Folding-Driven Reversible Polymerization of Oligo(*m*-phenylene ethynylene) Imines: Solvent and Starter Sequence Studies

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ABSTRACT: Bis(imino) end-functionalized oligo(*m*-phenylene ethynylene)s were equilibrated in a closed system under conditions that promote reversible imine metathesis. The metathesis reaction joins two oligomers and produces a small molecule byproduct. In polar solvents, equilibration gave high molecular weight polymers while equilibration in chloroform produced only low molecular weight oligomers. This polymerization is hypothesized to be driven by the free energy gained from the folding of the long polymer chains directed by the noncovalent, intramolecular aromatic stacking and solvophobic interactions. This polymerization was also conducted in a series of solvents in which *m*-phenylene ethynylene oligomers have previously shown varied, intermediate folding stabilities. These experiments revealed a good correlation of the product molecular weight with the stability of the *m*-phenylene ethynylene helix. The equilibrium state of the metathesis reaction was also demonstrated to depend on the chain length of the starter sequences. With a pair of trimeric precursors, macrocyclization instead of polymerization takes place. Consistent with the notion that the polymerization is a consequence of the intramolecular solvophobic chain association, higher degrees of polymerization followed from enhanced solvophobicity of the *m*-phenylene ethynylene backbone, achieved by appending a methyl substituent to half of the repeat units. The considerably longer equilibration time required by these more stabilized sequences suggests that the elongation process may involve unfolding or partial unfolding of the chain; alternatively, intermolecular association may be responsible for the slow chain growth.

Introduction

The folding of proteins into well-defined globular structures requires very specific sequences and composition of the constituent amino acids.[1,2] Both theoretical and experimental studies have suggested that only a fraction of all possible sequences give rise to globular, soluble structures.[2,3] For synthetic polymers, the design of tyligomers[4a] that possess a sequence that is able to adopt a desired secondary or tertiary structure (i.e., the "masterpiece" sequence)[4b] presents a significant challenge for chemists. One of the major obstacles comes as a consequence of the enormous magnitude of all possible sequences of a heteropolymerization. Even for a binary monomer system, the number of available sequences is large enough to make the identification of a specific sequence almost impossible. Conventional irreversible polycondensations inevitably generate representatives of all possible sequences in a copolymerization, regardless of the structures resulting from the sequences.[3e] On the other hand, in a reversible polymerization system wherein all sequences are interconvertible by dissociation and reassociation of the comprising subunits, the relative population of each different sequence is determined by their relative thermodynamic stabilities. Therefore, it is reasonable to hypothesize that a reversible polymerization would give rise to a smaller subset of the entire sequence library, selectively producing structures that are thermodynamically most stable. To induce the production of certain sequences, conditions can be selected to stabilize the desirable structures. If a polymerization is set up under conditions that favor folding, uniquely folded structures may be generated.

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The goal of the current work, as the first step toward identifying tyligomer sequences through reversible polymerizations, is to demonstrate that the free energy gained from folding provides the driving force for high polymer formation. We show that high molecule weight can be achieved from a reversible polymerization by appropriately choosing starter sequences that are only stabilized in long polymer chains that adopt compact form. Toward this end, a system that can undergo a reversible unfolded-to-folded conformational transition must first be identified. The oligo(*m*-phenylene ethynylene)s that have extensively been studied in our laboratory exhibit a reversible conformational transition in solution.[5] These oligomers are comprised of a hydrocarbon-rich, aromatic backbone appended with tris(ethylene glycol) monomethyl ether side chains via an ester linkage. They adopt an ordered helical conformation in polar solvents such as acetonitrile but exist in a random conformational state in chlorohydrocarbon solvents such as chloroform. Such a coil-to-helix transition was explained to result from solvophobically favored aromatic stacking interactions among the aromatic backbone units in polar media.[6] For folding to take place, a critical chain length (nucleation size) is required for the oligomers to achieve sufficient enthalpy gain from stacking interactions to overcome the entropy loss of restricted conformation.[5b] Therefore, the polymerization of the *m*-phenylene ethynylene oligomers may exhibit a unique nucleation process (i.e., formation of short sequences incapable of folding followed by favorable elongation of the chain into stable, folded polymers).[7]

To clearly elucidate the role of folding in the polymerization of *m*-phenylene ethynylenes, imine metathesis[8] (Scheme 1) was specifically chosen to perform the reversible, covalent ligation of starter sequences in the

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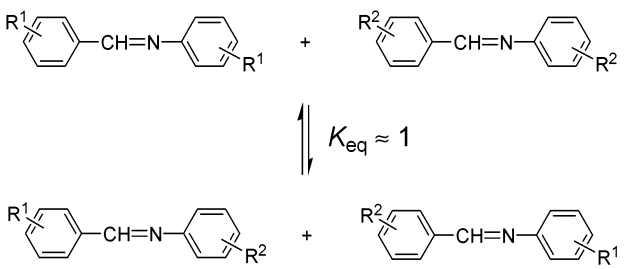
Scheme 1



polymerization reaction. Many features of the metathesis reaction[9] qualify it as a suitable choice for coupling monomers or sequences to test the concepts put forth in. Most notably, the sum of the bond energies on one side of the equilibrium will be nearly identical to those on the other. Thus, for a metathesis reaction, the equilibrium distribution will not be biased to a particular product by bond energy changes. Therefore, the formation of high molecular weight products, should they be observed, can reasonably be attributed to the energy gained by folding or collapsing of the polymer chains. For several reasons that are noted below, metathesis reaction between imine units appeared favorable for *m*-phenylene ethynylene system. First, the imine unit is nondisruptive to aromatic interactions[10] and imine metathesis can be conducted in a variety of solvents. Additionally, while the metathesis is reversible and quickly equilibrates in the presence of catalytic acid, the interconversion can conveniently be "switched off" (e.g., via addition of excess triethylamine) to "quench" the equilibrated product distribution.[11] As expected, the equilibrium constant of this reaction is nearly unity,[11a] which ensures that little, if any, favorable energy is gained from new covalent bonds generated during polymerization.

In a previous communication, we demonstrated that the folding of the *m*-phenylene ethynylene chains can drive the imine metathesis polymerization to generate high polymers in acetonitrile.[12] As a control, only low molecular weight oligomers were observed when the metathesis took place under nonfolding conditions, i.e., in chloroform. The correlation of the molecular weight of the resulting polymers with the solvent composition of a series of acetonitrile/chloroform binary mixtures, which dictates the stability of the folded conformation of *m*-phenylene ethynylene molecules,[5b] supported the proposition that folding shifts the metathesis equilibrium toward high polymers. Furthermore, the insensitivity of the equilibrated molecular weight of the products to the concentration indicated that intramolecular association (i.e., folding) rather than intermolecular aggregation was the dominant driving force for the high polymer formation.[12] Herein we report detailed studies elucidating the effect of solvent, starter sequence, and backbone chemical features on the polymerization reaction.

Results and Discussion

Calculations of MW Distribution under Nonfolding Conditions. To explicitly elucidate the effect of folding in driving high polymer formation, calculations were first conducted to determine the product molecular weight distribution of a metathesis polymerization in the absence of folding. If the equilibrium constant for reversible coupling of monomers or oligomers is assumed to be unity,[11a] the molecular weight distribution can be calculated by statistical methods (Figure 1).[13] An average degree of polymerization of 2.0 is predicted with the products distributed in the low molecular weight region. In other words, only oligomers with low degrees of polymerization are expected for a reversible polymerization conducted in a closed system. As the equilibrium constant for imine metathesis between monofunctional *m*-phenylene ethynylene oligomers has been shown to be close to unity, we expect to observe low molecular weight products under nonfolding conditions. Significant deviation from this calculated distribution suggests the presence of an alternate driving force that shifts the equilibrium.

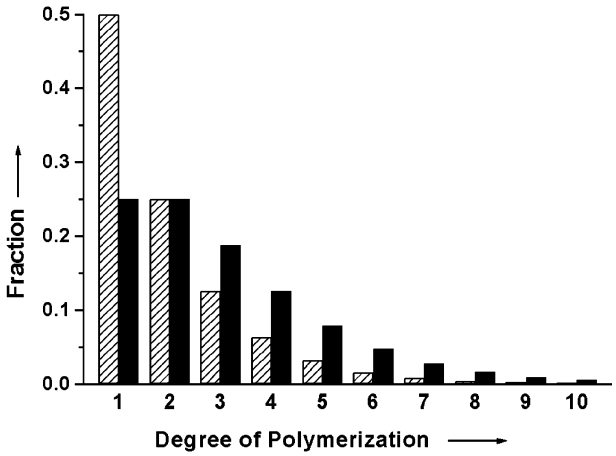


Figure 1. Histogram of the calculated chain length distributions (slashed bar, mole fraction; solid bar, weight fraction) at equilibrium for a closed-system metathesis polymerization in which the equilibrium constant of the coupling reaction is unity. The average degree of polymerization is calculated to be 2.0.

Solvent Studies: Polymerization of 1 and 2. As previously reported,[12] the imine metathesis polymerization of a pair of α,ω-imine functionalized, tetrameric *m*-phenylene ethynylenes **1** (N-terminal bis(imine)) and **2** (C-terminal bis(imine)) in chloroform resulted in a set of low molecular weight oligomers, the distribution of which was in qualitative agreement with the calculation mentioned above. In contrast, high polymers were obtained when the same metathesis reaction was carried out in acetonitrile under otherwise identical conditions (Scheme 2). Since the *m*-phenylene ethynylene chains are believed to be stabilized by compact, helical conformations in acetonitrile, as opposed to a random conformational state in chloroform, it can be concluded that the free energy gained from folding shifted the equilibrium toward high polymer formation (assuming there is no aggregation, vide supra).

If folding is responsible for the equilibrium shifting and consequently the elongation of the polymer chains, the degree of polymerization should correlate to the folding energy of the resulting products. In previous studies, we showed that the degree of polymerization systematically depended on the amount of chloroform in acetonitrile/chloroform binary solvent mixtures.[12] The observed dependence of the molecular weight on the solvent composition supported the role of folding as the driving force for shifting the equilibrium toward high polymers.

An obvious alternative approach to confirming the relationship between the folding energy and the degree of polymerization was to perform the equilibration in solvents that provide various folding stabilities. On the

Scheme 2

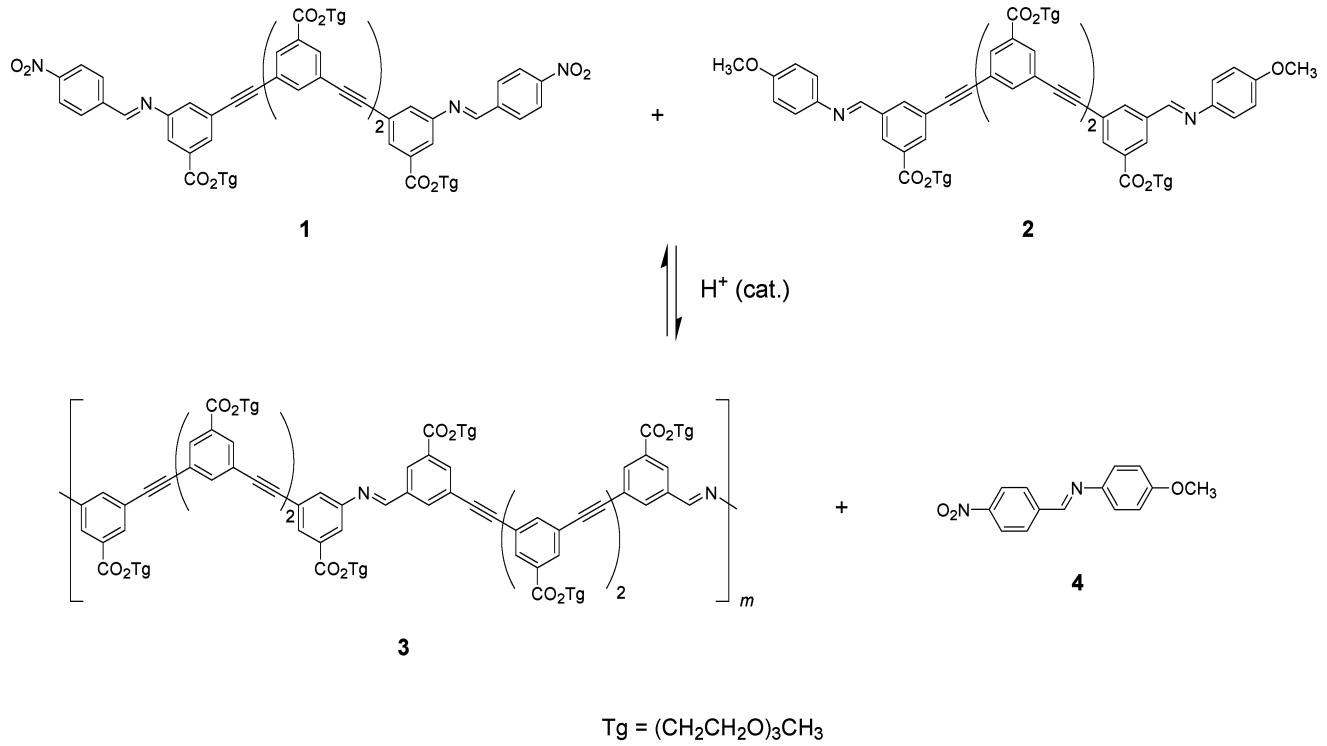


Table 1. Molecular Weight Data of 3 from Starter Sequences 1 and 2[a]

	solvent	A_{313}/A_{295}[b]	integration limits (min)	M_n (kDa)	M_w (kDa)	polydispersity (M_w/M_n)
a			26.0−27.8	1.8	1.8	1.0
b	$CHCl_3$	0.938	22.7−27.6	3.0	3.9	1.3
c	THF	0.860	22.6−27.6	3.0	3.9	1.3
d	1,4-dioxane	0.811	22.3−27.6	3.4	4.5	1.3
e	MeOAc	0.739	19.7−27.4	5.8	10.3	1.8
f	EtOAc	0.719	18.0−27.5	7.5	34.0	4.5
g	CH_3CN	0.672	15.3−27.5	13.5	350.2	26.3

[a] Metathesis conditions: 1:1 equiv of reactants at 5 mM equilibrated in the presence of 0.1 equiv of oxalic acid at room temperature for 6 days. The first column is keyed to Figure 2.[b] UV absorbance data are as previously reported.[14]

basis of the results from independent solvent studies,[14] metathesis polymerization was conducted in a series of solvents in which the folding propensity of a *m*-phenylene ethynylene oligomer has been shown to vary between that in chloroform and acetonitrile (Table 1). Previous studies have found that the ratio of UV absorbances at 313 and 295 nm (A_{313}/A_{295}) serves as a qualitative index of the helical stability and thus reflects the solvent quality for the promoting the folding of *m*-phenylene ethynylene oligomers.[5] The cisoid (helical) and transoid (nonhelical) states of the *m*-phenylene ethynylene unit give rise to different absorbance ratios at these wavelengths, and a decrease in this ratio corresponds to a larger fraction of the helical conformation.

Equimolar quantities of tetrameric starter sequences **1** and **2** were dissolved in the various solvents listed in Table 1 at a concentration of 5 mM in the presence of 0.1 equiv of oxalic acid as a catalyst. These sequences were equilibrated at room temperature for 6 days at which time the reaction was quenched with an excess amount of triethylamine. Exposing the reactants to the catalyst solution for a longer period of time led to no significant change in the molecular weight, indicating that for these sequences equilibrium could be reached within this time. The size exclusion chromatography (SEC) traces of the equilibrium products obtained from selected solvents are shown in Figure 2, and the corresponding molecular weight data are provided in Table 1. A consistent increase in the number- and weight-average molecular weight of the products was observed as the A_{313}/A_{295} absorbance ratio decreased. This further demonstrated that folding was responsible for shifting the equilibrium, driving the chain to elon-

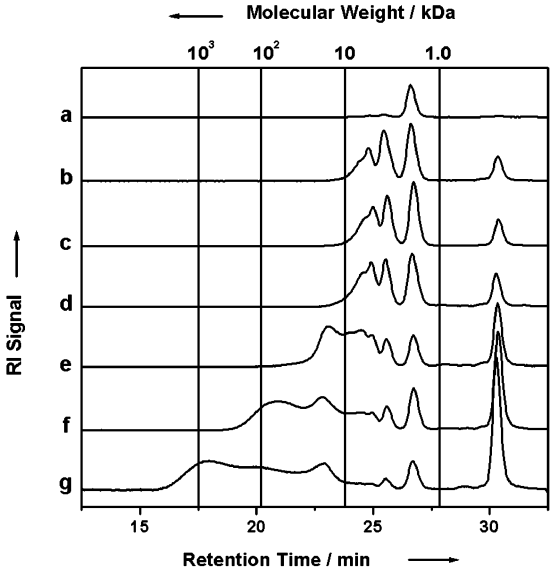


Figure 2. SEC traces of starter sequences **1** and **2** (a) and products **3** equilibrated for 6 days at 5 mM and room temperature in chloroform (b), tetrahydrofuran (c), dioxane (d), methyl acetate (e), ethyl acetate (f) and acetonitrile (g) solutions (the traces eluted at ca. 30 min are from the byproduct **4**). Samples were eluted from SEC columns with THF and detected by a refractive index (RI) detector. The molecular weight calibration is based on narrow molecular weight polystyrene standards. In trace a, starter sequences **1** and **2** coelute.

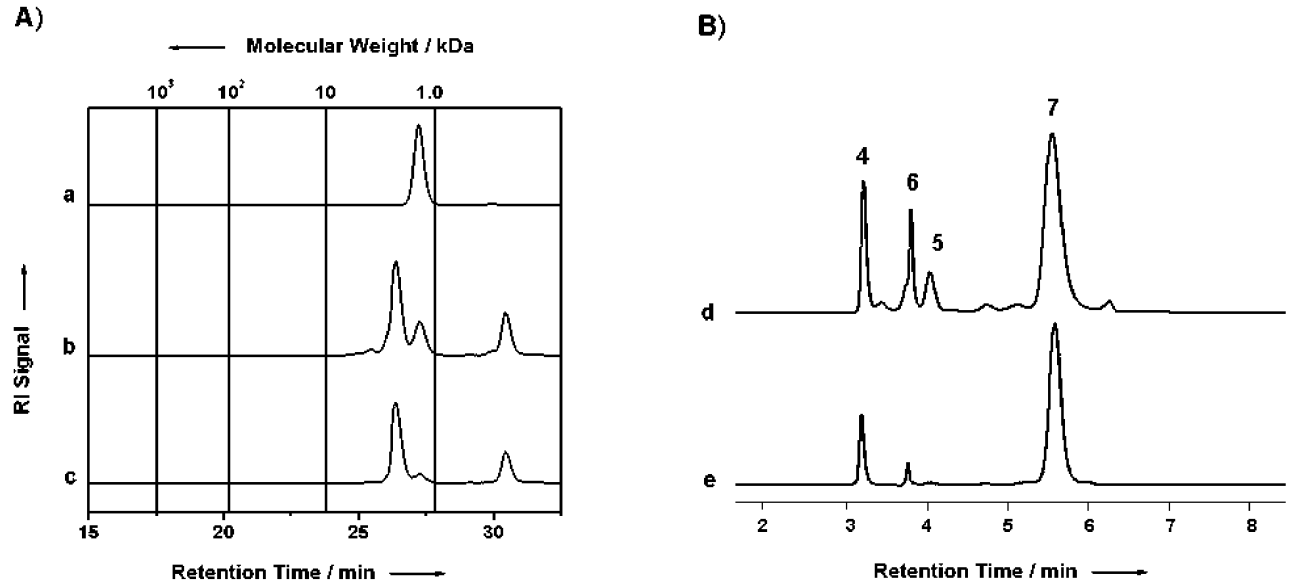
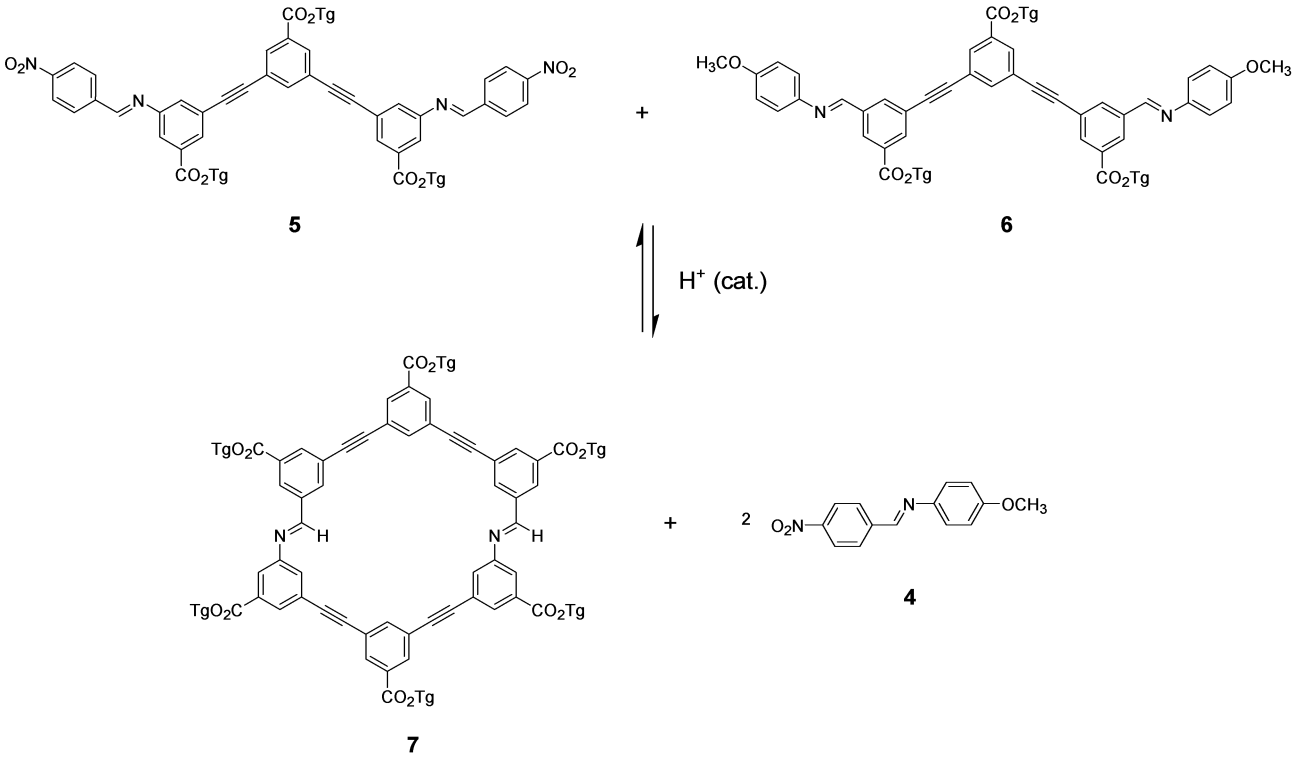


Figure 3. SEC (A) and HPLC (B) traces of starter sequences **5** and **6** (a) and their products following equilibration for 40 h at 5 mM and room temperature in chloroform (b and d) and acetonitrile (c and e). Starter sequence **6** was in excess in both reactions. SEC analyses were conducted under the same conditions as in Figure 2. Samples were eluted from silica gel HPLC columns with $CHCl_3$/*i*PrOH (3.0 vol %) and detected by a UV detector operating at 290 nm. In the SEC trace a, starter sequences **5** and **6** coelute.

Scheme 3



gate into high polymers. These results also indicate that folding driven polymerization is a general feature of *m*-phenylene ethynylene imine sequences under solvophobic conditions, rather than a unique observation that only takes place in acetonitrile.

Macrocyclization of Oligomers 5 and 6. In contrast to the polymerization of tetrameric starter sequences **1** and **2**, no high molecular weight product was obtained when trimeric *m*-phenylene ethynylene oligomers **5** and **6** were allowed to equilibrate under the same metathesis conditions. This pair of starter sequences contains the same imine end groups as **1** and **2**, but each is shorter in length by one phenylene ethynylene unit. On the basis of SEC studies, a monodispersed product with a molecular weight approximately twice that of either starting material was obtained from a catalyzed mixture of **5** and **6** equilibrated in either chloroform or acetonitrile (Figure 3A). Subsequent HPLC analyses on the same reaction mixtures (Figure 3B) confirmed the generation of a single, low molecular weight product. This product was found to coexist with a considerable amount of the starting materials when the equilibration was conducted in chloroform, while the reaction was driven to nearly

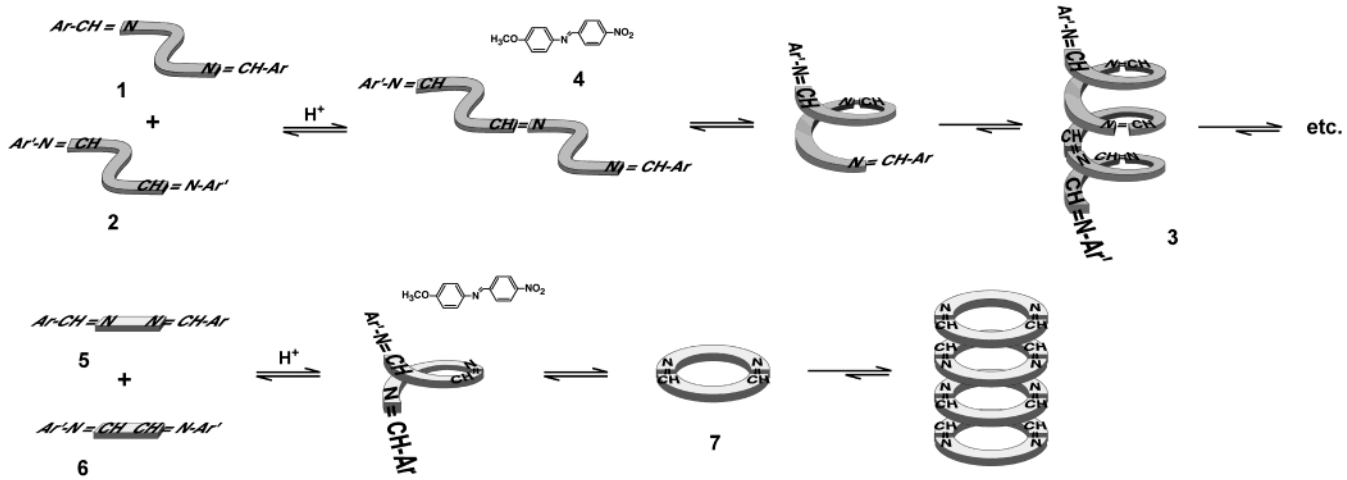


Figure 4. Schematic illustration of the metathesis polymerization and macrocyclization.

quantitative conversion when it takes place in acetonitrile. This monodisperse product was then identified by ^{1}H NMR and MS (FAB) as macrocycle **7**. On the basis of the integrations of the end group resonance in the ^{1}H NMR spectrum, the equilibrium constant of the reaction shown in Scheme 3 was determined to be ca. 13 mM in chloroform. However, this macrocycle exhibited extraordinary stability in acetonitrile. Even when one of the reactants (i.e., **6**) was present in excess, **7** was obtained in nearly quantitative yield (based on the amount of the quantity limiting compound **5**).

Macrocycle **7** is known to aggregate into columnar assemblies in polar solvents, including acetonitrile,[10] driven by the solvophobically favored aromatic stacking. On the basis of this evidence, we propose that the macrocycle is stabilized by the free energy gained from the intermolecular, noncovalent interactions upon aggregation in acetonitrile and that the aggregates therefore became the thermodynamically most stable species. Accordingly, the metathesis equilibrium was shifted in favor of cyclization and the macrocycle was afforded as the predominant product. Since unimolecular cyclization is intrinsically disfavored by entropy, low reaction yield has long presented a challenge for macrocycle syntheses. Significantly, the aggregation-driven synthesis of macrocycle **7** illustrates a possible approach to synthesize macrocyclic structures in high yield. From the standpoint of polymerization, however, these cyclic products are recognized as another type of "deep trap" that can interfere with high polymer formation.

The different product distributions obtained from the two sets of starter sequences (i.e., **1** + **2** vs **5** + **6**) under the same metathesis conditions may be explained by the structural differences of the corresponding macrocycles (Figure 4). On the basis of our previous studies,[15] macrocycle **7** is expected to possess a planar or nearly planar conformation in solution, which is optimal for efficient intermolecular π-stacking interactions and aggregation. Unlike **7**, an analogous octameric macrocycle (resulting from **1** and **2**) should be strained, having a nonplanar conformation, and would not be able to efficiently form stacked aggregates. Instead, a crescent broken ring would be formed, which upon further reaction would develop into long polymeric chains that maximize aromatic stacking intramolecularly. Consequently, polymerization dominates for **1** and **2**.

Metathesis Polymerization of 2 and 5. Since it has been illustrated that metathesis between a pair of tetrameric oligomers gives rise to higher polymers while macrocyclization occurs when the reaction starts with a pair of trimeric species, a question naturally arises as to what would happen if a trimer is metathesized with a tetramer. To answer this question, a metathesis reaction was performed under the same conditions as described earlier, with a mixture of oligomers **2** and **5**. The SEC traces of the equilibrated products showed that polymerization dominated in acetonitrile and low molecular weight oligomers were generated in chloroform. In the MALDI MS of the reaction mixture equilibrated in chloroform, both the open chain and the cyclic dimers of **2** and **5** were detected. The presence of two different forms of dimers in chloroform explained the disproportionally large peak that was eluted right before the starting material mixture in the SEC trace (Figure 5b). Although MALDI MS was not able to provide information on the sequence identity of the products obtained from acetonitrile solution due to the broad molecular weight distribution, the presence of high polymers was evidenced by SEC analysis (Figure 5c). This suggests that the cyclic dimer of **2** and **5** is at most of modest stability and is insufficient to produce an energy trap that prevents polymerization.

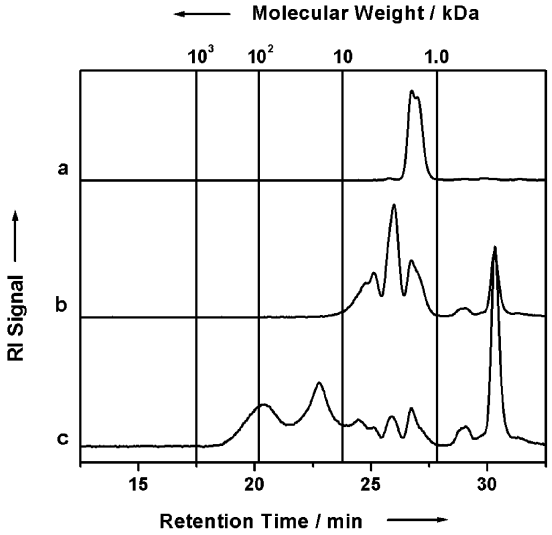
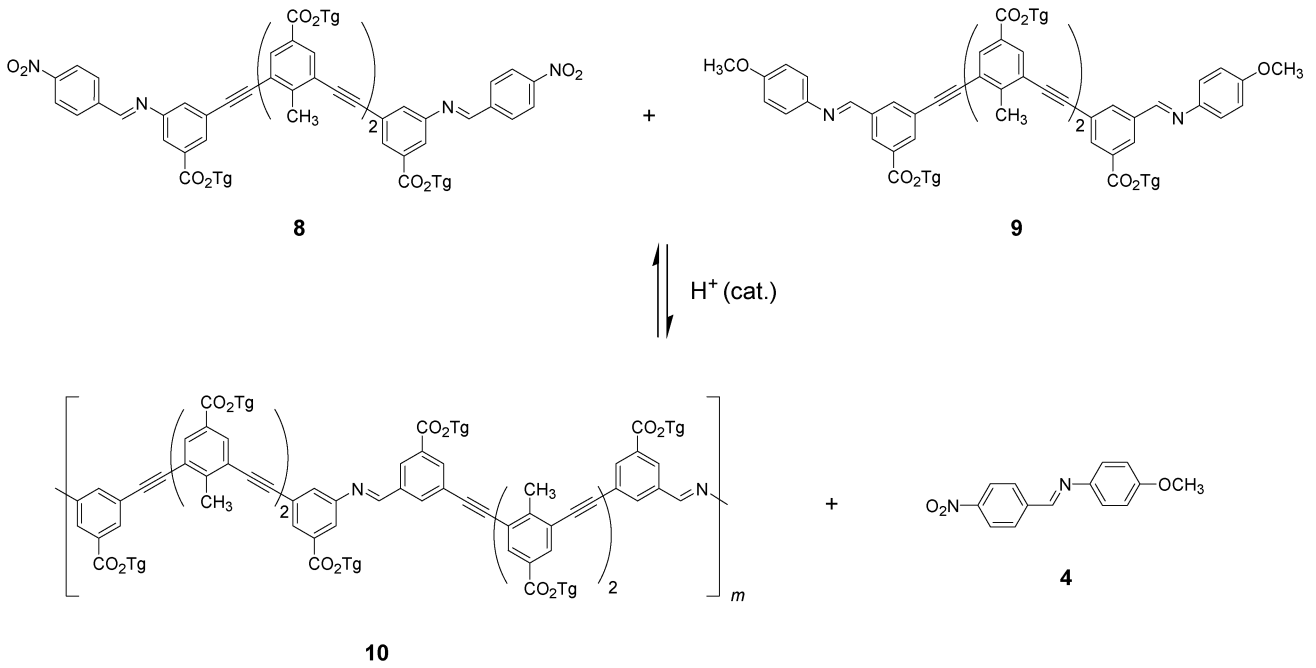


Figure 5. SEC traces of starter sequences **2** and **5** (a) and products following equilibration for 6 days at 5 mM and room temperature in chloroform (b) and acetonitrile (c).

Scheme 4



Starter Sequences with a Larger Polymerization Driving Force. Since the extent of equilibrium shifting is dependent on the stability of the polymer's solution conformation, higher molecular weights should be attainable from sequences giving rise to polymers that self-associate more strongly or fold with greater stability. Previous studies in our laboratory revealed that replacing the cavity-directed hydrogen atoms of the *m*-phenylene ethynylene oligomers with methyl groups generates a more stable folded structure.[16] The enhanced folding stability is attributed to the higher solvophobicity of the hydrocarbon backbone, which further strengthens the π-stacking interactions.[6,17] Therefore, a higher degree of polymerization should arise when corresponding methyl-substituted starter sequences are employed. To test this hypothesis, a new pair of starter sequences **8** and **9** (the methyl-substituted analogues of **1** and **2**) were synthesized and subjected to polymerization investigations (Scheme 4). For the purpose of simplifying the synthesis, only half of the phenylene units contained in **8** and **9** were substituted with methyl groups. Such a structural alteration was envisioned to increase solvophobicity to a degree that would cause a distinct molecular weight change in the products.

Oligomers **8** and **9** were prepared in a similar fashion as previously reported for **1** and **2**.[12] They were then reacted under the same metathesis conditions as applied to **1** and **2** (i.e., equilibration in catalytic solution at room temperature for 6 days before quenching with base). After analysis of the reaction products by SEC, it was apparent that the methyl-containing polymers afforded a higher number-average molecular weight (M_n) than the H-substituted analogues in the entire series of solvents investigated. However, when the weight-average molecular weights (M_w) were compared, the methyl modified sequences gave lower values than their H analogues in ethyl acetate and acetonitrile (Table 2).[18] These unexpected observations were explained upon examining the product molecular weight at prolonged reaction times (Figure 6). In solvents such as chloroform, THF and dioxane that furnish low to medium molecular weight products, no discernible change in molecular weight distribution occurred after 6 days indicating that the equilibrium state had been reached in each case. However, much higher molecular weight products were observed in acetonitrile solution after the reaction was allowed to equilibrate for 44 days at room temperature. Further extending the reaction time revealed that in either methyl acetate or ethyl acetate, equilibrium could be reached within approximately 19 weeks,[19] while in acetonitrile the product molecular weight continued growing slowly even after 25 weeks at which point the monitoring was stopped (Figure 6). On the basis of the molecular weight data from these experiments (Figure 7 and Table 2), it can be concluded that given sufficient reaction time to reach the equilibrium much higher molecular weights are achieved by the methyl-substituted sequences in methyl acetate, ethyl acetate, and acetonitrile.[20] These results agreed with our original premise that the product molecular weight can becontrolled through structural modifications that vary the folding energy.

The significantly longer equilibration time required by the methyl-substituted sequences indicates much slower kinetics as these more solvophobic chains elon-

Table 2. Molecular Weight Data of Metathesis Products 3 and 10[a]

	3[b]		**10**					
solvent	M_n	M_w	M_n[b]	M_w[b]	M_n	M_w	M_n[c]	M_w[c]
$CHCl_3$	3.0	3.9	3.1	3.6				
THF	3.0	3.9	3.1	3.7				
1,4-dioxane	3.4	4.5	4.4	6.0				
MeOAc	5.8	10.3	12.0	27.0	18.1[d]	701[d]	21.6	268
EtOAc	7.5	34.0	13.3	27.8	19.9[d]	1470[d]	23.1	355
CH_3CN	13.5	350	18.7	41.7	33.5[e]	382[e]	40.0	234

[a] All molecular weight data are in kDa and metatheses were performed at 5 mM reactant concentration in the presence of 0.1 equiv oxalic acid. [b] Data were obtained after equilibrating reaction mixtures at room temperature for 6 days. [c] After equilibration at 40 °C for 6 days followed by 10 days at room temperature. [d] After equilibration at room temperature for 19 weeks. [e] After equilibration at room temperature for over 25 weeks (the equilibrium state may have yet to be reached).

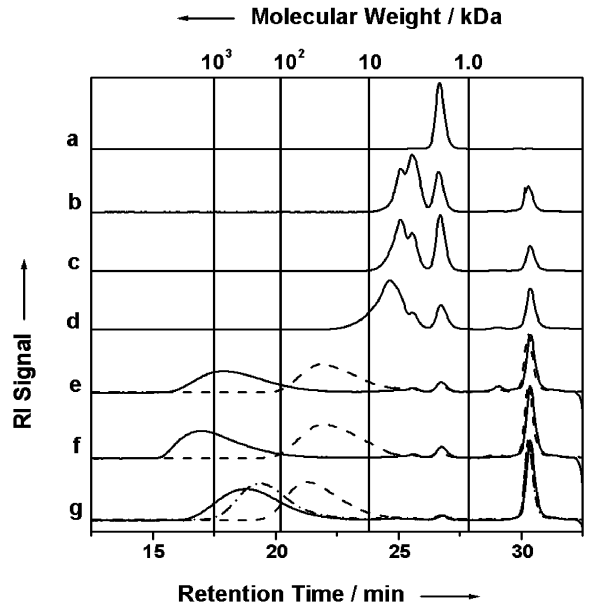


Figure 6. SEC traces of starter sequences **8** and **9** (a) and products equilibrated at 5 mM and room temperature in chloroform (b, 6 days), tetrahydrofuran (c, 6 days), dioxane (d, 6 days), methyl acetate (e, - - - 6 days; — 19 weeks), ethyl acetate (f, - - - 6 days; — 19 weeks) and acetonitrile (g, - - - 6 days; —·— 44 days; — 25 weeks) solutions. In trace a, starter sequences **8** and **9** coelute.

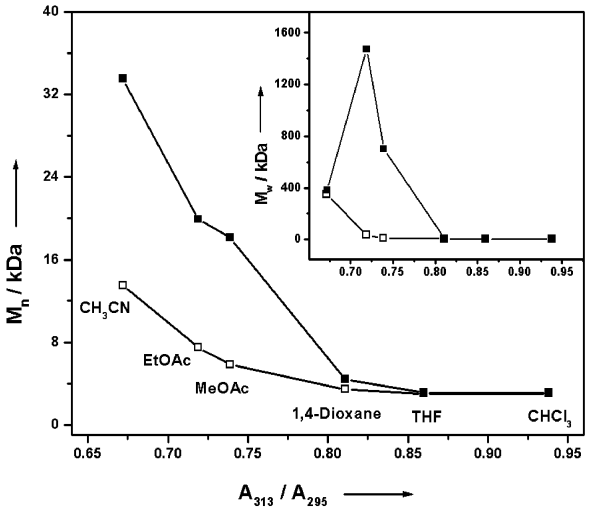


Figure 7. Molecular weight (number-average M_n (main plot) and weight-average M_w (inset)) of the metathesis products **3** (—□—) and **10** (—■—) vs the UV absorbance ratio A_{313}/A_{295} of a *m*-phenylene ethynylene oligomer in given solvents.

gate. On the basis of this observation, we hypothesize that the metathesis of the imine bond may require at least partial unfolding the *m*-phenylene ethynylene chain. Under conditions that strongly stabilize the helical conformation, the unfolded state is considerably disfavored. Thus, a larger energy barrier must be overcome before additional stabilizing energy can be attained from incorporation of more monomer units. Consequently, chain elongation is kinetically impeded. An alternative explanation is that intermolecular association, which is absent or less severe in the case of H-substituted sequences,[11a] becomes significant for the more solvophobic backbone in polar media. In either case, slow kinetics of metathesis likely resulted from disfavored dissociation and the imine bonds buried within stacked helices.

Additional evidence for slow kinetics came from experiments with metathesis between **8** and **9** at varied temperatures. At a given equilibration time (e.g., 6 d), the molecular weight of polymer **10** was found to increase with the reaction temperature up to 30 °C; however, it decreased at even higher equilibration temperatures (Figure 8). This result suggests that the observed lower molecular weight of the more stabilized polymer is a kinetic rather than thermodynamic limitation. At elevated temperatures the unfolded state (or the dissociated state of the aggregated species) becomes more accessible and chain elongation via metathesis is facilitated. The rate at which equilibrium is approached increased and higher molecular weight products were achieved within a shorter period of time. On the other hand, although increasing the reaction temperature increases the approach to equilibrium, the thermodynamic stability of the folded conformation is probably reduced at higher temperature, leading to a diminished molecular weight at equilibrium. Therefore, the maximum observed in the molecular weight as a function of temperature can be rationalized as slow kinetics at low temperature and decreased stability at high temperature. Further investigations at elucidating the kinetics of this polymerization are underway.

Since raising the temperature was effective in accelerating the approach to equilibrium, efforts were made to modify the polymerization procedure for **8** and **9** in order to achieve high molecular weight within a reasonable period of equilibration time. As the experimental results showed that heating the catalyzed reactant mixture at 40 °C for 6 days followed by equilibration at room temperature for ca. 10 days generates products with a molecular weight close to that obtained at the most prolonged equilibration time (Table 2), the subsequent polymerizations of **8** and **9** in a series of chloroform/acetonitrile binary solvent mixtures were all conducted under such modified conditions (Figure 9). Although the equilibrium state is most likely not reached by the end of 16 days in the solvents with a high acetonitrile composition, these experiments allowed us to obtain information on the product molecular weight close to equilibrium at room temperature. The molecular weight variation of **10** with solvent composition was compared to that of **3**. As the plot in Figure 10 shows, an escalation of the average molecular weight occurred at higher chloroform composition for **10** than for **3**, and an overall higher molecular weight was obtained from the methyl-substituted polymers than from the parent analogues at corresponding solvent composition (except for M_w in pure acetonitrile).[18] Thus, even though the equilibrium may not have been reached for the methyl-substituted polymers in high acetonitrile composition solutions, these results are consistent with our expectation of higher molecular weight polymers arising from better stabilized, folded structures. Again, the drop in molecular weight at high acetonitrile composition was likely a consequence of slow kinetics with an insufficient equilibration time.

Conclusion

The solvent and sequence effects on the closed-system reversible, imine metathesis polymerization of *m*-phenylene ethynylene oligomers have been investigated. In these polymerizations, the folding or collapsing of the

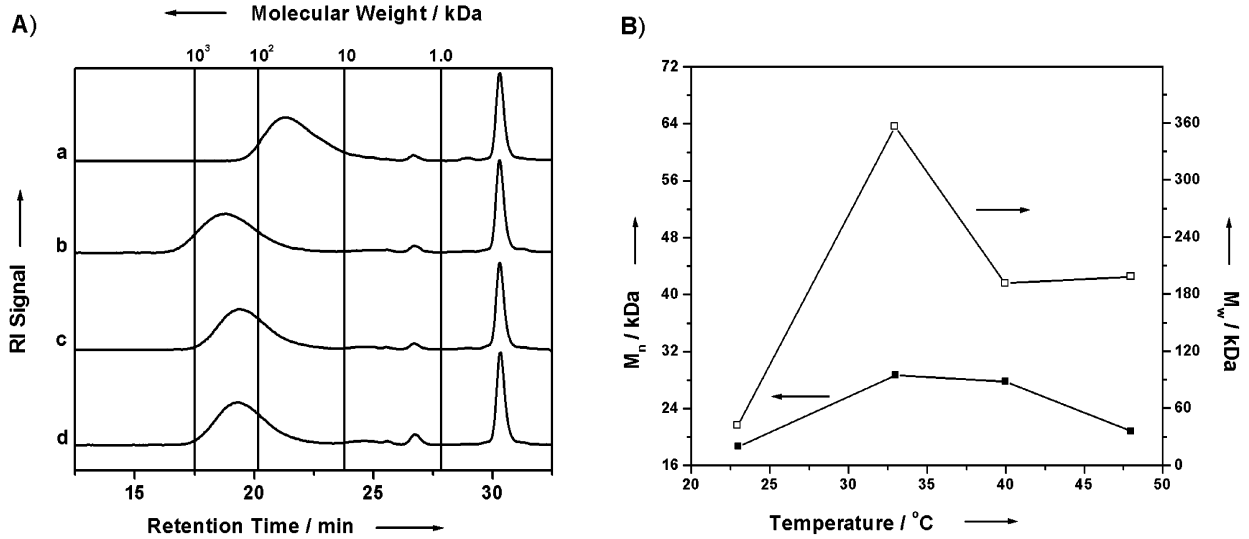


Figure 8. SEC traces (A) and corresponding molecular weight of metathesis products **10** equilibrated at 5 mM in CH_3CN for 6 days at 23 (a), 33 (b), 40 (c), and 48 °C (d).

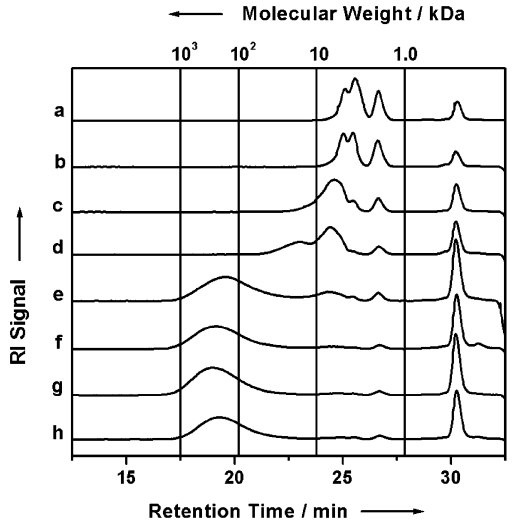


Figure 9. SEC traces of metathesis products **10** equilibrated at 5 mM for 6 days at 40 °C followed by 10 days at room temperature in $CHCl_3$ (a), $CHCl_3/CH_3CN$ (vol % of $CHCl_3$: b, 75%; c, 50%; d, 25%; e, 22%; f, 12.5%; g, 5%), and CH_3CN (h) solutions.

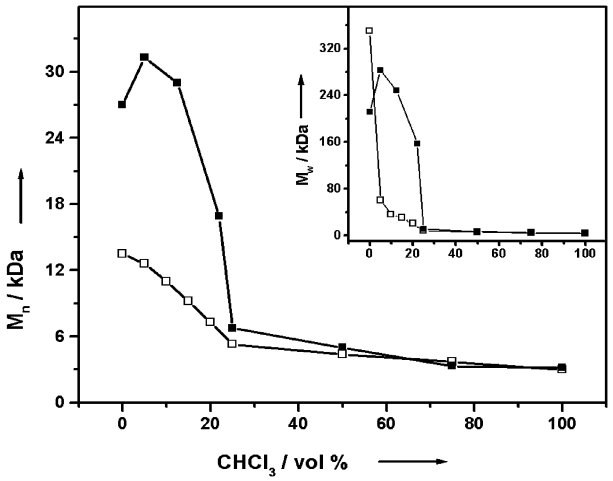


Figure 10. Molecular weight (number-average M_n (main plot) and weight-average M_w (inset)) of metatheses products **3** (—□—, equilibrated at room temperature for 6 d) and **10** (—■—, equilibrated for 6 days at 40 °C followed by 10 days at room temperature) at 5 mM in $CHCl_3/CH_3CN$ mixtures.

polymer chain was shown to provide a sufficient driving force to push the equilibrium toward high polymers. By means of tuning the solvent quality and/or temperature, the folding propensity of *m*-phenylene ethynylene imine chains can be modulated, and as a result, the control over the molecular weight of the resulting polymers can be achieved. By varying the chain length of the starter sequences, macrocyclization can be either favored or circumvented. When the chain growth proceeds via an oligomeric intermediate containing six *m*-phenylene units, macrocycles form exclusively. This was attributed to the stabilization of the intermolecular aggregates by solvophobic and π-stacking interactions. When the starter sequence lengths do not allow the formation of the hexameric macrocycle, chain elongation into polymers dominates. Besides the chain length, the structural characteristics of the starter sequence strongly influence the kinetics and equilibrium state of the final product. Improving the folding capability of *m*-phenylene ethynylene chain resulted in higher molecular weight polymers. This agrees with the folding-driven nature of the polymerization.

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Supporting Information Available: Text giving calculations on molecular weight distribution of a reversible polymerization based on statistical methods, syntheses, and characterization data of **5**, **6**, **8**, and **9** and a scheme showing the syntheses of these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Small variations in the values of M_n and M_w observed in a number of cases shown here result from different polydispersities. Number average molecular weight value is much more sensitive than weight average molecular weight to the presence of the nonfoldable, low molecular weight oligomers. The stability and correspondingly the relative amount of these short oligomers vary with solvent and temperature conditions in a different manner than the long, foldable polymers. This inconsistency complicated the distribution of the products, which leads to the variation in M_n and M_w. For example, the narrow distribution of **10**, in which nearly all the low molecular weight species that are present in **3** have disappeared, gives rise to the higher M_n. Polymer **3** obviously contains some high molecular weight components that are absent from **10**, which accounted for the higher M_w of **3**.

(19) Equilibrium may have been reached in methyl acetate and ethyl acetate in less than 19 weeks, but the product was not monitored day-to-day. The equilibration time and the molecular weight were also found to be sensitive to the amount of water introduced into the system; longer reaction times corresponding to higher molecular weights were necessary for reactions in solvents that had been rigorously dried.

(20) The lower M_w observed in acetonitrile compared to methyl acetate and ethyl acetate is mostly likely the result of a very slow approach to equilibrium in this solvent.

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