



Feature Article

Topological polymer chemistry by programmed self-assembly and effective linking chemistry

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ARTICLE INFO

Article history:

Received 15 July 2010

Received in revised form 14 October 2010

Accepted 17 October 2010

Available online 17 November 2010

Dedicated to Professor Nikos Hadjichristidis

Keywords:

Topological polymer chemistry

Cyclic and multicyclic polymers

Electrostatic self-assembly and covalent

fixation (ESA–CF)

Metathesis reaction

Click chemistry

ABSTRACT

Ongoing challenges in topological polymer chemistry are reviewed. In particular, we focus on recent developments in an “electrostatic self-assembly and covalent fixation (ESA–CF)” process in conjunction with effective linking/cleaving chemistry including a metathesis process and an alkyne–azide click reaction. A variety of novel cyclic polymers having specific functional groups and unprecedented multicyclic macromolecular topologies have been realized by combining intriguing synthetic protocols.

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1. Introduction

The construction of sophisticatedly designed topologies has been a challenging issue in synthetic polymer chemistry. Particularly, cyclic topologies attract an increasing attention due to the distinctive properties arising from the unique structure that lacks chain ends [1]. For example, a monocyclic polymer, in comparison with the linear counterpart, has distinctive static and dynamic properties including a smaller hydrodynamic volume, less entanglement, and higher glass transition temperature as well as a non-reptational diffusion. Recently, new synthetic protocols have been developed to produce a variety of cyclic polymers of guaranteed purity, providing rational polymer materials designs relied on the novel topologies [2,3].

The most straightforward synthetic approach for ring polymers is a reaction between a linear polymer precursor having reactive groups, i.e., telechelics, and bifunctional coupling reagent [4]. This *bimolecular* cyclization protocol

should be performed with strictly equimolar amounts of the telechelics and coupling reagent in dilution. Consequently, this process is often considered unattractive in practice. Alternatively, *unimolecular* processes, which do not require the exact equivalence of two components, have been developed. Recently, Grayson et al. have prepared a telechelic polystyrene having an alkyne and an azide groups, which was subjected to the end-to-end polymer cyclization via click chemistry [5]. However, this methodology suffers from the synthetic difficulties to prepare asymmetric telechelics.

For the effective construction of cyclic polymer topologies, we have developed an *electrostatic self-assembly and covalent fixation* (ESA–CF) process using a linear or star telechelic precursor having cyclic ammonium salt end groups accompanied by a plurifunctional carboxylate counterion [6–8]. The self-assembly of telechelic polymer precursors through non-covalent interactions, typically with ionic salt groups [9,10] with multiple hydrogen-bonding groups [11,12], or with transition metal–ligand complexes [13] has been exploited to provide polymer materials exhibiting unique properties in solution and in bulk due

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to their dynamic equilibrium nature. In the ESA–CF process, the combination of a set of the telechelic prepolymers and counteranions forms a predesigned self-assembly via the electrostatic interaction, in which the initially resulted kinetic agglomerate restructures into a thermodynamically favored ionic complex with the smallest number of components in dilution by keeping the balance of the electric charges. Subsequently, the solution was heated to cause the selective ring-opening reaction of the cyclic ammonium end groups by the carboxylate counterion to construct covalently linked polymer topologies (Scheme 1) [6].

This methodology has been demonstrated to produce a variety of polymers, such as polytetrahydrofuran (poly(THF)) [6], polyethylene glycol [14], polystyrene [15], and polydimethylsiloxane [16] using the relevant prepolymers obtained by living polymerization and subsequent transformation of end groups. Furthermore, a monocyclic polymer possessing a prescribed functional group at a designated position was also prepared by making use of either a telechelic precursor having a functional group or dicarboxylate counterion with a functional group [17]. Such prepolymers, namely *kyklo*-telechelics, thus formed were exploited to construct various complex multicyclic polymer topologies [18].

In the present feature article, we show recent developments in the “*electrostatic self-assembly and covalent fixation* (ESA–CF)” process, particularly in conjunction with effective linking/cleaving chemistry including metathesis process and alkyne–azide click reaction to afford a variety of novel cyclic polymers having specific functional groups and unprecedented multicyclic macromolecular topologies.

2. New tailored cyclic polymers designed through the ESA–CF process

By an extension of the ESA–CF process, we have prepared a cyclic polymer having a fluorescent group for a single molecule spectroscopic study of cyclic and linear polymers to elucidate topology effects in polymer diffusion [19]. Thus, we employed a linear telechelic poly(THF) having *N*-phenyl piperidinium (6-membered ring) salt groups accompanied by a perylene dicarboxylate counteranion ($M_p = 6000$, PDI = 1.13). The subsequent heating of the ionic complex resulted in the formation of a cyclic polymer having a perylene unit mostly connected by a simple ester linkage via the elimination of *N*-phenylpiperidine in 65% yield (Scheme 2a) [20]. According to NMR, 88% of the *N*-phenyl piperidinium groups

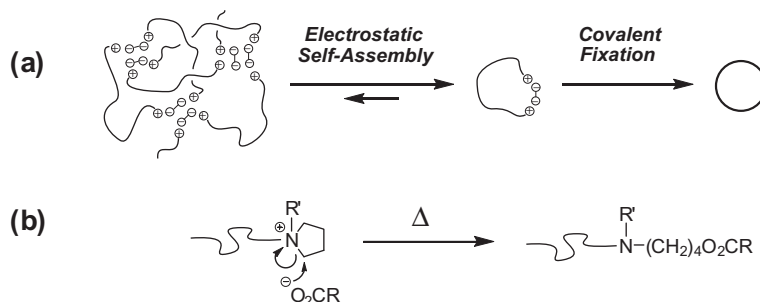
were eliminated, while the rest underwent a ring-opening reaction. We have subsequently disclosed the multiple-mode diffusion process uniquely observed in a cyclic polymer in contrast to the linear counterpart [19].

Notably, a relevant ring polymer was accessible by using an alternative telechelics having *N*-phenyl pyrrolidinium (five-membered ring) groups. However, the latter was inapplicable to single-molecule spectroscopy due to the photo-quenching by the *N*-phenyl amine group formed through the ring-opening reaction of the pyrrolidinium salt groups (Scheme 2b).

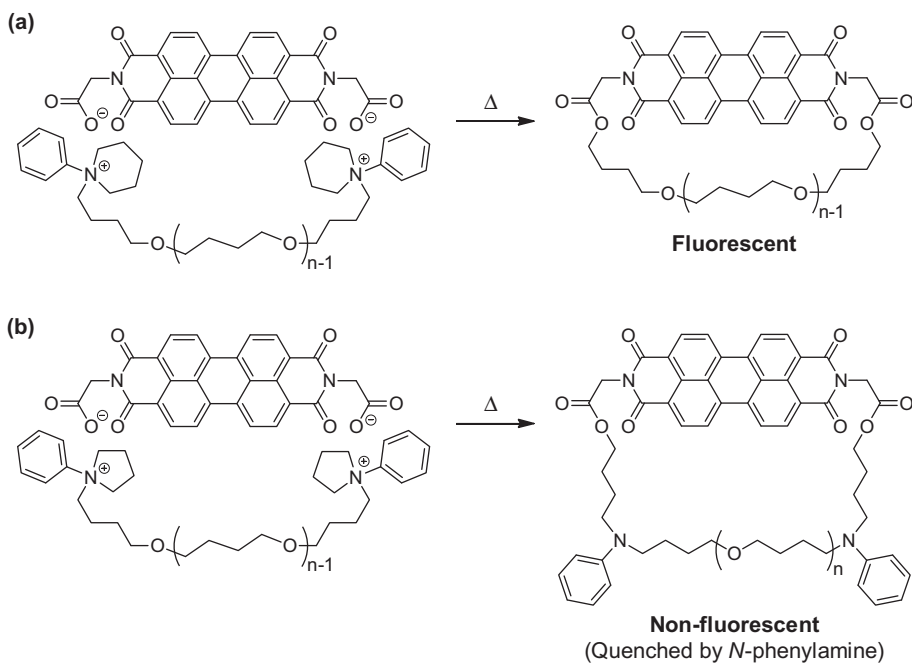
As another development of the ESA–CF process to construct tailored cyclic polymers having specific functional groups, we have newly prepared cyclic poly(THF)s having a hydrogen-bonding isophthaloyl benzylic amide group. The cooperative electrostatic and hydrogen-bonding self-assembly of the polymer precursors and a subsequent covalent conversion have been demonstrated as an effective means for the synthesis of polymer catenanes [21]. Thus, a telechelic poly(THF) having an isophthaloyl benzylic amide group at the center position and having *N*-phenylpyrrolidinium salt end groups carrying a biphenyldicarboxylate counteranion ($M_p = 2500$, PDI = 1.39 after cyclization by itself) was prepared and subjected to a covalent conversion reaction in the presence of another type of a pre-formed cyclic poly(THF) having the hydrogen-bonding unit ($M_p = 2400$, PDI = 1.32) (Scheme 3). A polymer [2]catenane comprised of the two different cyclic poly(THF) components was isolated up to 7% yield as an acetone-insoluble fraction and unambiguously characterized by means of MALDI-TOF mass spectroscopy together with ^1H NMR and SEC.

3. ESA–CF process coupled with an olefin metathesis process

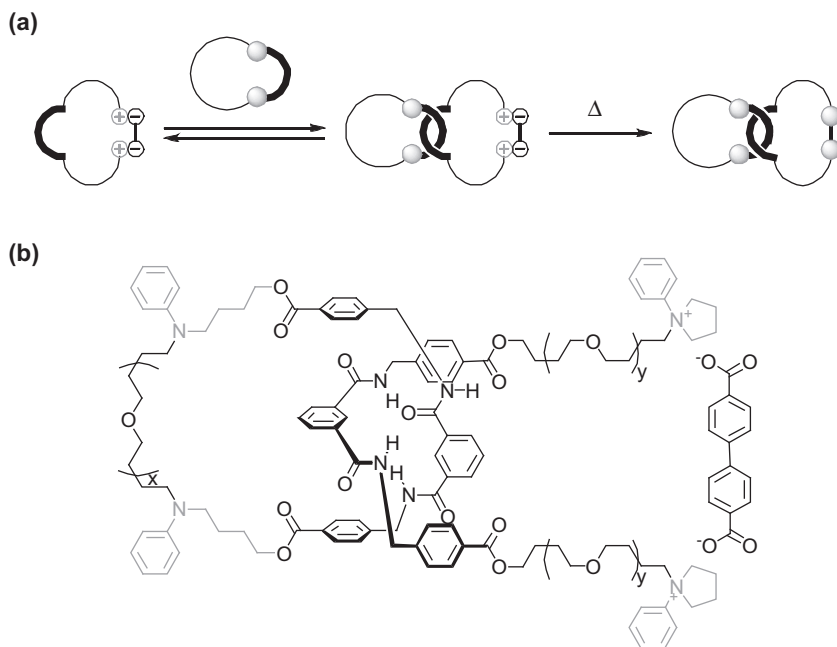
Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) have extensively been utilized in synthetic polymer chemistry [22]. Moreover, new functional group-tolerant catalysts have recently been developed and successfully applied for the synthesis of topologically unique molecules like catenanes [23,24] as well as cyclic polymers through ring-expansion polymerization [25–27]. We prepared α,ω -diallyl telechelic poly(THF)s and poly(acrylic ester)s through the living polymerization followed by an end-capping reaction. The subsequent metathesis condensation, i.e., metathesis polymer cyclization (MPC), under dilution produced the corresponding



Scheme 1. (a) Schematic representation of the ESA–CF process. (b) Selective ring-opening reaction of a cyclic ammonium salt end group by heating.



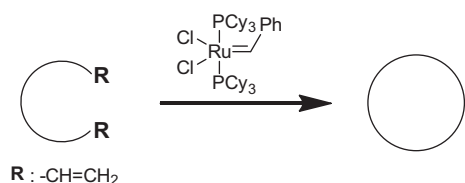
Scheme 2. Formation of cyclic polymers through the covalent fixation of (a) *N*-phenyl piperidinium and (b) *N*-phenyl pyrrolidinium end groups via ring-eliminating and ring-opening reactions, respectively.



Scheme 3. Synthesis of a polymer hetero [2] catenane through a cooperative electrostatic/hydrogen-bonding self-assembly and covalent fixation.

cyclic polymers in high yields (Scheme 4) [28,29]. The MPC process has also been applied for the synthesis of an amphiphilic cyclic block copolymer [30,31]. In case of the cyclization of a linear telechelic AB diblock copolymer ($M_p = 9700$, PDI = 1.34), the cyclized product ($M_p = 8900$, PDI = 1.42) was formed almost quantitatively (96%). On the other hand,

a linear telechelic ABA triblock copolymer ($M_p = 7800$, PDI = 1.16) yielded the corresponding AB diblock copolymer ($M_p = 6700$, PDI = 1.09) in 37% isolated yield. It is notable, in the latter case, that the ring polymer product was formed effectively from the starting telechelic block copolymer, but a part of the product was lost during purification.



Scheme 4. MPC using a Grubbs catalyst.

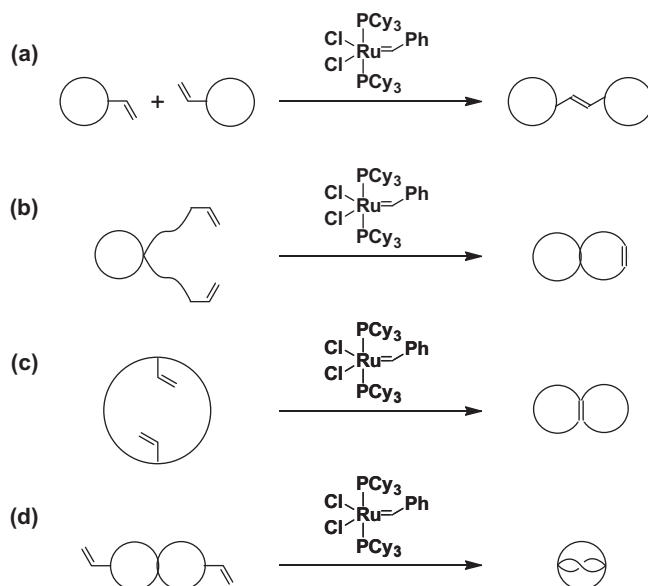
Moreover, we have shown the ESA–CF process in conjunction with a metathesis condensation as an effective means to produce multicyclic polymer structures. Thus, a cyclic prepolymer having an allyloxy group ($M_p = 4500$, PDI = 1.23, [Scheme 5a](#)), an allyloxy-terminated twin-tailed tadpole polymer precursor ($M_p = 8100$, PDI = 1.06, [Scheme 5b](#)), and a cyclic polymer precursor having two allyloxy groups at opposite positions ($M_p = 6400$, PDI = 1.20, [Scheme 5c](#)) have been employed to produce 8-shaped polymers (28%, 45%, and 66%, respectively) [32]. Furthermore, an 8-shaped *kyklo*-telechelic precursor having two allyl groups at opposite positions ($M_p = 7800$, PDI = 1.16) has also been prepared by the ESA–CF process with a self-assembly consisting of two units of a cationic linear precursor having an allyl group and tetracarboxylate counteranion ($M_p = 4800$, PDI = 1.11), and subjected to the metathesis condensation to construct a polymeric δ -graph having a doubly-fused tricyclic topology ($M_p = 7000$, PDI = 1.18) in 67% yield ([Scheme 5d](#)) [33]. The values of M_p/M_n for the benzoate-terminated linear precursor, 8-shaped prepolymer, and δ -graph were 0.96, 0.82 and 0.63, respectively, indicating the progressive contraction of the 3D-size of multicyclic polymers along with the increases of the chain segments in the fused ring.

A cross metathesis process has also been combined with the ESA–CF process to accomplish the unique topological conversion of multicyclic polymers [34]. Thus, an

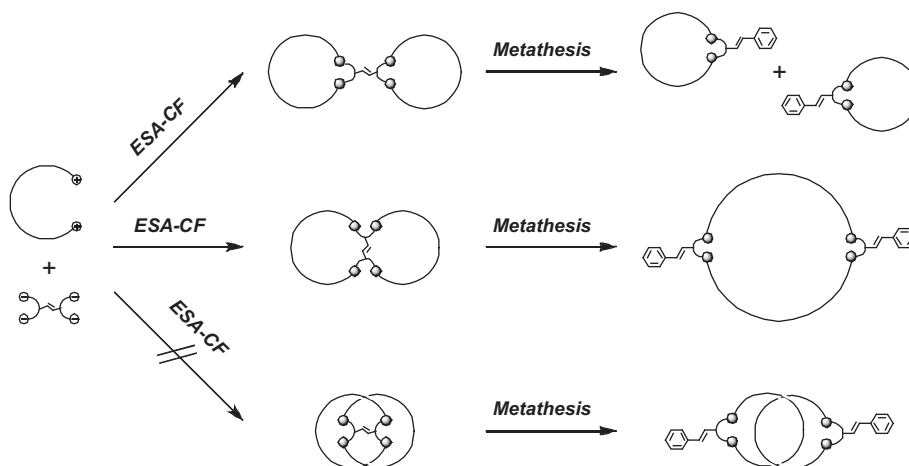
8-shaped poly(THF) having a metathesis-cleavable olefinic unit at the focal position ($M_p = 4900$, PDI = 1.13) was synthesized through the ESA–CF process in 38% yield. The subsequent metathesis cleavage reaction of the olefinic group proceeded effectively in the presence of a second generation Grubbs catalyst, and the subsequent quenching by the addition ethyl vinyl ether to give the end-capped products in 99% yield. Thus, the topology of the polymer was converted from 8-shaped dicyclic to monocyclic. In this system, moreover, the cyclic polymer products having two distinctive ring sizes, consisting of one or two prepolymer units, were expected due to the linking mode of the two prepolymer segments on the employed tetracarboxylate having an olefinic unit. MALDI-TOF mass indeed showed the formation of both products. It was noticed also the absence of a visible fraction corresponding to a polymer [2] catenane during this topological conversion, implying that the entanglement of the two prepolymer segments appears reluctant to proceed even they are placed spatially close by each other ([Scheme 6](#)).

4. ESA–CF process coupled with the click chemistry

Typically, multicyclic polymer topologies with the lower symmetry are difficult to construct by a single-step process. For example, the selective synthesis of a manacle-shaped polymer is hard to achieve by the simple application of the ESA–CF process, but a θ -shaped product is formed concurrently. Accordingly, an alternative effective cross-coupling process has extensively been explored. Initially, such condensation-type cross-coupling as Sonogashira and Suzuki reactions were applied to connect two cyclic prepolymers to form an 8-shaped topology [35]. A series of cyclic prepolymers having a bromophenyl, pentynoyl, or phenylboronate group was prepared through the esterification of the hydroxyl group of a *kyklo*-telechelics. They were subsequently



Scheme 5. ESA–CF process coupled with olefin metathesis for the constructions of (a–c) 8-shaped and (d) δ -graph polymers.



Scheme 6. Formation of 8-shaped polymers by the ESA–CF process and subsequent topological conversion by a cross metathesis process, resulting two distinguishable monocyclic products (top and middle). However, the entanglement of the polymer chains placed closely in space scarcely took place to form a polymer [2] catenane (bottom).

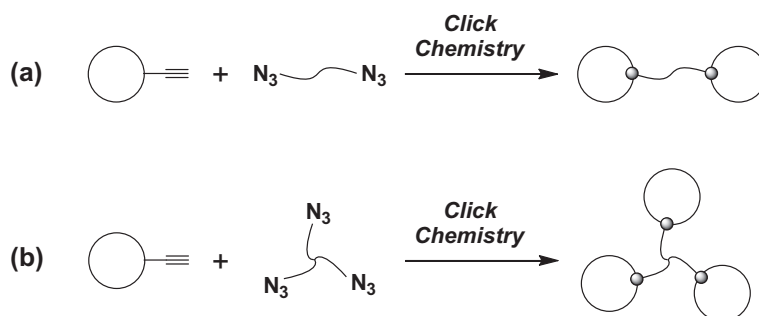
subjected to palladium-mediated condensation cross-coupling reactions. SEC showed that the Sonogashira coupling produced the corresponding product effectively. On the other hand, Suzuki coupling failed to proceed under the examined conditions.

Recently, we have discovered an alternative addition-type cross-coupling by a click chemistry process as an extremely versatile protocol in conjunction with the ESA–CF process [36,37]. Thus, a *kyklo*-telechelics having an alkyne group ($M_p = 2500$) was prepared by the ESA–CF process and subsequently subjected to click chemistry with a linear telechelic precursor having azide end groups ($M_p = 2100$), resulting in the selective formation of a *bridged*-type manacle-shaped polymer ($M_p = 6700$) in 48% yield (Scheme 7a) [38]. Similarly, the *kyklo*-telechelics having an alkyne group ($M_p = 2400$) was subjected to a click reaction with a three-armed star telechelics having azide end groups ($M_p = 4600$), leading to the selective formation of a *bridged*-tricyclic paddle-shaped polymer ($M_p = 11,100$) in 57% yield (Scheme 7b) [38].

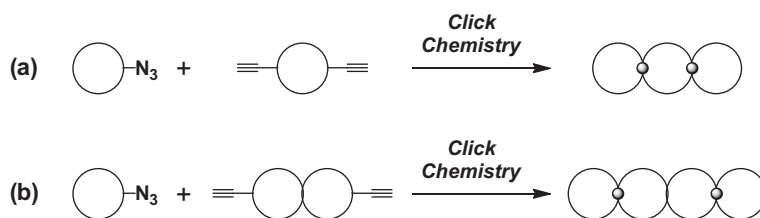
Moreover, this combinational process was applicable for the construction of *spiro*-type multicyclic polymers. A bifunctional *kyklo*-telechelics having two alkyne groups at the opposite positions ($M_p = 3100$) was also prepared

by the ESA–CF process using a linear telechelic precursor having an alkyne group at the center position and an accompanying alkyne-functionalized dicarboxylate anion. The bifunctional *kyklo*-telechelics was subjected to click chemistry with another *kyklo*-telechelics having an azide group ($M_p = 2100$), which was also obtained by the ESA–CF process with an azide-functionalized counterion, giving a tandem *spiro*-tricyclic topology ($M_p = 7400$) in 76% yield (Scheme 8a) [38]. Furthermore, the use of an 8-shaped dicyclic dialkyne prepolymer ($M_p = 5900$) afforded a tandem *spiro*-tetracyclic construction ($M_p = 9200$) in 71% yield (Scheme 8b) [38].

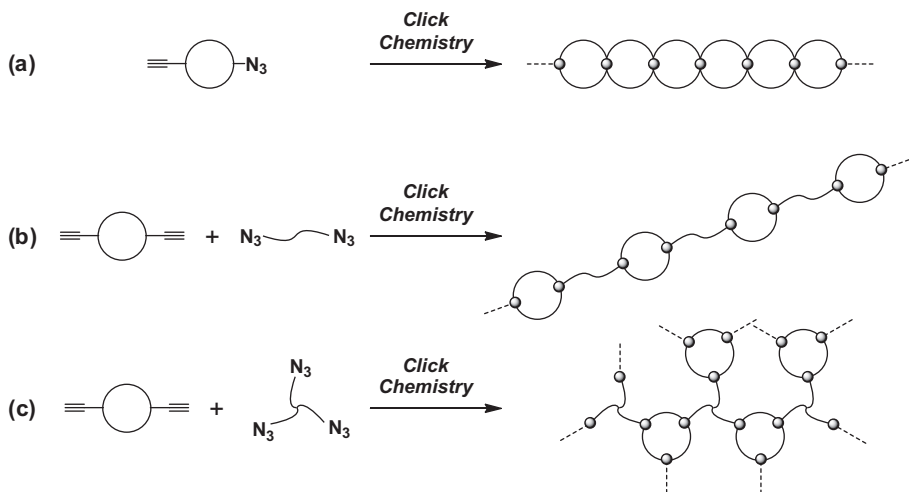
Click chemistry was further applied to the polyaddition of an asymmetrically bifunctional *kyklo*-telechelics having an alkyne group and an azide group at the opposite positions ($M_p = 1700$), obtainable by the ESA–CF process, leading to the formation of a linearly connected *spiro*-type multicyclic polymer in 82% yield (Scheme 9a) [38]. The SEC analysis of the resulting polymer product showed the construction of hexameric cyclic polymer units on average. Copolyaddition of the aforementioned bifunctional *kyklo*-telechelics having two alkyne groups ($M_p = 1800$) and a linear ($M_p = 2000$) or three-armed star-shaped ($M_p = 4500$) telechelics having azide end groups was performed to form



Scheme 7. Click chemistry between a *kyklo*-telechelics having an alkyne group and (a) linear and (b) three-armed star telechelic precursors having azide end groups to selectively form *bridged*-dicyclic and *bridged*-tricyclic polymers, respectively.



Scheme 8. Construction of tandem (a) *spiro*-tricyclic and (b) *spiro*-tetracyclic polymer topologies via click chemistry.



Scheme 9. Construction of (a) *Spiro*-type multicyclic, (b) *bridged*-type cyclic/linear and (c) *Bridged*-type cyclic/star polymer topologies.

multicyclic polymers having alternating ring/linear (67%) or ring/star (72%) segments, respectively (Schemes 9b and c) [38]. The SEC trace of the *bridged*-type linear multicyclic polymer showed that the product was composed of four rings connected with three linear segments on average.

5. Conclusions and future perspectives

This article has highlighted recent remarkable developments in topological polymer chemistry. Through the intensive research efforts, a variety of polymers having novel topologies have now been synthesized and convincingly characterized, and ongoing challenges will extend the frontier of synthetic polymer chemistry. Furthermore, the designs of functional polymeric materials, which are currently restricted mostly to conventional linear and branched polymers, could be radically refurbished by the precisely controlled synthesis and by extraordinary properties of cyclic and multicyclic polymers.

Acknowledgements

We thank Sekisui Chemical Grant Program for Research on Manufacturing Based on Learning from Nature (Y.T.), The Mitsubishi Foundation (Y.T.), Tokyo Tech Innovative Research Engineering Award (Y.T.), Tokyo Tech Young Investigator Engineering Award (T.Y.), KAKENHI (21850013, T.Y.), Mizuho Foundation for the Promotion

of Sciences (T.Y.), The Ogasawara Foundation for the Promotion of Science & Engineering (T.Y.), and Tokuyama Science Foundation (T.Y.) for financial support.

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