REVIEW

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Cage-Shaped Polymers Synthesis: A Comprehensive State-of-the-Art

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Dedicated to Rudolf Zentel on the occasion of his retirement.

Researchers have dedicated their efforts for the creation of a wide choice of complex and precise macromolecular architectures over the past 100 years. Among them, cyclic polymers benefit from their absence of terminal chains and from their singular topology to minimize their hydrodynamic volume in solution, increase their chemical stability, limit their number of possible conformations as well as a reduce their propensity to crystallize or to form entanglements in comparison to their acyclic counterparts. While monocyclic structures have already been widely investigated and reviewed, reports on more complex polycyclic structures are rare. In this regard, cage-shaped polymers—consisting of at least three polymer chains covalently interconnected through strictly two junction points—have received little attention over the past two decades. Although their synthesis is a worthy challenge, only a few synthetic methodologies of polymer cages were successfully developed so far. Thus, this review intends to highlight the key concepts of the conception of cage-shaped polymers in addition to propose an actual and exhaustive state-of-art concept of their synthesis to rationally promote the next-generation synthesis strategies.

1. Introduction

This review focuses specifically on the synthesis of cage-shaped polymers and by extension does not cover the synthesis of other complex cyclic polymer topologies. In a general manner, the synthesis of cyclic polymers can occur either by topological conversion of an acyclic polymer precursor via post-polymerization ring closing reaction or by ring-extension of a preexisting low-molecular cyclic initiator.[1–3] In analogy, the synthesis of covalently-bound polymer cages was expected to follow the same scheme. However, while several examples of polymer cage formations by topological conversion were reported since the beginning of the 20th century, only one example of a polymer cage obtained through the arm-expansion of low molecular polycyclic precursors was reported so far. In comparison to monocyclic polymer synthesis, the generation of polymer cages was found to be much more challenging, as it enforces more synthetical restrictions and suffers from an additional high predisposition to cross-link into networks. As a result, the diversity of synthesis approaches is still very much limited. This is why, in a concern of promoting the upcoming developments in this research area, it is crucial to critically look back at what has been accomplished so far before stepping forward. To do so, the different approaches were categorized in five subsequent sections, constituting and structuring the rest of this review, as summarized in **Scheme 1**.

2. Intermolecular Topological Conversion with Preorganization

Historically, the first example of isolated three-arm cage-shaped polymers was reported by Tezuka and Oike in the early 2000s.[4,5] Taking advantage of the electrostatic self-assembly and covalent fixation (ESA-CF) methodology, which they had previously codeveloped, a large library of exotic topologies was progressively constituted by simple variation of the nature and number of the ionic functionalities present in each precursor.[6,7] This method is based on the intermolecular electrostatic preorganization in high dilution of a mixture of macromolecules and low-molecular weight linkers, which create an electrostatic template for a subsequent formation of covalently-linked complex topologies. Once the polymer salt dissolved in a liquid medium, large electrostatic

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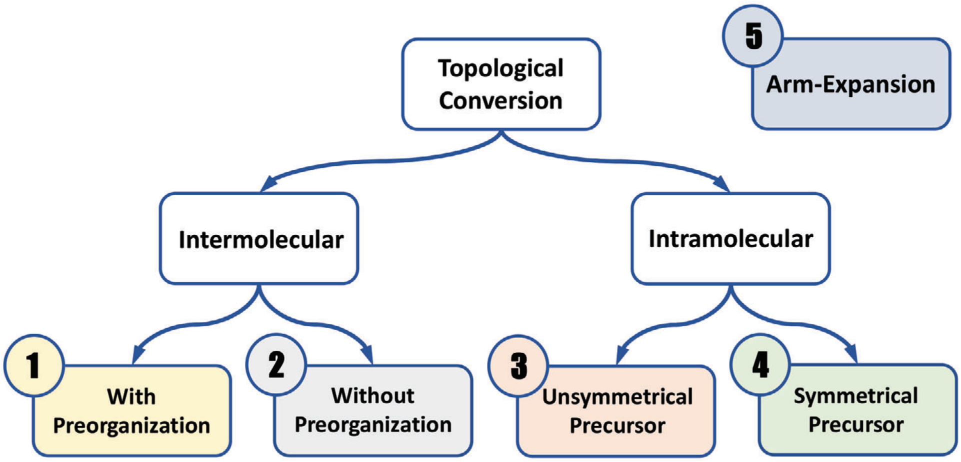


Scheme 1. Classification of all cage-shaped polymer synthesis methods into five subcategories.

Table 1. Intermolecular topological conversions with preorganization.

Entry	Closing system	Polymer type closing reaction	N° arm	Isolated yield [%]	Isolated mass [mg]	M_n, ^{1}H-NMR [kg mol^{-1}]	$Đ_{SEC}$
1a	$3A_2 + 2B_3$	PTHF/ESA-CF	3	15[a)]	n/a	13	1.11[a)]
1b	$A_3 + B_3$	PTHF/ESA-CF	3	52	n/a	14	1.06
2	$A_3 + B_3$	PTHF/ESA-CF	3	49	11.0	7.3	1.10
	$A_3 + B_3$	PTHF/ESA-CF	3	40	9.0	9.6	1.16
	$A_3 + B_3$	PTHF/ESA-CF	3	42	9.4	11.9	1.07
3	$A_4 + 2B_2$	PTHF/ESA-CF	3	4[b)]	5.0[b)]	9.2	n/a[b)]
	$A_4 + 2B_2$	PTHF/ESA-CF	3	3[b)]	3.1[b)]	9.1	n/a[b)]

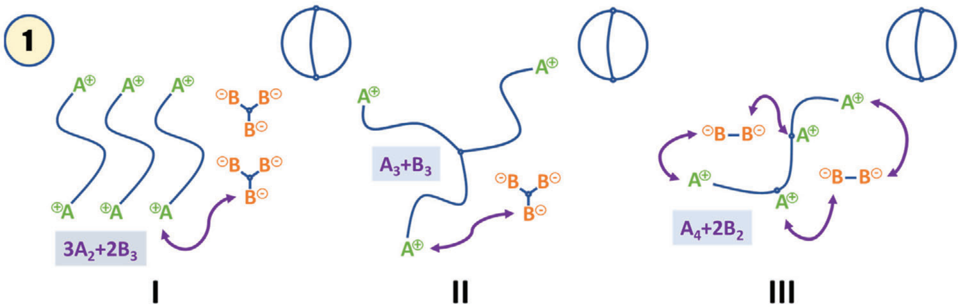
[a)] Values extrapolated from an isolated mixture of both cage- and barbell-shaped topologies. [b)] Values extrapolated from an isolated mixture mainly composed of eight-shaped polymer with minor barbell-shaped and cage-shaped polymers as side-products.

networks are kinetically favored. However, due to the dynamic exchange taking place between the solvated ionic species, the intermolecular connections within the network constantly reorganize themselves. Coupled with the diffusion resulting from the Brownian motion, the charged species progressively diffuse homogenously through the liquid until, below a critical polymer concentration limit, the formation of discreet electrostatic complexes becomes thermodynamically favored. Ultimately, once the equilibrium is reached, the covalent fixation of the electrostatic templates can be initiated by a thermal treatment, yielding the desired topology. Thus, three-arm polymer cages were assembled by ESA-CF from three-arm star-shaped poly(tetrahydrofuran) (PTHF) bearing cyclic quaternary amine end groups and trifunctional carboxylate linkers. Once the thermodynamic equilibrium was reached in high dilution, the $A_3 + B_3$ pairs were covalently linked in isolated yields between 40% and 52% (**Table 1**, Entries 1b–2 and **Scheme 2**,I).[4,5]

A second approach for the generation of three-arm polymer cages based on the same chemistry was reported shortly after from the same authors (Table 1, Entry 1a and Scheme 2,II).[4] The thermodynamic equilibrium took place between three telechelic linear polymer-chains and two trifunctional linkers in a $3A_2 + 2B_3$ intermolecular system. However, the reaction resulted in a 67% yield of a topological mixture which constituted of 78% intramolecularly favored barbell-shaped polymer cages and only of 22% three-arm polymer cages, yielding an extrapolated low 15% yield for cage polymers. More recently, a third example of three-arm cage-shaped polymer from a tetra-functionalized linear polymer and two bifunctional linker was reported (Table 1, Entry 3 and Scheme 2,III).[8] However, once again the reaction led to a mixture of polymer topologies mainly composed of eight-shaped polymers with minor barbell-shaped and cage-shaped polymer traces detectable by size exclusion chromatography (SEC) analysis. Nevertheless, although being restricted to the milligram-scale and necessitating some synthetical efforts to produce the ionic precursor species in high purity, the ESA-CF methodology shines by its unique ability to produce—beyond polymer cages—a large library of complex cyclic topologies.[6,7]

3. Intermolecular Topological Conversion without Preorganization

Unlike the previously discussed examples, the syntheses of polymer cages that involve an intermolecular step without any kind of preorganization strongly suffer from undesired competitive cross-linking, which ultimately leads to network formation. Thus, the topological conversion of two distinct four-arm star-shaped poly(ethylene oxide) (PEO) polymers, each end functionalized with *N*-hydroxysuccinimide (NHS) activated esters and primary amines, respectively, into an expected large four-arms cage was reported recently by Matsushita and colleagues (**Table 2**, Entry 4 and **Scheme 3**,I).[9] While the purification procedure



Scheme 2. Schematic overview of all intermolecular topological conversions with preorganization.

Table 2. Intermolecular topological conversion without preorganization.

Entry	Closing system	Polymer type closing reaction	N° arm	Isolated yield [%]	Isolated mass [mg]	M_{n}, ^{1}H-NMR [kg mol^{-1}]	$Đ_{\mathrm{SEC}}$
4	$A_4 + B_4$	PEO/NHS ester	4	0.5[a]	10	20.6[d]	1.08
5	$A_3 + B_3$	PS/CuAAC	3	37[b] /[d]	n/a	5.2[c]	n/a
	$A_3 + B_3$	PS/CuAAC	3	45[b] /[d]	n/a	8.2[c]	n/a
	$A_3 + B_3$	PS/CuAAC	3	48[b] /[d]	n/a	9.1[c]	n/a
6	$A_3 + B_3$	PS/CuAAC	3	17[a]	166	6.3[d]	n/a
	$A_3 + B_3$	PS/CuAAC	3	30[b] /[d]	n/a	4.2[d]	n/a
7	$A_4 + B_4$	PS/CuAAC	4	81[b] /[d]	n/a	6.7[d]	1.01
8	$A_4 + B_4$	PS/CuAAC	4	65[b] /[d]	n/a	6.8[d]	n/a
	$A_4 + B_4$	PS/CuAAC	4	51[b] /[d]	n/a	7.2[d]	n/a
9	$A_4 + B_4$	PS/CuAAC	4	63[b] /[d]	n/a	6.0[e]	n/a
10	$A_4 + B_4$	ϵ-PCL/DSPAAC	4	73[a]	89	4.1[d]	1.04
	$A_6 + B_6$	ϵ-PCL/DSPAAC	6	71[a]	85	6.2[d]	1.05

[a] Isolated yield; [b] Yields extrapolated from a mixture of topologies; [c] Estimated by ^{1}H-NMR; [d] Estimated by SEC; [e] Estimated by LS.

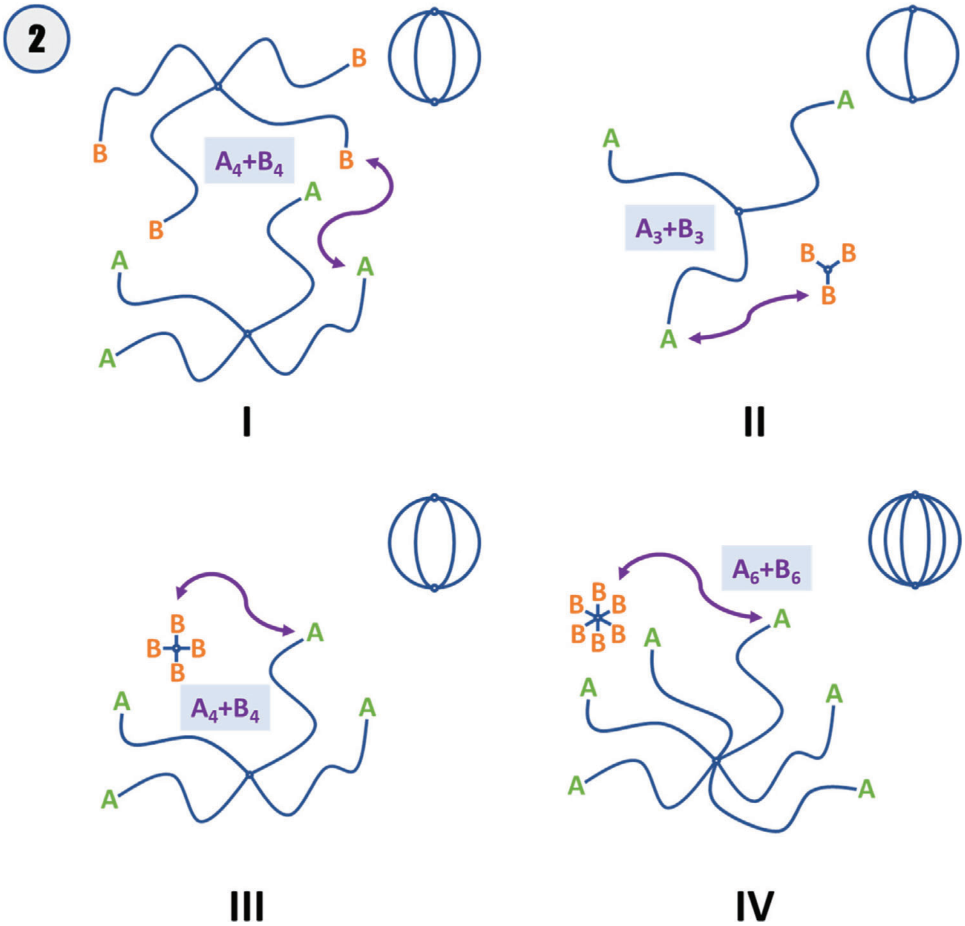
taking advantage of the interaction of α-cyclodextrin with chain-end PEOs is worth of interest, the $A_4 + B_4$ intermolecular topological conversion resulted in an extremely low 0.5% yield, that is, circa 10 mg product for 1.8 g of starting material. This particular example illustrates well the limitation of intermolecular systems, which do not include any preorganization to reduce network formation as intermolecular reactions are needed but have to be avoided at the same time to yield the desired product.

A few years earlier, the syntheses of three-[10,11] (Table 2, Entries 5 and 6 and Scheme 3,II) and four-arm[12–14] (Table 2, Entries 7–9 and Scheme 3,III) polystyrene (PS) cages through a combination of atom transfer radical polymerization (ATRP) and copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) were reported by Paik and coworkers. All topological conversions were designed to occur via intermolecular coupling between azide end functionalized star-shaped polymer precursors and tri- or tetra-functional alkyne linkers. However, despite the 17% yield reported for a three-arm polymer,[10] no information on the isolated yields was given. Instead, the yields were mainly extrapolated from SEC analysis. Considering the natural propensity of this kind of topological conversion to yield networks, it has to be feared that only the weakly crosslinked and discreet topologies might be able to eluate through the SEC column. In this regard, these values might not be sufficient to determine the efficiency of the topological conversion. In addition, the topological purity not only impacts the reaction yield but also the quality of the obtained material, and therefore only the characterizations obtained from a previously isolated topology should be ideally taken into account. Finally, all given molecular masses were only estimated either by SEC or light scattering (LS), and the values of dispersity for the cage-shaped polymers were almost never mentioned, making any comparison with other polymer cage synthesis very difficult.

Nonetheless, an additional synthesis of cage-shaped polymers by triazole formation was more recently reported by Zhang et al. (Table 2, Entry 10 and Scheme 3,III,IV).[15] Based on self-accelerating double-strain promoted azide-alkyne click reactions (DSPAAC), their work consisted of the synthesis of azide end-functionalized star-shaped poly(ϵ-caprolactone)s (ϵ−PCL) obtained by ring-opening polymerization (ROP). The polymer precursors were then reacted with small linkers containing two or three sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD) subunits to obtain the respective 4- and 6-arm polymer cages. Thanks to the fast kinetics of the double-strain promoted azide-alkyne click reactions (DSPAAC) reaction, the topological conversion was achieved in good yields (i.e., 71–73%) at the price of a more demanding linker synthesis than comparative studies.

4. Intramolecular Topological Conversion from an Asymmetrical Precursor

To overcome the intermolecular drawbacks, intramolecular topological conversions, which occur within a unique precursor macromolecule, were investigated. Taking advantage of their concentration-independent kinetics, unimolecular topological



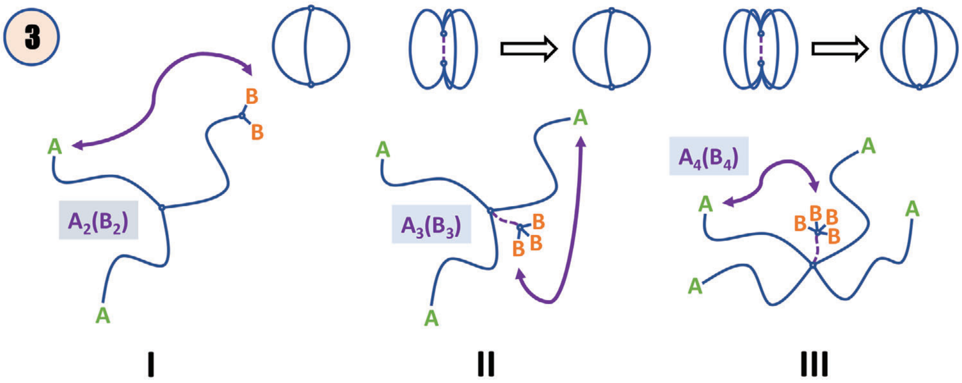
Scheme 3. Schematic overview of all intermolecular topological conversion without preorganization.

conversions were employed in a high dilution condition to suppress the undesired intermolecular side-reactions without impacting their intramolecular reaction rate. While their synthesis suffered from being usually more complex and challenging than their intermolecular analogues, the intramolecular closing systems can be further subdivided in two distinct groups in respect to their complexity. Thus, if the use of low or non-symmetrical precursors tends to be easier to conceptualize, their synthesis turns out to be usually particularly challenging. On the contrary, the synthesis of precursors with a high degree of symmetry in their structure are less resource- and time-demanding, but require more care in their conception to ensure an efficient topological conversion. The unsymmetrical intramolecular precursors are discussed in more detail below while the symmetrical ones will be subsequently addressed in Section 5. A pioneering example of unsymmetrical precursors that reacted intramolecularly to deliver polymer cages was reported by Pan and Shi in 2009 (**Table 3**, Entry 11 and **Scheme 4**,I).[16] This specific example was based on the synthesis of a series of four different three-arms A_2B miktoarm star-shaped polymers consisting of one ϵ-PCL and two PS arms obtained by ROP and atom transfer radical polymerization (ATRP), respectively. The intramolecular topological conversion was performed by CuAAC reaction in an $A_2(B_2)$ manner via the slow addition of the precursor polymer into the reaction medium. It is particularly interesting to note that the term of theta-shaped polymer was preferred to the one of cage-shaped by the authors, due to the independent length of the PS and ϵ-PCL arms, respectively. However, the authors failed to report yields for the higher molecular weight theta-shaped polymers, and the absence of any network removal measures before the given isolated 70% yield along the monomodal SEC trace leaves uncertainties about the reaction workup. Alternatively, an intramolecular approach involving unsymmetrical trefoils- and quatrefoils shaped polymer precursors was later proposed by Satoh et al. in 2016 (Table 3, Entry 12 and Scheme 4,II,III).[17] In order to prepare the precursors, tri- and tetra-functional ROP initiators bearing three and four azide groups, respectively, separated by a benzyl linker were first synthetized. Subsequently, ROP and the introduction of terminal alkynes at each arm chain ends by post-polymerization modification were performed. The intramolecular topological conversions of the respective three and four-arm star polymers into trefoils- and quatrefoils shaped polymers were then achieved by CuAAC. This first topological conversion was directly followed by the palladium-catalyzed cleavage of the benzyl linker to finally form three- and four-arm polymer cages. This initial work was expanded in 2021 with the analysis of three polymer cages consisting of diblock copolymer and triblock terpolymer chain-arms, respectively (Table 3, Entry

Table 3. Intramolecular topological conversions from asymmetrical precursor.

Entry	Closing system	Polymer type Closing reaction	N° arm	Isolated yield [%]	Isolated mass [mg]	M_n, ^{1}H-NMR [kg mol^{-1}]	$Đ_{SEC}$
11	$A_2(B_2)$	star-(PS; PCL)/CuAAC	3	70	70	9.4$^{a)}$	1.12
	$A_2(B_2)$	star-(PS; PCL)/CuAAC	3	n/a	n/a	16.5$^{a)}$	1.10
	$A_2(B_2)$	star-(PS; PCL)/CuAAC	3	n/a	n/a	19.2$^{a)}$	1.09
	$A_2(B_2)$	star-(PS; PCL)/CuAAC	3	n/a	n/a	27.0$^{a)}$	1.09
12	A_3B_3	PBO/CuAAC	3	48	78	3.3$^{b)}$	1.04
	A_3B_3	$^{c)}$/CuAAC	3	72	511	22.9$^{b)}$	1.03
	A_4B_4	PBO/CuAAC	4	78	359	3.8$^{b)}$	1.02
	A_4B_4	$^{c)}$/CuAAC	4	61	336	23.4$^{b)}$	1.02
13	A_3B_3	$^{c)}$/CuAAC	3	66	592	22.6$^{b)}$	1.02
	A_3B_3	$^{c)}$/CuAAC	3	31	337	22.6$^{b)}$	1.02
	A_3B_3	$^{c)}$/CuAAC	3	69	719	22.6$^{b)}$	1.03

$^{a)}$ Estimated by SEC; $^{b)}$ Estimated by ^{1}H-NMR; $^{c)}$ Poly(*n*-decyl glycidyl ether)-*block*-poly[2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether].



Scheme 4. Schematic overview of all intramolecular topological conversions from asymmetrical precursors.

13 and Scheme 4,II).[18] Nevertheless, although both approaches are elegant in their conception, the particularly high number of preliminary steps prior to their cage shaped synthesis makes further development in a similar direction particularly arduous.

5. Intramolecular Topological Conversion from Symmetrical Precursors

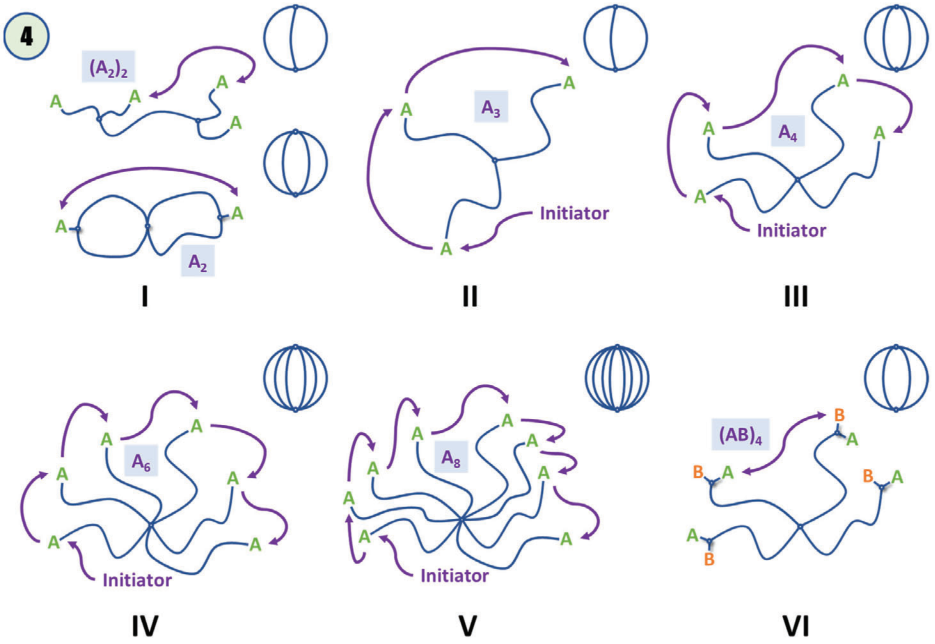
As previously mentioned in Section 4, not all precursors require high synthetical investment due to the introduction of a higher degree of symmetry within their structure. In this regard, the first two examples of polymer cages obtained by intramolecular conversion of symmetrical precursors were published both by Tezuka and colleagues in 2005 (**Table 4**, Entries 14 and 15 and **Scheme 5**,I).[19,20] The synthesis of the H- and eight-shaped poly(tetrahydrofuran) PTHF precursors bearing four and two terminal alkene groups, respectively, were achieved by ESA-CF, before being intermolecularly converted into three- and four-arm polymer cages by ring-closing metathesis (RCM) in high dilution conditions. While the eight-shaped polymer topological conversion resulted in a good 67% yield, the H-shaped precursor approach suffered from the competitive formation of barbell-shaped polymers as the major product, negatively impacting the reaction yield to 20% requiring product isolation by preparative SEC.

However, none of these two examples reached the simplicity and efficiency expected for symmetrical precursors. Actually, it was only recently that the intramolecular topological conversion from simple and symmetrical precursor truly matured when Satoh and coworkers proposed the intramolecular closing step by ring-opening metathesis oligomerization (ROMO) of norbornene end functionalized ϵ-PCL stars in 2019 and 2021 (Table 4, Entries 16 and 17 and Scheme 5,II–V).[21,22] While the addition of the 3rd generation Grubbs catalyst on the first arm is strictly speaking an intermolecular process, the kinetic of the following oligomerization was found to be fast enough to make a second catalyst addition unlikely. Thus, once the stoichiometric ratio between polymer and catalyst was optimized to [1:6], the reaction proceeded with an intramolecular-like kinetic in a strict oxygen-free atmosphere. In this way three-, four-, but also six-, and eight-arm ϵ-PCL cages with various molecular weights were obtained in very high isolated yields comprised between 80% and 99%. Also, by further twisting the reaction conditions, the authors were able to create graft(cage-shaped) polymers with $M_{n,MALS}$ up to 303 and 95 kg mol^{-1} for graft(3- and 4-arm cage-shaped) polymers, respectively (**Scheme 6**,I,II).[23]

This major breakthrough is not only the first example of cages possessing more than four arms, but constitutes also an efficient way to synthetize polymer cages with virtually any number of arms. In fact, only the prerequisite to obtain defect-free

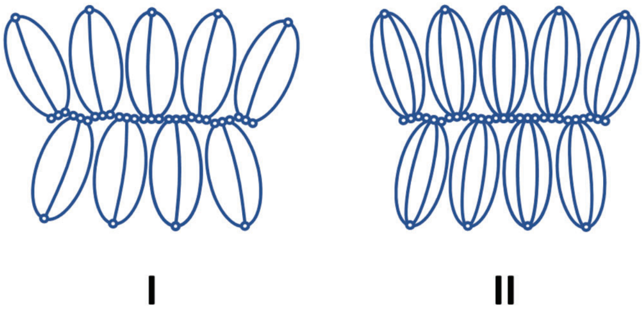
Table 4. Intramolecular topological conversion from symmetrical precursor.

Entry	Closing system	Polymer type closing reaction	N° arm	Isolated yield [%]	Isolated mass [mg]	M_n, ^{1}H-NMR [kg mol^{-1}]	$Đ_{SEC}$
14	A_2	PTHF/RCM	4	67	20.2	10.6	1.18
15	A_4	PTHF/RCM	3	20	14	14.7	n/a
16	A_3	ϵ-PCL/ROMO	3	92	27.6	6.1	1.09
	A_3	ϵ-PCL/ROMO	3	80	24.0	8.0	1.09
	A_3	ϵ-PCL/ROMO	3	84	25.2	10.7	1.09
	A_4	ϵ-PCL/ROMO	4	97	29.1	6.1	1.08
	A_4	ϵ-PCL/ROMO	4	94	28.2	8.9	1.08
	A_4	ϵ-PCL/ROMO	4	91	27.3	10.4	1.08
	A_6	ϵ-PCL/ROMO	6	91	27.3	6.1	1.08
	A_6	ϵ-PCL/ROMO	6	99	29.7	9.5	1.09
	A_6	ϵ-PCL/ROMO	6	91	27.3	11.9	1.07
	A_8	ϵ-PCL/ROMO	8	98	29.4	7.4	1.06
	A_8	ϵ-PCL/ROMO	8	98	29.4	9.6	1.08
	A_8	ϵ-PCL/ROMO	8	85	25.5	13.2	1.06
17	A_3	ϵ-PCL/ROMO	3	68	74.5	10.6	1.08
18	$(AB)_4$	ϵ-PCL/CuAAC	4	78	39	5.3	1.08
	$(AB)_4$	ϵ-PCL/CuAAC	4	72	36	7.3	1.06
	$(AB)_4$	ϵ-PCL/CuAAC	4	64	32	10.5	1.08
	$(AB)_4$	ϵ-PCL/CuAAC	4	36	18	14.6	1.07
19	$(AB)_4$	PEO/CuAAC	4	43	1548	6.4	1.14



Scheme 5. Schematic overview of all intramolecular topological conversions from symmetrical precursor.

polymer stars as well as end functionalization fidelity might limit the number of arms. Furthermore, as long as the end functionalization with norbornene remains effective, the functional tolerance of the 3rd generation Grubbs catalyst ensures a large scope of polymer composition and functionalization. Thenceforth, a critical question has been raised whether the synthesis of polymer cages on the milligram-scale could have reached an optimal efficiency through the ROMO approach. On the contrary, once aiming for larger scales, the necessity to quench the living oligomers to prevent further cage oligomerization prior to any further precursor addition suppresses the possibility to run the reaction in semi-batch mode, making



Scheme 6. Schematic representation of I) graft(3-arm cage-shaped) and II) graft(4-arm cage-shaped) polymers.

any gram-scale material synthesis and subsequent tangible application unlikely.

In line with this statement, a new intramolecular strategy to obtain polymer cages was recently proposed by our research group (Table 4, Entries 18 and 19 and Scheme 5,VI).[24,25] Starting from alkyne-azide end-bifunctionalized symmetric four-arm ϵ-PCL stars, the topological conversion was intramolecularly achieved by CuAAC tetramerization of the four end-groups into a thermodynamically favored D_{4h}-[3_4]triazolophane macrocycle, resulting in isolated yields between 36% and 78% depending on their molecular size. While this strategy is currently restricted to four-arm cage synthesis and therefore lacks the versatility of the previously mentioned ROMO approach, its real strength arises from its capacity to be easily upscaled with acceptable yields and precursor accessibility on the gram scale and in a semi-batch process. This approach can therefore be considered very relevant to investigate some possible applications related to these types of polymer cage architectures. In this sense, a first milestone to future applications was reached recently by synthesis of four-arm cage-shaped PEG in a single semi-batch process with 43% yield at the gram-scale (Table 4, Entry 19).[25] Taking advantage from the reduction of crystallinity in the cage PEG structure, its application as polymer electrolyte in lithium batteries was investigated.

However, even if there is no doubt that further intramolecular closing systems will be reported in the near future, further upscaling to multigram or even kilogram scale might remain out of reach by topological conversions and might be rather achieved by arm-expansion methods, as shown in Section 6.

6. Cage-Shaped Polymer Synthesis by Arm Expansion

Besides the topological conversion methods, the use of arm expansion methods might constitute a valuable alternative to efficient gram-scaled synthesis of high-molecular weight polymer cages without the requirement to work under high-dilution conditions in analogy to what has been reported for the synthesis of polymer rings.[1–3] In particular, ring-expansion mechanisms that occur by thermodynamically-driven monomer coordination/insertion polymerization though labile bonds are highly promising to achieve this purpose. However, most of these mechanisms could not simply be transferred to a polymer cage synthesis due to their inability to elongate three or more polymer chains simultaneously from a single reactive center. In this context, the only report of polymer three-arm cage synthesis achieved though arm-expansion was published—to the best of our knowledge—by Shea and coworkers in 2003 (**Table 5**, Entry 20 and **Scheme 7**).[26] Taking advantage of C1 methylene insertion-polymerization from a borane-adamantane precursor, high-molecular weight three-arm polyethylene (PE) cages with over 35 kg mol^{-1}, and low dispersities were obtained.

Table 5. Cage-shaped polymers obtained through arm-expansion.

Entry	Closing system	Polymer type polymerization method	N° arm	M_n [kg mol^{-1}]	$Đ_{SEC}$
20	Arm-expansion	PE/C1 methylene insertion	3	2.4$^{a)}$	1.06
	Arm-expansion	PE/C1 methylene insertion	3	5.6$^{a)}$	1.09
	Arm-expansion	PE/C1 methylene insertion	3	10.5$^{a)}$	1.08
	Arm-expansion	PE/C1 methylene insertion	3	19.6$^{a)}$	1.08
	Arm-expansion	PE/C1 methylene insertion	3	21.7$^{b)}$	1.12
	Arm-expansion	PE/C1 methylene insertion	3	35.4$^{b)}$	1.12

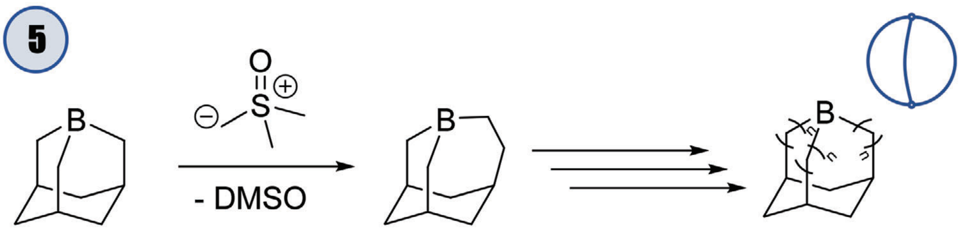
$^{a)}$ Estimated by SEC; $^{b)}$ Estimated by LS.

The mechanism of the polyhomologation consisted in the migration insertion of a methylene group to a trialkyl borane center. While the migration-insertion steps did not require any particular dilution to avoid network formation, the unstable nature of the trialkyl borane in presence of dioxygen or water strongly restricted the polymer characterization and applications of this specific polymer cage. Furthermore, besides the well-known solubility issue of polyethylene in organic solvents, two-third of the borane-adamantane precursors were reported to be kinetically trapped at low degree of polymerization due to the probability to lead to sterically hindered conformations.

Nevertheless, the use of similar arm-expansion methods might constitute in future an interesting alternative to the synthesis of covalently stable cage-shaped polymers at the multigram-scale, and therefore paving the way to further applications for polymer cages.

7. Conclusion

In conclusion, many generations of organic and polymer chemists focused their efforts during the last century on the synthesis of macrocyclic structures featuring unique sets of properties. Regardless of the nature of the final product, their concerted achievements constitute a solid basis allowing inter alia for the synthesis of even more sophisticated cyclic polymer architectures. Thus, several synthesis protocols for polymer cages were proposed since the early 2000s, resulting in a series of different polymer cages varying in composition, molecular mass, and the number of arms obtained through various synthesis protocols differing in reaction scale, yield, and accessibility. Nevertheless, the development and optimization of synthetical methods over the gram-scale will remain essential for the



Scheme 7. Schematic overview of all intramolecular topological conversions from symmetrical precursor.

concretization of any future potential applications related to cage-shaped polymer-based materials.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

arm expansion, cage polymers, cyclic polymers, cyclization, star polymers, topological conversions

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