distribution partitions into folded polymers that coexist with the excess starter sequence (Figure 5).

An equilibrium model that captures the features of nucleation–elongation mechanism under imbalanced stoichiometry has been constructed.²⁰ In the simplest case, all different units within the polymerization system can be categorized into three energetically distinct groups: monomer, end group, and internal repeating unit. Each type of moiety includes two energetically equivalent species bearing different functional groups. Equation 1 represents the transformations among these species,²¹ wherein A and B represent the bifunctional A–A and B–B type monomers, respectively, EgA and EgB stand for the corresponding units at the end of an oligomer or polymer, while PA and PB are internal repeating units of a chain containing more than two monomer segments.²² Each reaction in this mechanistic scheme involves a reversible process with a corresponding equilibrium constant. When the equilibrium equations (eqs 2–4) are combined with the monomer mass balance equations (eqs 5 and 6) and the sequence composition rule (eq 7), the equilibrium concentrations of all six different species in eq 1 can be numerically solved.²³

When $K_1 \approx K_2$, the model corresponds to an isodesmic polymerization;²⁴ if $K_1 \ll K_2$, the model describes a polymerization that has a single nucleation step (i.e., the nucleus is a dimer) with all subsequent monomer addition steps having an

(19) (a) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793. (b) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114–3121.

(20) Previous models used to describe nucleation–elongation (or more generally, nonisodesmic) polymerizations do not differentiate species bearing different functional groups and are therefore not suitable for nonstoichiometric analyses. Moreover, these models do not consider the small-molecule byproduct that results from metathesis. For examples of equilibrium models of indefinite association, see: Martin, R. B. *Chem. Rev.* **1996**, *96*, 3043–3064.

(21) Because only the thermodynamic equilibrium state is under investigation here, the equations do not necessarily have to be the kinetically most favorable pathways. As long as the correlations of concentrations with thermodynamic constants are appropriately expressed, the choice of a certain set of expressions over another will not alter the analysis result.

(22) The equilibrium model represented by eq 1 should generally be applicable to various polymerizations that have a single nucleation step and form a small-molecule byproduct. See the Supporting Information for details on the specific chemical structure correlation of the model with the *m*PE metathesis polymerization.

(23) The calculations were conducted using Mathematica 4.2. Numerical solutions were acquired as the software failed to generate algebraic solutions.

(24) It was found that K_1 has to be 4 times as large as K_2 for the results from this model to exactly match those of an isodesmic model derived in ref 3. The reason for this coefficient 4 is currently unclear.

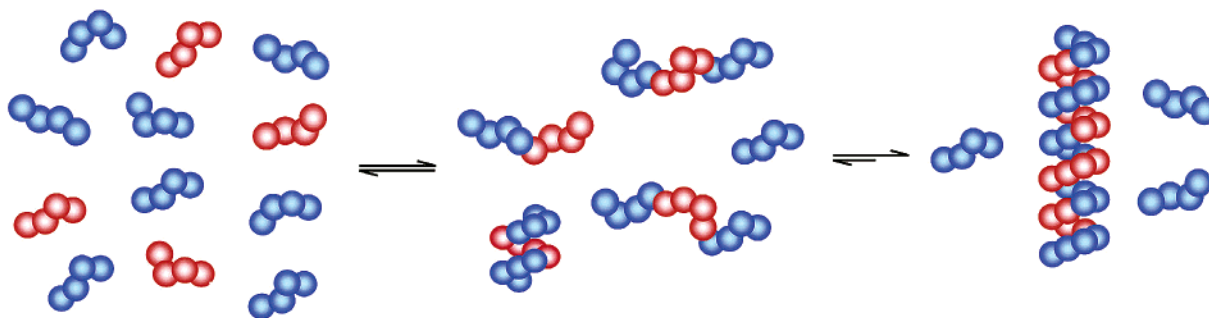
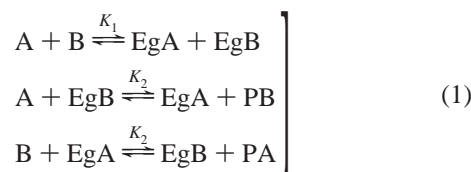


Figure 5. A schematic representation of a nucleation–elongation polymerization of **1** and **2** under imbalanced stoichiometry. The coexistence of foldable polymer and the excess monomer are favored over oligomers of no or diminutive folding stability (the red and blue segments represent starter sequences bearing N-terminus and C-terminus imine end groups, respectively).

identical free energy change. The key results from this model are summarized in Figure 6. Given the same value of elongation equilibrium constant, K_2 , a significantly higher number-average degree of polymerization was found for polymeric products (i.e., $\langle dp \rangle'_n$ is the number-average molecular weight of products not including the unreacted monomers²⁵) from a nucleation–elongation polymerization than from an isodesmic reaction.²⁶ Consistently, the monomer concentration at equilibrium of a



$$K_1 = \frac{[\text{EgA}][\text{EgB}]}{[\text{A}][\text{B}]} \quad (2)$$

$$K_2 = \frac{[\text{EgA}][\text{PB}]}{[\text{A}][\text{EgB}]} \quad (3)$$

$$K_2 = \frac{[\text{EgB}][\text{PA}]}{[\text{B}][\text{EgA}]} \quad (4)$$

$$[\text{A}]_0 = [\text{A}] + [\text{EgA}] + [\text{PA}] \quad (5)$$

$$[\text{B}]_0 = [\text{B}] + [\text{EgB}] + [\text{PB}] \quad (6)$$

$$[\text{PA}] + \frac{1}{2}[\text{EgA}] = [\text{PB}] + \frac{1}{2}[\text{EgB}] \quad (7)$$

nucleated system is significant higher than that found in an isodesmic system. Naturally, when the stoichiometry is substantially imbalanced, the monomer that remains unreacted at equilibrium is almost exclusively the one that is in excess. It is clear from Figure 6 that, with respect to monomer concentration and $\langle dp \rangle'_n$, there are important differences between isodesmic

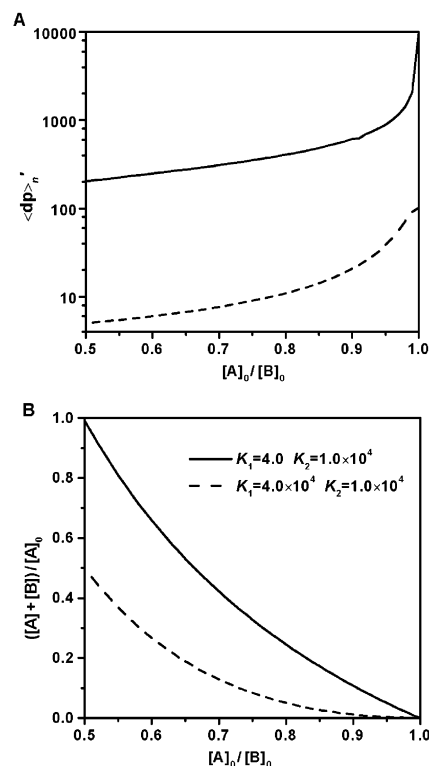


Figure 6. Representative plots of (A) number-average degree of polymerization ($\langle dp \rangle'_n$) of the polymer product (excluding the monomer) and (B) the relative monomer concentration at equilibrium as a function of the initial monomer molar ratio in a nucleation–elongation polymerization. For comparison, corresponding results for an isodesmic reaction are also shown. The data were obtained from numerical calculations based on the model shown in eqs 1–7.

and nucleation–elongation polymerizations under conditions of imbalanced stoichiometry. The experimentally observed monomer concentrations at metathesis equilibria of **1** and **2** (the last column in Table 1) are close to the calculated values based on the nucleation–elongation mechanism.²⁷

Conclusion

Reversible metathesis polymerizations of *m*PE imines generating helical polymers have resulted in novel size distributions under imbalanced stoichiometries. In the presence of a large excess of one of the bifunctional starter sequences, or a

(25) The number-average degree of polymerization of polymer product excluding unreacted monomer: $\langle dp \rangle'_n = 2([\text{PA}] + [\text{PB}] + [\text{EgA}] + [\text{EgB}])/([\text{EgA}] + [\text{EgB}])$.

(26) Theoretically, the polymer portion of the product (excluding the monomer) from the nucleation–elongation polymerization should have a polydispersity index of ca. 2.0. However, in the current reactions broader distributions were observed. Moreover, certain specific chain lengths appeared to be more abundant than the others according to SEC analyses. The presence of such potentially stable species is consistently reproducible and seems to be sequence dependent (for another set of starter sequences with a slightly different backbone structure, monomodal SEC traces were recorded, cf. ref 5b). Although a number of possibilities may be proposed (e.g., the existence of higher order structures), unambiguous evidence that can lead to a definitive explanation for this phenomenon is currently unavailable.

(27) Although the equilibrium constant used in these calculations may not accurately reflect the values of the real system, it is reasonable to conclude that the *m*PE starter sequences exhibit the predicted characteristics of a nucleation–elongation polymerization.

monofunctional analogue, polymers having significant molecular weight were produced, coexisting with the excess monomer. Such distributions are distinct from those obtained from isodesmic reactions, which give rise mainly to low molecular weight oligomers under highly imbalanced stoichiometry. The observed distribution is proposed to be the result of a cooperative, nucleation–elongation chain growth mechanism. The nucleation event originates from an intrinsically less favorable initiation process of forming the helical structure adopted by the polymer products.

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Supporting Information Available: Characterization data of compounds **1**–**6**, SEC traces of products from polymerizations of **1** and **2** with **1** in excess, and more polymerizations in the presence of **5** or **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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