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Architecture-transformable polymers: Reshaping the future of stimuli-responsive polymers

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A B S T R A C T

The field of stimuli-responsive, or smart polymers, has commanded significant interest over the past decade. However, most examples of stimuli-responsive polymers have relied on macroscopic changes that arise via simple alterations in chain conformation or changes in polymer-polymer or polymer-solvent interactions. In recent years, there has been an effort to expand the scope of modifiable variables to include the covalent architecture of a polymer through the use of reversible covalent bonds. Polymers capable of architectural transformation are those that can undergo changes in their chain topology (e.g., linear to branched, star to comb, etc.) via rearrangement in the chain structure. This approach has proven particularly interesting because it allows access to materials capable of dramatic macromolecular property changes that cannot be replicated by the more traditional approaches to responsive polymer systems, which often rely on solubility or swelling transitions in solution. This review aims to highlight the main synthetic strategies to architecture-transformable polymers, including dynamic-covalent and supramolecular chemistry approaches. In addition, the properties and applications of those smart polymers are highlighted. It is clear from recent research in this area that macromolecules capable of undergoing transformations in topology represent a paradigm shift in the field of stimuli-responsive materials.

Contents

Abbreviations: RDRP, reversible-deactivation radical polymerization; ATRP, atom-transfer radical polymerization; RAFT, reversible addition-fragmentation chain transfer; PNIPAM, poly(*N*-isopropylacrylamide); LCST, lower critical solution temperature; DMAEMA, *N*,*N*-dimethylaminoethyl methacrylate; DC, dynamic-covalent; DA, Diels-Alder; Fur-Mal, furan-maleimide; DLS, dynamic light scattering; GPC, gel permeation chromatography; MMA, methyl methacrylate; PMMA, poly(methyl methacrylate); TAD, triazolinedione; PS, polystyrene; PBA, poly(butyl acrylate); ROP, ring-opening polymerization; NB, *o*-nitrobenzyl; CL, ε-caprolactone; CMA, 7-(2-methacryloyloxyethoxy)-4-methylcoumarin; PLLA, poly(L-lactide); PDLA, poly(D-lactide); DSC, differential scanning calorimetry; PEO, poly(ethylene oxide); PTHF, polytetrahydrofuran; PL, photoluminescence; δ-VL, δ-valerolactone; PVL, poly(δ-valerolactone); HL, hexanolactone; UPy, ureido-pyrimidinone; DAT, thymine-diaminotriazine; PBO, poly(butylene oxide); T_g, glass transition temperature; T_m, melting point.

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1. Introduction

Hermann Staudinger's pioneering work in macromolecular science led to his theory defining polymers as long chains of repeating units bound covalently together, rather than as aggregates of small molecules or colloids as was widely maintained at the time [1]. Since then, the field of polymer chemistry has flourished and is now ingrained in nearly every facet of daily life, from industrial use (e.g., textiles, painting, packaging, and building materials) to high-value-added applications including biomaterials and microelectronics [2–7]. Synthetic polymers are ubiquitous, reaching a staggering production of 300 million tons in 2015 [8]. While simple commodity polymers comprise much of this volume, the ever-expanding toolbox of macromolecular synthetic techniques has greatly improved access to more sophisticated polymeric materials. Little could Staudinger have imagined that polymer science would one day expand into advanced applications such as molecular-level information storage (supported by DNA-mimic sequence-controlled polymers) [9–12] and high-efficiency chemical separation using a single-layer 2D polymeric network [13–15]. The role of synthetic advances in these innovations should not be understated, but many of the insights we will discuss herein also arose from a careful consideration of the effect of *architecture*, not just functionality or molecular weight, on macromolecular properties.

The development of reversible-deactivation radical polymerization (RDRP) (e.g., atom-transfer radical polymerization (ATRP) [16–19], nitroxide-mediated polymerization [20], and reversible addition-fragmentation chain transfer (RAFT) polymerization [21–25]) has empowered polymer chemists with the ability to easily prepare topologically unique macromolecules with diverse functionality. Indeed, the ability to control molecular weight, dispersity, and chain-end functionality has enabled the preparation of a remarkable array of innovative and sophisticated polymers [26–30]. RDRP has been particularly useful for the generation of polymers with hyperbranched, [31–35] star-shaped [36–40], and cyclic [41–45] architectures that are generally inaccessible by many other polymerization methods. Importantly, the architecture of a polymer dictates many properties, including the extent of entanglement with neighboring chains [46,47], the ability to modify solution viscosity [48,49], and the propensity for self-assembly into complicated nano-objects with tailored morphologies [50–54]. As structure begets function, a consideration of how architecture may be advantageously exploited can be a powerful guiding principle for the design of new polymers.

A growing subset of functional polymers, made possible by the continuous improvement of synthetic tools in polymer chemistry, includes polymers that can adapt to their surrounding environment by responding to external signals, resulting in changes in material physical and/or chemical properties [55,56]. These tailor-made polymers, referred to as stimuli-responsive or smart polymers, can respond to a broad range of stimuli (e.g., pH, temperature, the presence of reducing agents, mechanical force, electric/magnetic field, etc.) [4,57] and, as such, are garnering significant interest in the fields of triggered drug release/delivery, tissue engineering, optical systems and biosensors, as well as in coatings, environmental remediation, and self-healing materials [55]. Of the numerous examples of stimuli-responsive polymers, the best known involve triggered changes in polymer chain conformation by changing polymer-polymer and/or polymer-solvent interactions [58–61]. Perhaps the quintessential example of this is poly(*N*-isopropylacrylamide) (PNIPAM), a thermoresponsive polymer that exhibits a lower critical solution temperature (LCST) in aqueous solution [62–65]. Below the LCST, PNIPAM chains are hydrophilic and exist as random coils in solution. As the temperature is increased above the LCST, PNIPAM expels bound water molecules and undergoes a transition to a compact globular conformation, sometimes also accompanied by macroscopic phase separation. Similarly, the conformation of pH-responsive polymer chains can be tuned by altering the environmental pH to change the degree of ionization of the polymer, and therefore hydrophilicity, *via* protonation or deprotonation of ionizable moieties [58,66]. Common examples include polymers that contain carboxylic acid or tertiary amine moieties, such as (co)polymers of acrylic acid or *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) [67–69].

These traditional smart polymers enjoy the advantage of great synthetic accessibility and have been most frequently exploited for stimuli-responsive materials. In the pursuit of ever more dramatic stimulus-induced property modifications, however, increasing attention has been devoted to a class of polymers that can undergo topological transformations (i.e., changes due to rearrangement of the constituent parts to achieve a new chain architecture) in response to an external stimulus [70–72]. The nascent concept of macromolecular topological transformation is becoming more widespread, largely for two reasons: (*i*) the development of a sufficiently large chemical toolbox to facilitate the construction of diverse responsive architectures and (*ii*) the recognition that architectural transformations are typically accompanied by significant changes in the physical properties of the resultant polymers [73,74]. In acknowledgment of this field's burgeoning prevalence, we aim to first critically assess the state-of-the-art synthetic strategies that enable architecture-transformable polymers, including the variety of stimuli that can induce topological transformations and the various architectures that can be interconverted. Additionally, we will discuss the property changes that can arise from topological transformations and how this may translate into potential applications for these materials. Finally, we believe it is important to evaluate practical challenges that may hinder the field's further expansion, such as purification of the desired architecture from (often macromolecular) impurities after topological transformation and the feasibility of conducting topological transformations in bulk polymeric materials.

2. Synthetic strategies of architecture-transformable polymers

We begin our exploration of the synthetic directions towards architecture-transformable polymers by reasserting that architecture or topology critically influences polymer properties in solution and in bulk [31,75–79]. Therefore, the development of architecture-transformable polymers is particularly interesting from the viewpoints of expanding the scope of stimuli-responsive polymers and understanding structure-property relationships. As a general concept, a polymer with the ability to transform its architecture should contain segments that are connected by reversible linkages, facilitating disassembly and reassembly of these segments with high efficiency. Two illustrative approaches to architecture-transformable polymers are considered (Fig. 1). The first involves incorporation of dynamic-covalent (DC) bonds that link the segments of polymers [80,81]. These labile bonds should respond to a particular stimulus that induces cleavage of the linkages and leads to transformations of the polymer architecture. The second method harnesses supramolecular interactions, such as hydrogen bonding or rotaxane structures. For example, the latter mechanically "locks" a wheel polymer and an axle polymer [70,82,83]. Upon the removal of supramolecular interactions, the wheel polymer is able to move along the axle chain to induce a net architecture transition. Many supramolecular interactions are comparatively weak, so the efficient and selective formation and perturbation of these dynamic links can often prove challenging.

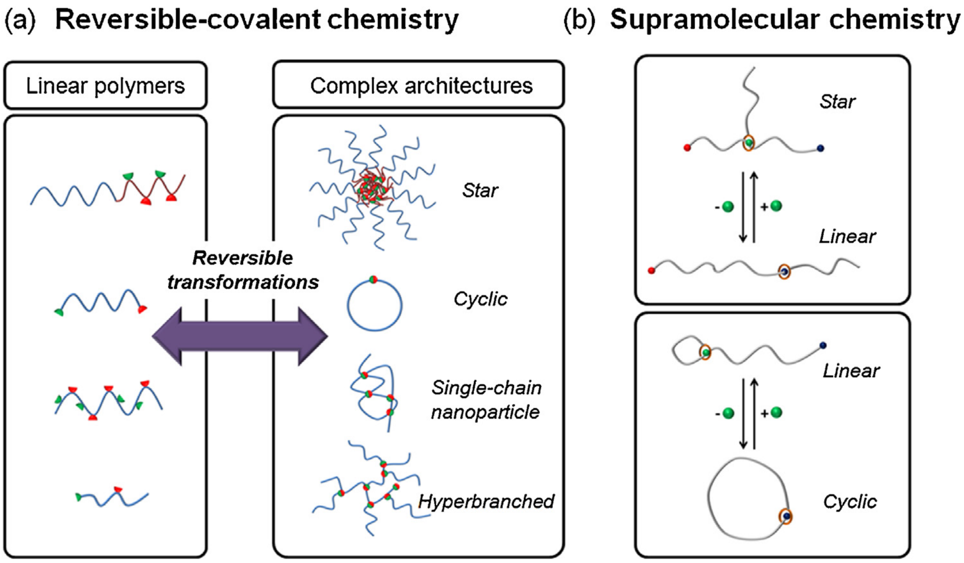


Fig. 1. Two approaches to architecture transformation of polymers. (a) Various topological transformations through disconnections and reconnections of dynamic covalent bonds; (b) Macromolecular topological transformation using a mechanically-linked (rotaxane) system.

2.1. *Dynamic-covalent chemistry approach*

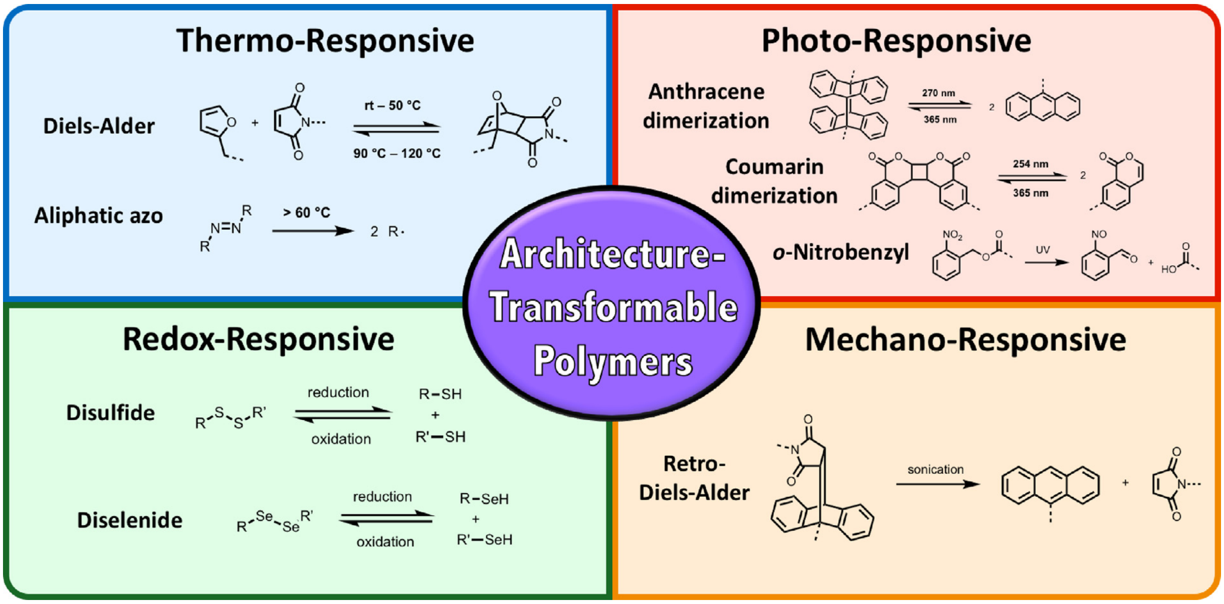
Compared to supramolecular interactions, DC bonds are typically more robust, leading to enhanced structural stability. Moreover, many DC chemistries are orthogonal; that is, they only respond to specific stimuli while remaining stable otherwise [36]. Therefore, it is no surprise that a variety of DC bonds have been applied to the design of smart polymers that can change their architecture upon receiving an appropriate signal (Scheme 1). This section will primarily cover recent examples of architecture-transformable polymers, sorted by applied stimulus (Table 1).

2.1.1. *Thermally-induced topological transformations*

The popularity of temperature as a stimulus arises from the fact that temperature changes can be applied to a material in a straightforward and inexpensive manner, can be spatiotemporally controlled (albeit to a limited extent compared to light), and do not necessarily involve drastic changes in the chemical environment that may interfere with other present structural units. Temperature-triggered architectural transformations are typically achieved through the use of thermally labile functional groups (e.g., azo groups and Diels-Alder (DA) adducts). For example, DA linkages based on the furan-maleimide (Fur-Mal) reaction can be formed at relatively low temperatures (room temperature to ~60 °C). However, further increasing temperature above 90 °C results in cycloreversion of Fur-Mal adducts, liberating free furan and maleimide moieties [84]. These adducts and those derived from other pericyclic reactions are attractive because they can be cleaved and re-formed with perfect atom economy under different magnitudes of the same stimulus (i.e., higher and lower temperatures, respectively).

Several illustrative examples of architectural transformations involving Fur-Mal chemistry have been reported by the Sumerlin group [31,85,86]. First, a star-to-linear transformation was achieved by preparing star polymers with cores linked by Fur-Mal adducts. These core-crosslinked stars were prepared by reacting furan-functional block copolymers with a bismaleimide crosslinker at 50 °C. This approach conferred thermal reversibility to the star polymers since the core of the star was completely crosslinked by labile DA bonds. Dynamic light scattering (DLS) and gel permeation chromatography (GPC) analyses demonstrated that the core-crosslinked stars were capable of dissociating back to individual arms by heating to 120 °C, yielding the original linear block copolymers [85]. A later report described the first example of thermally-reversible segmented hyperbranched polymers that contain DA-derived branch points [31]. These hyperbranched polymers (120–515 kg/mol) were synthesized *via* self-condensing vinyl copolymerization [87,88] of methyl methacrylate (MMA) and an inimer with a Fur-Mal linkage located between the polymerizable methacrylate group and initiating alkyl bromide moiety. Upon heating, the Diels-Alder linkages were cleaved, rapidly reducing the polymer molecular weights and forming linear poly(methyl methacrylate) (PMMA) segments (3.5–8.7 kg/mol) with terminal maleimide and pendent furan groups. Importantly, the retention of these reactive moieties allowed the partial reconstruction of hyperbranched PMMA by simply incubating the crude degraded sample at 50 °C. Most recently, *in situ* retro-Diels-Alder and DA cascade reactions were exploited to effect dramatic changes in polymer topology (Fig. 2). The process by which one macromolecular architecture is efficiently transformed into another was termed “macromolecular metamorphosis”[86]. In this process, an anthracene-containing “template” and an amphiphilic block copolymer joined by a central Fur-Mal linkage were heated at 120 °C, inducing retro-Diels-Alder reaction of the Fur-Mal cycloadduct and the resultant cleavage of the copolymer into its corresponding homopolymers. The resulting maleimide-containing polymer subsequently reacted with an anthracene-containing template (*i.e.*, anthracene-terminated linear polymer, trifunctional anthracene reagent, or copolymers bearing pendent anthracene groups) present in solution, giving rise to various new architectures, including hydrophobic block, star, and comb copolymers, respectively.

The Alder-ene reaction has also recently shown promise for reversible topology transformations. Du Prez and coworkers have specifically pioneered the use of the reaction between triazolinediones (TAD) and indoles to rapidly form robust macromolecular linkages, even at room temperature [89]. In a seminal report, they linked indole end-functional polystyrene (PS) and TAD end-functional poly(butyl acrylate) (PBA) to form a block copolymer (PS-*b*-PBA) within 30 min at room temperature. The exceptional rapidity and efficiency of this reaction is due to the extreme enophilic character of TAD moieties. To demonstrate the dynamic properties of the Alder-ene linkages, PS-*b*-PBA was readily converted to its constituent homopolymers (PS and PBA) when heated



Scheme 1. Various dynamic-covalent chemistries which have been utilized to design architecture-transformable polymers.

Table 1
Summary of architecture-transformable polymers via dynamic-covalent chemistry.

Polymer type	Stimulus	Chemistry	Shape transformation	Reversibility	Ref.
Vinyl polymer	Thermal	Diels-Alder	Star to linear	Yes	Sumerlin [85]
Vinyl polymer	Thermal	Diels-Alder	Hyperbranched to linear	Yes	Sumerlin [31]
Vinyl polymer	Thermal	Diels-Alder	Linear to star Linear to comb Hyperbranched to linear Hyperbranched to comb	No	Sumerlin [86]
Vinyl polymer	Thermal	Azo	Star to linear	No	Sumerlin [94]
Vinyl polymer+ polyester	Light	*o*-Nitrobenzyl	Hyperbranched to a mixed set of architecture	No	Zhao [100]
Vinyl polymer	Light	Coumarin	Linear to SCNP	Yes	Zhao [74]
Polyester	Light	*o*-Nitrobenzyl	Cyclic to linear	No	Yamamoto [71]
Polyether	Light	Anthracene	Linear to cyclic	Yes	Yamamoto [72]
Polyester	Light	*o*-Nitrobenzyl	Cyclic to linear	No	Yamamoto [122]
Vinyl polymer	Redox	Disulfide	Hyperbranched to linear	Yes	Tsarevsky [103]
Vinyl polymer	Redox	Disulfide	Cyclic to linear	Yes	Perrier [104]
Vinyl polymer	Redox	Disulfide	Star to linear	Yes	Sumerlin [37]
Vinyl polymer	Redox	Diselenide	Cyclic to linear	Yes	Zhu [105]
Vinyl polymer	Mechanical	Diels-Alder	Star to linear	No	Boydston [78]

at 120 °C in the presence of excess 2,4-hexadien-1-ol, which can efficiently react with liberated PBA-TAD and prevent reformation of PS-*b*-PBA at room temperature. This suggests that even reactions involving highly reactive precursors can be reversible under accessible conditions and therefore applicable for achieving architectural transformations.

Beyond pericyclic chemistry, Sumerlin and coworkers have recently investigated the triggered transformation of architectures containing aliphatic azo linkages. Drawing upon previous work demonstrating the degradability of linear polymers containing backbone azo moieties [90–93], the group synthesized a novel star polymer containing thermally labile azo linkages in the core via post-polymerization crosslinking of a PEG-*b*-poly(*N*-hydroxypropyl methacrylamide) copolymer with the azo initiator, 4,4′-azobis(4-cyanovaleric acid) [94]. Upon heating at 90 °C, a gradual reduction in hydrodynamic volume was observed as a result of azo cleavage. After 12 h, the size was reduced from an initial 27 nm to 3 nm, in good accordance with the size of linear chains. As an alternative to direct thermally induced degradation, stars that were loaded with a photosensitizing dye (in this case, indocyanine green) could be rapidly degraded under near-IR ($\lambda > 715$ nm) irradiation, presumably due to localized heating in the core. This approach exemplifies what we envision to be a major future direction in the field of architecture-transformable polymers: adapting one moiety to achieve transformations using multiple stimuli.

2.1.2. *Photoinduced topological transformations*

Light has recently attracted tremendous attention as a stimulus for smart polymers because it provides spatiotemporal control and can be triggered externally [95–97]. In addition, the irradiation parameters such as wavelength, luminous intensity, and irradiation time can be easily modulated to accommodate the system [98,99]. Various photoresponsive moieties have been employed in the synthesis of architecture-transformable polymers, most of which involve photoinduced cleavage of the moiety via either generation and subsequent fragmentation of an excited state, or [2 + 2] retrocyclization. Common examples of the former include *ortho*-nitrobenzyl esters and ethers, and the latter is typified by photoinduced dimerization and de-dimerization of coumarins and anthracenes (Scheme 1).

In 2015, Mo and Zhao et al. reported the synthesis of a photocleavable hyperbranched graft copolymer by successive RAFT-self-

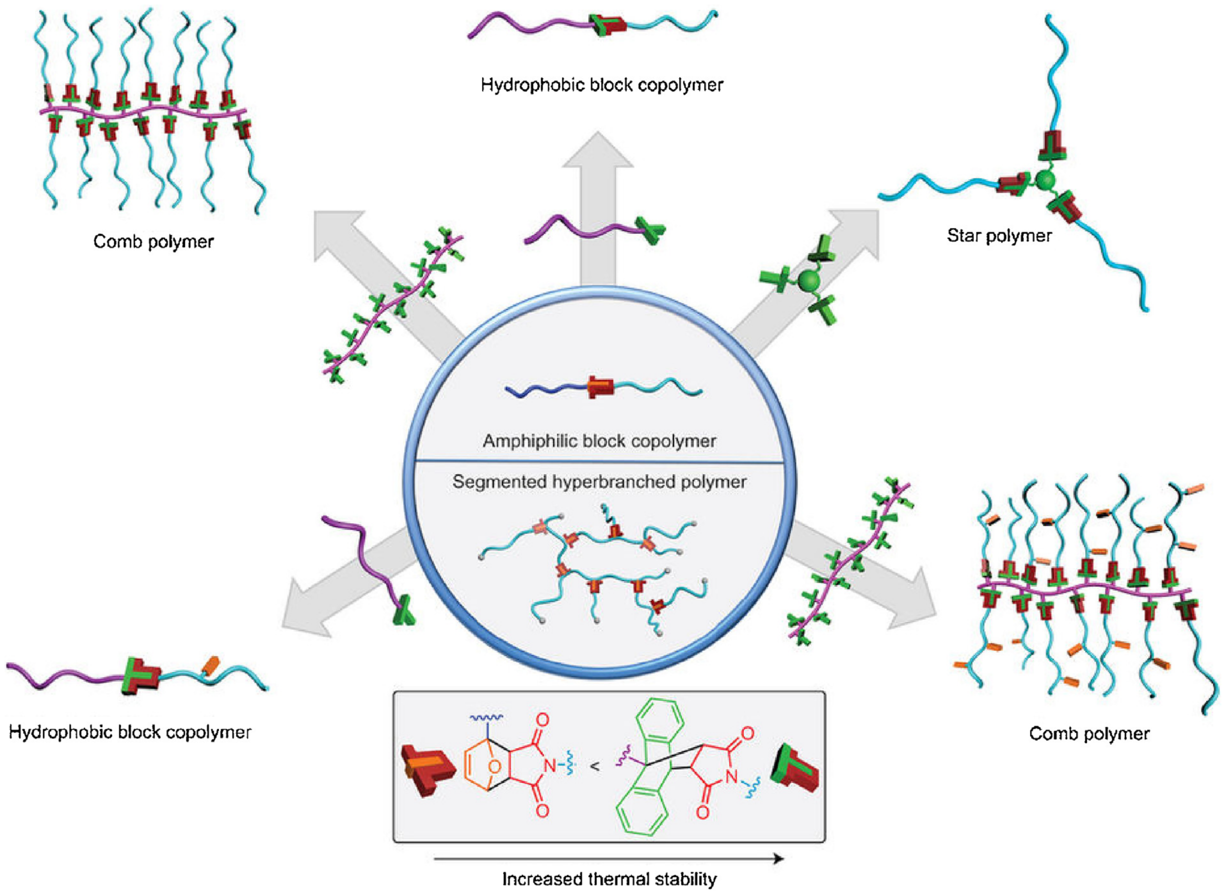


Fig. 2. Diels-Alder chemistry under thermodynamic control was used to induce "macromolecular metamorphosis" between polymer architectures. Thermally labile furan-maleimide bonds were cleaved at elevated temperatures in the presence of anthracene-containing templates, which subsequently formed maleimide-anthracene cycloadducts and resulted in transitions in polymer architecture. Examples include transformation from an amphiphilic block copolymer to comb polymer, hydrophobic block copolymer, and star polymer, as well as from a segmented hyperbranched polymer to hydrophobic block copolymer and comb polymer [86], Copyright 2017. Reproduced with permission from the Nature Publishing Group.

condensing vinyl copolymerization and ring-opening polymerization (ROP) using a multifunctional chain transfer monomer [100]. In this approach, hyperbranched poly(poly(ethylene glycol) acrylate) was formed first *via* self-condensing vinyl copolymerization of poly(ethylene glycol) acrylate and a chain transfer monomer containing an *o*-nitrobenzyl (NB) ester linkage. The resulting polymer was decorated with hydroxyl groups at each branch point that were further utilized to initiate ROP of ε-caprolactone (CL), creating hyperbranched graft copolymers. Because light-sensitive *o*-nitrobenzyl ester moieties were present at the branch points, these hyperbranched graft copolymers were capable of transitioning into a mixed set of architectures including linear, star-like, and graft copolymers under long-wave UV irradiation (365 nm).

A reversible linear-to-"chain loops" transformation triggered by UV light was reported by Zhao and coworkers, taking advantage of the reversible photoinduced dimerization of coumarins (Fig. 3) [74]. In their study, a well-defined random copolymer of DMAEMA and 7-(2-methacryloyloxyethoxy)-4-methylcoumarin (CMA), poly(DMAEMA-*co*-CMA), was prepared by RAFT polymerization. The authors showed that chain loops can be introduced into a linear polymer structure via the intra-chain photodimerization of coumarin groups upon exposure to long-wave UV irradiation ($\lambda > 310$ nm) in a dilute polymer solution. GPC was used to support the occurrence of intra-chain crosslinking events, displaying a peak shift to longer elution times as compared to the original linear polymer. The reversibility of chain-folding was further investigated by exposing the aqueous solution of intrachain-folded poly(DMAEMA-*co*-CMA) to short-wave UV light ($\lambda < 260$ nm). UV–vis spectral measurements revealed that only partial de-crosslinking occurred, with approximately half of the coumarin groups still remaining in their dimeric form.

In a recent report, Yamamoto and coworkers were able to prepare cyclic poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) that contained an *o*-nitrobenzyl group as a photocleavable linker [71]. Photoirradiation of cyclic polylactides resulted in the cleavage of *o*-nitrobenzyl linkers and concomitant topological transformations to their linear analogues. Despite observing the same molecular weights for cyclic and linear polymers, differential scanning calorimetry (DSC) indicated that the melting temperature of a stereocomplex of cyclic PDLA/PLLA ($T_m = 167\,^\circ$C) was significantly lower than the stereocomplex composed of the cleaved linear analogues ($T_m = 211\,^\circ$C). The same group developed an approach to reversible linear-cyclic topological transformations through a photoinduced cyclization and thermally-induced retrocyclization series (Fig. 4) [72]. The authors demonstrated that cyclic poly(ethylene oxide) (PEO) or polytetrahydrofuran (PTHF) was efficiently formed in both organic solvent and water by photodimerization of terminal anthryl groups on linear telechelic polymers. Moreover, the linear telechelic polymers could be regenerated by heating the cyclized polymers at 150 °C under dilute conditions. Up to 5 cycles of linear-cyclic transformations were achieved, indicative of extremely efficient topological transformations.

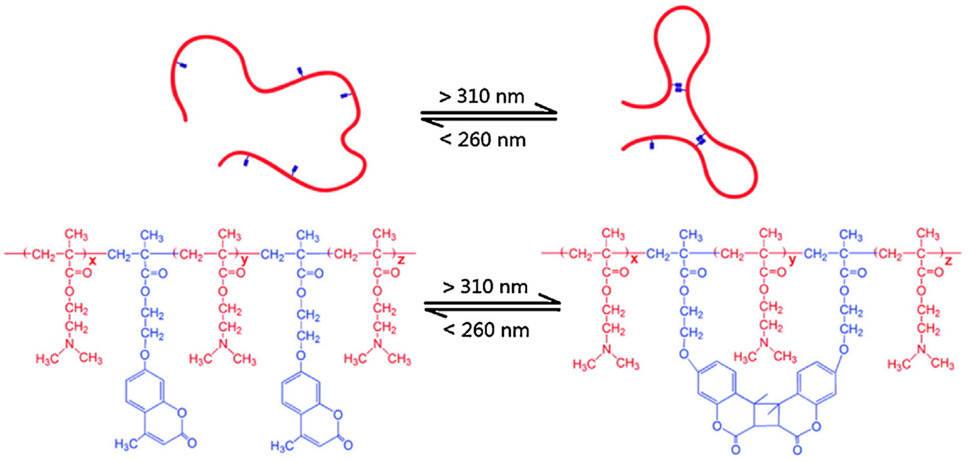


Fig. 3. Schematic illustration of reversible transformations from linear PDMAEMA to polymers with intramolecular chain loops *via* photodimerization (λ > 310 nm) and retrocyclization (λ < 260 nm) of pendent coumarin functionality [74], Copyright 2011. Reproduced with permission from the American Chemical Society.

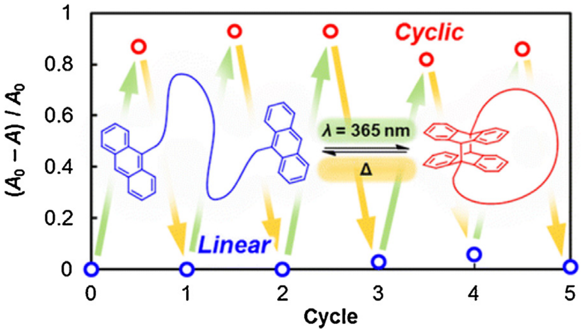


Fig. 4. Reversible architecture transformation of linear telechelic polymers to their cyclic analogues by irradiation at 365 nm (cyclization) and heating to 150 °C (retrocyclization) [72], Copyright 2016. Reproduced with permission from the American Chemical Society.

2.1.3. Redox-mediated topological transformations

Redox reactions are less commonly encountered as stimuli for adaptive polymeric materials, yet they are no less important because, unlike heat and light, they are biologically relevant (along with other stimuli like pH, glucose, enzymes, etc.). For example, redox-responsive polymers have been designed to take advantage of the tremendous difference in redox conditions between extracellular and intracellular locations [101,102]. Many redox-responsive polymers are fabricated by the incorporation of reducible linkages such as disulfides and diselenides [37,103–107]. For example, degradable hyperbranched polymers containing disulfide-based branch points were reported by Tsarevsky and coworkers [103]. Self-condensing vinyl copolymerization of methyl methacrylate and an inimer bearing a disulfide group resulted in segmented hyperbranched polymers that could dissociate in the presence of reducing agents (e.g., tributylphosphine) and morph their architecture from hyperbranched into low-dispersity linear poly(methyl methacrylate). In an example involving a cyclic-to-linear transformation, Monteiro and Perrier et al. reported the synthesis of cyclic polystyrene through oxidation of α,ω-thiol-difunctional PS in dilute solution, conditions that were necessary to minimize the effects of intermolecular disulfide formation (that is, step-growth polymerization of telechelic polymers) (Fig. 5) [104]. The resultant monocyclic PS structure was supported by GPC analysis, which showed a characteristic shift to longer elution times following oxidation, likely due to the lower hydrodynamic volume of cyclic polymers relative to linear polymers. More importantly, the disulfide bonds were readily reduced by zinc/acetic acid, providing the original linear PS with regenerated terminal mercaptan functionalities and showing potential for use in recyclable polymer materials.

In a similar demonstration of reversible architectural transformation mediated by disulfides, Sumerlin and coworkers synthesized redox-responsive star polymers that could reversibly transition into linear unimers [37]. In their approach, well-defined block copolymers containing a reactive poly(styrene-*alt*-maleic anhydride) segment were prepared by RAFT polymerization, and subsequent ring-opening reactions of the anhydride groups in the block copolymers with cystamine led to core-crosslinked stars. Thereafter, the transformation from star polymers to linear unimers bearing pendent thiols was realized by reductive cleavage of disulfide linkages. Moreover, the original star architecture could be reformed by oxidation of the free thiols in the presence of air. Multiple cycles of reversible star-linear transformations were achieved.

As an intriguing alternative to disulfide-containing architectures, polymers containing diselenide bonds have recently attracted interest due to their redox sensitivity and potential application in biologically-relevant areas. Compared to disulfides, diselenides can be reduced or oxidized under milder conditions [108] and have even been found to exhibit dynamic behavior under visible light irradiation [109]. Although we only cover here a single representative report of a diselenide-linked architecture, we wish to emphasize that this is an expanding frontier in stimuli-responsive polymers and direct readers interested in a more comprehensive survey to a review by Zhang et al. [108] Zhu et al. illustrated the utility of diselenides for topological transformations by demonstrating the synthesis and reversible cleavage of cyclic diselenide-linked PS [105]. To start with, well-defined linear PS was synthesized by RAFT polymerization using a bifunctional diselenocarbonate chain transfer agent. Then, aminolysis of the terminal selenocarbonates yielded selenol chain ends that spontaneously oxidized (even in the absence of oxygen) to monocyclic PS or multiblock cyclic PS, depending on the concentration of α,ω-telechelic PS in solution. Taking advantage of the unique redox responsive performance of diselenide linkers, the topology change from cyclic to linear could be accomplished under both reductive and oxidative conditions by cleaving the mid-chain diselenides with either sodium borohydride or hydrogen peroxide.

2.1.4. Mechanically-induced topological transformations

The use of mechanical force to achieve unique and selective chemical reactivity has become one of the fastest growing directions in polymer chemistry. The applications of the burgeoning

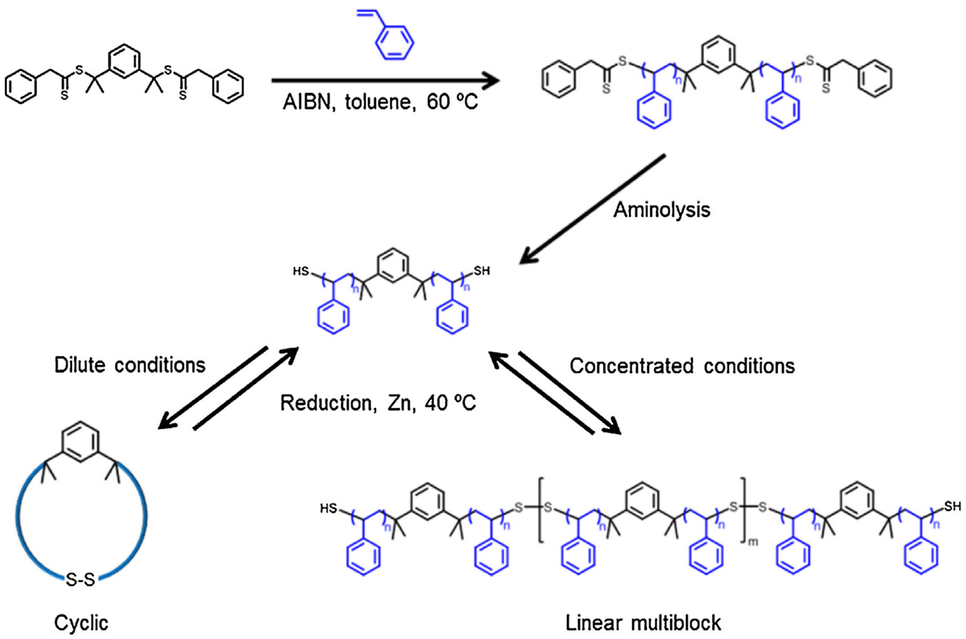


Fig. 5. Redox-triggered reversible topological transformation from linear PS to monocyclic (one disulfide linkage) and multiblock PS [104], Copyright 2006. Reproduced with permission from the American Chemical Society.

field of polymer mechanochemistry abound from those of purely synthetic interest, as in the mechanically assisted synthesis of semiconducting polyacetylenes [110], to those of materials engineering interest, such as the additive manufacturing of force-responsive materials [111]. A central concept in mechanochemistry is that of the *mechanophore*, that is, a moiety that undergoes chemical transformation when subjected to mechanical force [112]. Polymers have emerged as useful facilitators of mechanochemistry largely because their long chain lengths allow efficient transduction of macroscopic stresses, such as material deformation, into atomic-scale forces such as elongation and eventual rupture of weak covalent bonds (commonly present in mechanophores). There has been relatively little attention directed towards the mechanically induced conversion of one discrete polymeric topology into another, yet we believe this is another stimulus poised to be productively exploited for architectural transformation.

Boydston et al. achieved a star-to-linear transformation through the use of a three-arm star poly(methyl acrylate) containing an anthracene-maleimide DA adduct mechanophore that was located in the core of the star polymers (Fig. 6) [78]. The solvodynamic shear generated upon sonication of a solution of the star polymers led to cycloreversion of the DA adducts, resulting in a maleimide terminal linear PMA and an anthracene-centered PMA diblock copolymer. Photoluminescence (PL) spectra displayed increasing PL intensities as a function of sonication time, corresponding to the generation of anthracene functional groups and confirming the retrocyclization of the DA adduct. This was an especially intriguing finding considering the high thermodynamic stability of anthracene-maleimide adducts, the retro-DA reaction energy barrier of which has been computationally found to exceed 75 kcal/mol [86]. This stability renders these adducts virtually inert to thermal activation, yet the mechanical force provided by a ultrasonic probe at room temperature provided sufficient energy to induce scission.

2.2. Supramolecular chemistry approach

The promiscuity of noncovalent interactions render them more challenging to rationally apply to complex polymeric architectures, but they can induce structural changes that arguably rival those achieved with dynamic-covalent bonds and are evocative of the architectural transformations observed in Nature's intricate molecular machinery. In the forthcoming section, we will broadly assess recent work involving the use of host-guest and hydrogen-bonding interactions to illustrate the promise of supramolecular chemistry for topological transformations (Table 2).

In the past two years, several topology-transformable polymers based on rotaxane chemistry have been systematically studied by Takata, et al. (Fig. 1) [70,73,82,83,113,114]. In comparison with the dynamic-covalent chemistry approach (*vide supra*), these rotaxane-based protocols enabled topological transformations without changes in molecular weight and composition. In 2015, the authors' pioneering work in this concept described the synthesis of a mechanically linked star polymer and its transition into a linear polymer (Fig. 7) [70]. In their approach, a pseudo [2]rotaxane bearing three hydroxyl groups, one at each end of the axle and a third on the wheel component, was employed to facilitate ROP of δ-valerolactone (δ-VL), followed by end-capping with bulky functional groups (3,5-dimethylphenyl isocyanate) after polymerization. The resulting three-arm star poly(δ-valerolactone) (PVL) was composed of an axle PVL chain that was connected to the wheel PVL segment via ammonium/crown ether interactions. The star structure could then be disassembled by acylating the central nitrogen with excess acetic anhydride, causing the crown ether wheel to move from the now poorly interacting acetamide to the terminal urethane groups. This star-to-linear transformation was driven by the stronger urethane-crown ether interaction relative to that of esters (in the PVL backbone) with crown ethers. Both GPC and viscometry were used to analyze the initial star polymer and the corresponding linear polymer that was produced after *N*-acetylation. This analysis clearly showed the apparent number-average molecular weight of linear PVL (9.5 kDa) was larger than that of its star counterpart (8.0 kDa), suggesting a relatively larger hydrodynamic volume of the linear analogue. Furthermore, there was a clear increase in intrinsic viscosity after acylation, corroborating the formation of more greatly viscosifying linear polymers. It should be emphasized that, unlike the examples that utilize dynamic-covalent chemistry, this system involved a star-to-linear transformation with no reduction in molecular weight and no for-

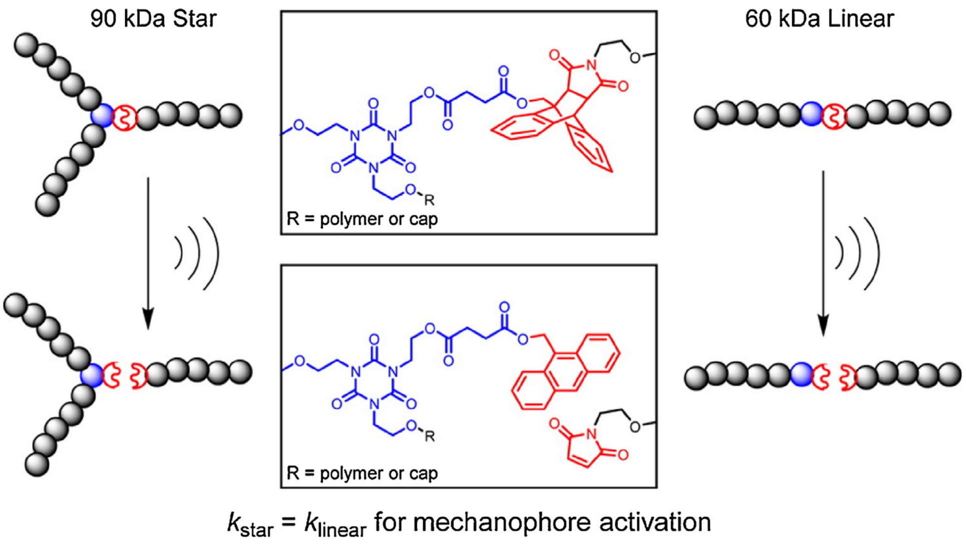


Fig. 6. Architecture transition from star to linear polymer through mechanochemically induced Diels-Alder bond scission [78], Copyright 2014. Reproduced with permission from the American Chemical Society.

Table 2
Summary of architecture-transformable polymers via supramolecular chemistry approach.

Polymer type	Chemistry	Shape transformation	Reversibility	Ref.
Polyester	Rotaxane	Star to linear	No	Takata [70]
Vinyl polymer+ polyester	Rotaxane	Star to linear	No	Takata [82]
Polyether	Rotaxane	Linear to cyclic	Yes	Takata [113]
Polyester	Rotaxane	Linear block to cyclic block	Yes	Takata [114]
Vinyl polymer	Hydrogen bond	Linear to cyclic	No	Barner-Kowollik [119]
Vinyl polymer	Hydrogen bond	Linear to SCNP	No	Meijer [120]
Polyether	Hydrogen bond	Linear to comb	Yes	Richter [121]

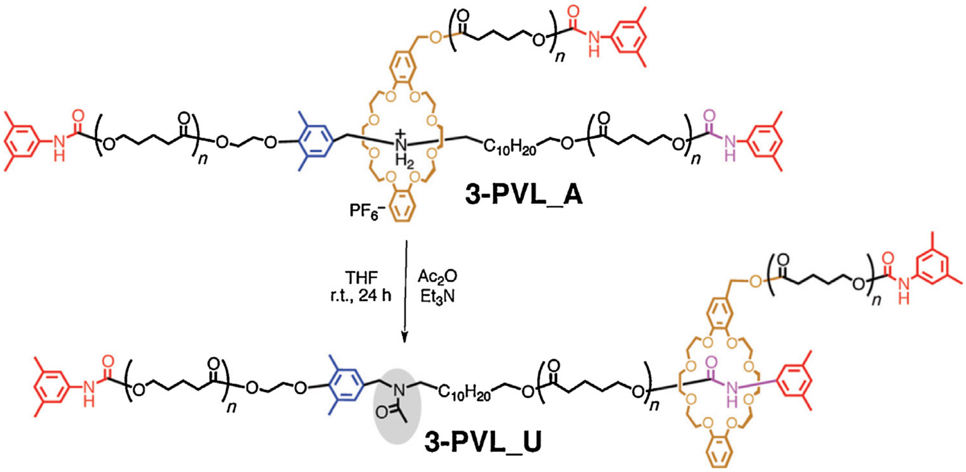


Fig. 7. Architecture transformation of a 3-arm star polymer to its linear analogue by *N*-acetylation [70], Copyright 2015. Adapted with permission from John Wiley and Sons.

mation of lower-molecular-weight byproducts, so the effects of architecture on properties could be probed independent of other macromolecular parameters.

To increase the scope of architectural transformations that can be achieved by supramolecular interactions, the same authors further applied a similar strategy to realize the transformation of an ABC star terpolymer to a linear ABC terpolymer [82]. By using a pseudo [2]rotaxane initiator that comprised three different functionalities (*i.e.*, trithiocarbonate, hydroxyl, and alkyne), the synthesis of an ABC star copolymer was achieved by successive ROP, RAFT polymerization, and copper(I)-catalyzed alkyne-azide cycloaddition click chemistry. Similar to their first report of rotaxane-based star to linear transformation, the ABC star terpolymer could readily transition to an ABC linear terpolymer by removing the interaction between the positively charged ammonium group and crown ether via *N*-acetylation.

Rotaxane chemistry has also been extended to linear-cyclic transformations [73,113–115]. Takata and coworkers demonstrated the transformation of linear PTHF into an analogous cyclic polymer without the need for a macrocyclization reaction (Fig. 8) [113]. The general synthetic approach involved first threading a crown ether wheel onto its own pendent axle, then growing polyTHF from a terminal initiating group. The polymeric axle was end-capped with a sulfonamide that, after deprotection, could also

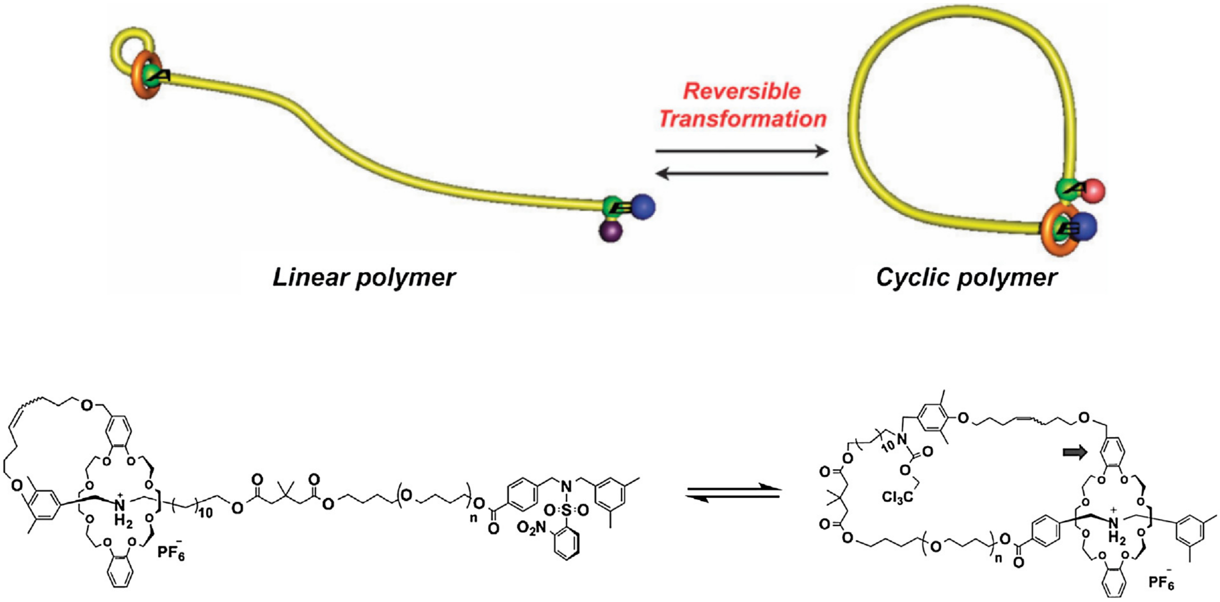


Fig. 8. Reversible transformation of linear polyTHF into cyclic polyTHF through shuttling of a covalently linked crown ether wheel between chain termini [113], Copyright 2015. Adapted with permission from the Royal Society of Chemistry.

serve as a guest for the crown ether wheel. Carefully cycling protection and deprotection steps finally allowed selective shuttling of the crown ether between chain ends, effectively achieving repeatable linear-cyclic transformations. From a synthetic point of view, this approach is potentially useful for large-scale cyclic polymer synthesis, since it does not require highly dilute conditions which are typically necessary for efficient and clean cyclization of linear polymer precursors.

The same group later extended a similar concept to linear-cyclic transformable block copolymers. Due to the ability of amphiphilic block copolymers to self-assemble in the bulk and in solution, there remains considerable interest in the field of block copolymer materials [51,116,117]. Likewise, cyclic polymers have intriguing bulk and solution state properties, owing to the absence of chain ends and therefore lessened chain entanglement and smaller hydrodynamic volumes than their linear analogues [76,118]. The ability to exploit architectural transformations to potentially merge the interesting properties of linear block copolymers with those unique to cyclic architectures is therefore highly intriguing. In this work, a stable pseudo [2]rotaxane was used as an initiator for sequential ROP of ε-caprolactone and hexanolactone (HL), creating a macromolecular [2]rotaxane with block copolymer poly(ε-caprolactone)-*b*-poly(hexanolactone) as its axle component. The axle and wheel were linked via a ring-closing metathesis reaction between an olefin on the crown ether wheel and an olefin on the terminus of the axle polymer, forming a lasso-shaped structure. Finally, *N*-acetylation of the ammonium group at the α-terminus (station A) eliminated its interaction with crown ether, prompting the wheel to translate along the axle and reach the other terminus (station B). Since station B contained a urethane moiety that could interact with crown ether, the wheel was thus "locked" again, resulting in the architecture transformation from linear block copolymer to cyclic block copolymer (Fig. 9) [114].

In addition to rotaxane chemistry, hydrogen bonding has often been utilized in architectural transitions. The Barner-Kowollik group demonstrated the cyclization of linear polystyrene utilizing hydrogen bonding between a Hamilton wedge and a cyanuric acid [119]. ^{1}H NMR spectroscopy and DLS analysis showed cyclization mainly occurred below concentrations of 0.5 mM, where the concentration was low enough to preclude oligomerization. Meijer and coworkers employed hydrogen bonding to promote the transformation from linear to chain loops or single-chain nanoparticles [120]. A library of copolymers (including polyacrylates, polymethacrylates, polynorbornenes, and polystyrene) bearing pendent and protected ureido-pyrimidinone (UPy) functionalities were prepared via RDRP or ring-opening metathesis polymerization (Fig. 10). Upon UV-induced deprotection of UPy groups, dimerization via four-fold H-bonding induced intramolecular crosslinking and formation of chain loops, as evidenced by SEC and DLS. Remarkably, changes in backbone flexibility and molecular weights of the polymers had little effect on the efficiency of these topological transformations. Later, reversible transition from linear to comb architecture was achieved by Richter et al. using thymine-diaminotriazine (DAT)-based hydrogen bonding [121]. Their system consisted of a polybutylene oxide (PBO)-based backbone with pendent thymine groups, in combination with shorter DAT end-functional PBO graft chains. Heterocomplementary association between thymine and DAT resulted in the formation of a transient comb architecture. The examples highlighted above display the ease with which polymeric units can be assembled or manipulated using supramolecular interactions, providing dynamic control over the polymer architecture and as a consequence, regulation of the polymer physical properties.

3. Properties and applications of architecture-transformable polymers

Polymer science has historically resided at a unique crossroads of fundamental synthetic chemistry and applications-oriented engineering. Breakthroughs in synthetic methodologies often inspire the production of unique and useful materials; similarly, the need for materials with specific properties can drive the development of novel polymer reactivity. Architecture-transformable polymers lie at the center of this intersection, often utilizing state-of-the-art chemical transformations to achieve unique property modifications. As we stated at the outset of this review, morphing the architecture of a polymer can lead to dramatic changes in a variety of physical properties, such as the extent of chain entanglement, solution viscosification, rheological properties, the ability to self-assemble into nanostructures, thermal transitions in solution, glass

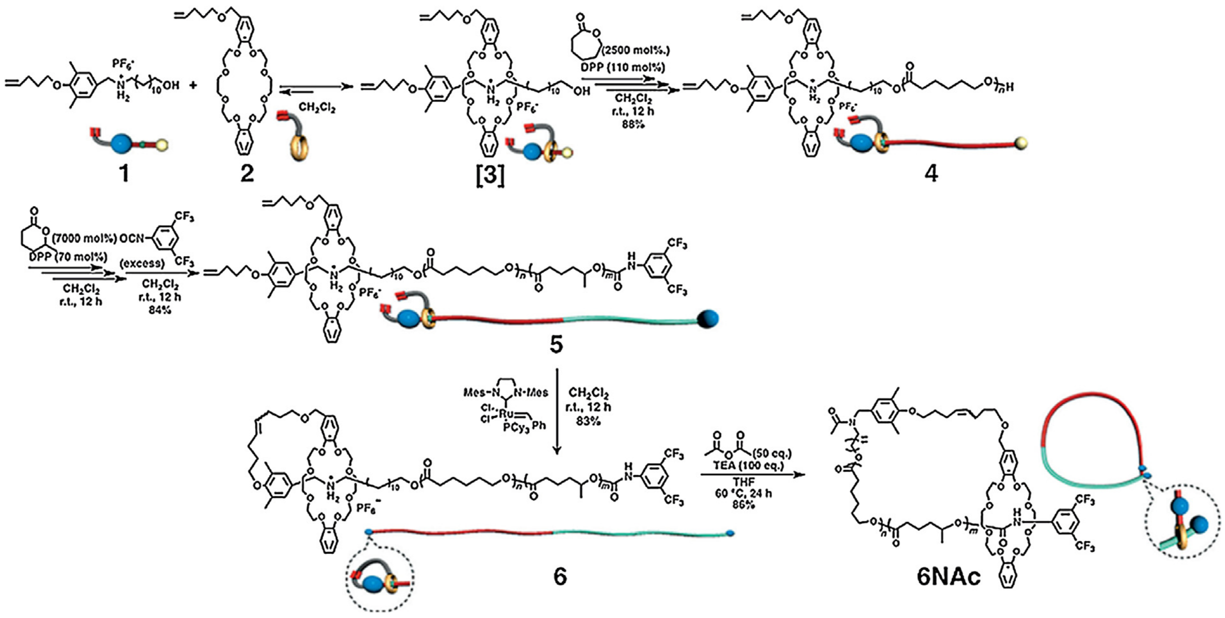


Fig. 9. Synthetic pathways of linear block copolymer and transformation to cyclic block architecture via *N*-acetylation [114], Copyright 2016. Adapted with permission from John Wiley and Sons.

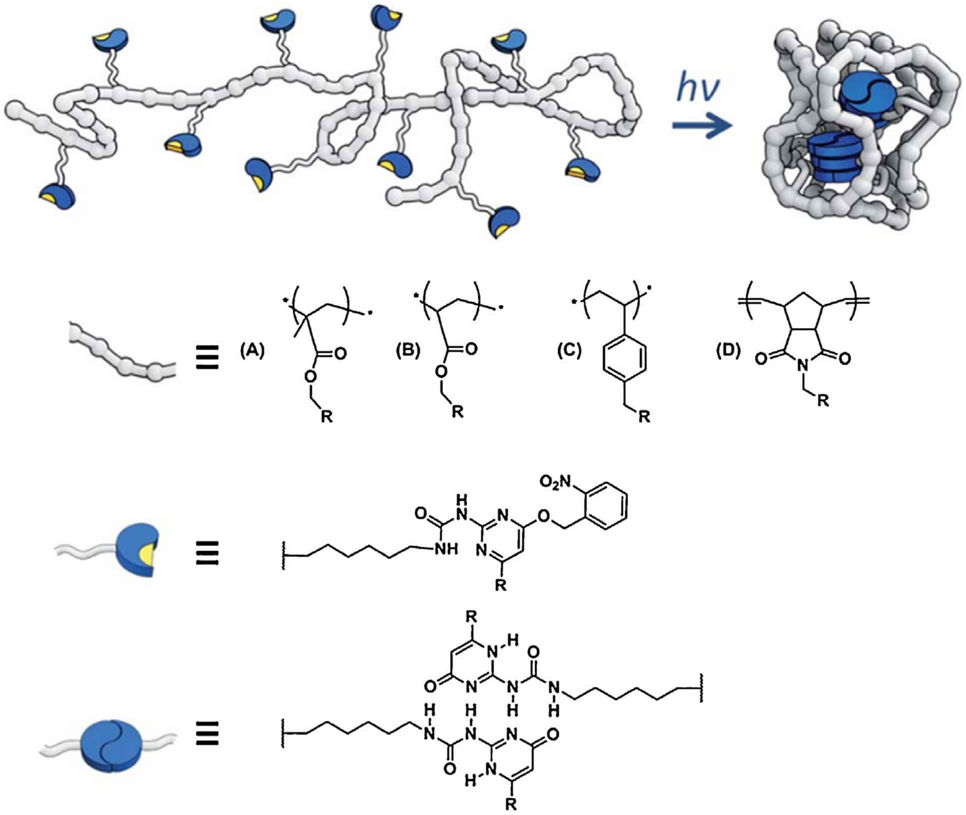


Fig. 10. Architecture transformation from linear to single chain loops via a cascade UV-triggered deprotection of UPy pendent groups and subsequent UPy dimerization through self-complementary quadruple hydrogen bonds [120], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.

transition temperature (T_g), and melting point (T_m), among others. In the upcoming section, we will explore examples that illustrate the extent to which properties depend on topology. In doing so, we hope to outline the utility of architecture-transformable polymers and inspire new efforts towards their application.

We begin our survey with work by Zhao et al., who were able to tailor the LCST of thermosensitive, water-soluble PDMAEMA through reversible photoinduced transformations between linear and chain-loop polymers [74]. This general approach involved photodimerization of pendent coumarin units that were installed through copolymerization of DMAEMA with a coumarin-bearing

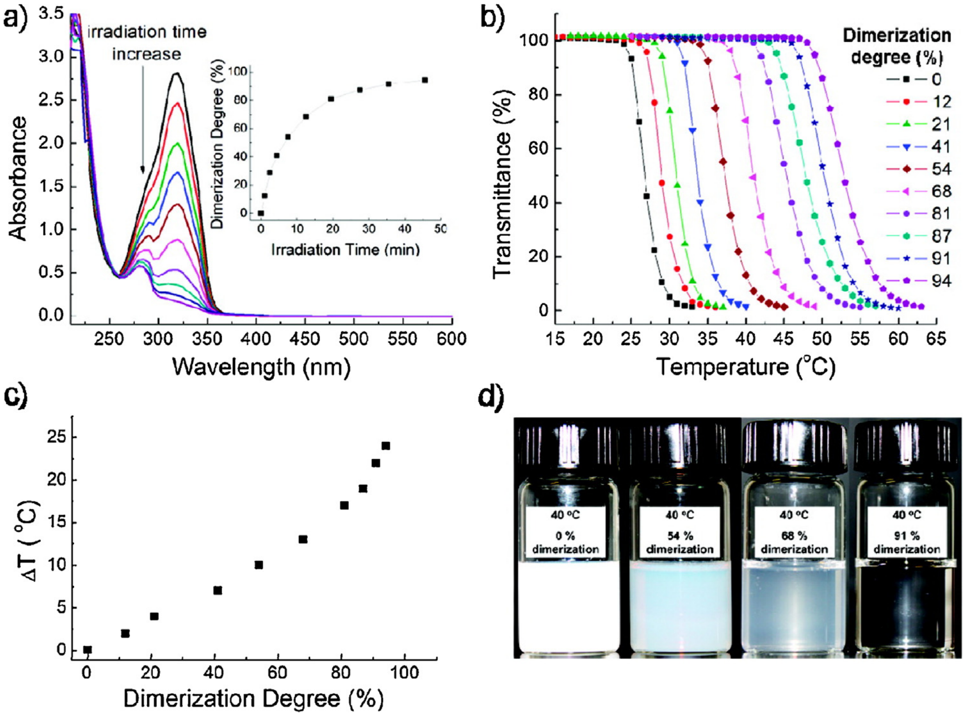


Fig. 11. (a) UV–vis spectra of poly(DMAEMA-*co*-CMA) in water exposed to UV light (λ > 310 nm) for photoinduced architecture transformation from linear to chain-loop; the inset is a plot of photodimerization degree versus irradiation time. (b) Transmittance change as a function of temperature for poly(DMAEMA-*co*-CMA) aqueous solutions (1.0 mg/mL) with samples photodimerized to different extents. (c) Cloud point temperatures of poly(DMAEMA-*co*-CMA) solutions increased as photodimerization degree increased (data from Fig. 10b). (d) Photographs of polymer solutions at 40 °C with various dimerization degrees (from left to right: 0, 54, 68, and 91%) [74], Copyright 2011. Reproduced with permission from the American Chemical Society.

methacrylate, resulting in the introduction of intra-chain loops and a large increase in LCST. The increased transition temperature is presumably due to a reduction of entanglement with neighboring chains, which leads to greater repulsive force and decreased chain aggregation. As the extent of coumarin dimerization (and therefore extent of chain folding) depended on the irradiation time, the authors also studied the ability to externally tune the LCST using different durations of irradiation. Transmittance measurements revealed that the cloud points increased with increasing degree of dimerization, shifting from 25 °C in the original sample to ~50 °C with 94% dimerization after 45 min of irradiation. Intermediate cloud points could be achieved by sampling shorter irradiation times (Fig. 11).

Mo and Zhao et al. later studied the effect of topology on the self-assembly behavior of a UV-cleavable hyperbranched graft polymer containing *o*-nitrobenzyl ester branch points [100]. Under UV irradiation, branch point cleavage transformed the original hyperbranched architecture into a mixture of linear, star, and comb polymers. This mixture of new topologies was found to self-assemble into vesicles and multi-compartmental vesicles in water, whereas the original hyperbranched polymer only self-assembled into micelles (Fig. 12). Further, Nile red that was encapsulated into the starting micelles could be released into solution upon UV irradiation. This on-demand release of Nile red suggests these polymers could prove useful in triggered drug delivery.

In the previously described work involving transformable cyclic block copolymers, the Takata group demonstrated that a transformation of polymer topology from linear to cyclic led to a large difference in crystallization behavior of the block copolymer poly(ε-caprolactone-*b*-hexanolactone) (PCL-*b*-PHL), despite both architectures being of the same composition and molecular weight [114]. According to DSC thermograms, linear PCL-*b*-PHL exhibited both a glass transition at approximately −40 °C (corresponding to the PHL block) and a melting transition at approximately 25 °C (corresponding to the PCL block). However, the cyclic PCL-*b*-PHL did not exhibit a melting temperature, suggesting that the organization of the PCL segments necessary for crystallization was hindered by the cyclic architecture. We also wish to reiterate the findings from the aforementioned linear-to-cyclic polyTHF system, in which the same group showed that solution viscosity behavior could be altered through topological transformations [115]. The transition from a linear to a cyclic polymer directly resulted in a decrease in the intrinsic viscosity from 0.17 dl/g to 0.13 dL/g. The ratio of the intrinsic viscosities of linear polymer to cyclic polymer of 0.76 is strongly suggestive of the formation of cyclic structures. Furthermore, GPC displayed longer elution times after acetylation, indicating a smaller molecular size that would be expected after cyclization.

Finally, Yamamoto and Tezuka et al. linked architectural transformations to material fabrication by developing an approach to rapid, phototriggered hydrogel formation *via* architecture transformation of cyclic block copolymers (PLLA-*b*-PEO and PDLA-*b*-PEO) into linear stereocomplexes [122]. As shown in Fig. 13, a mixture of micellar dispersions of linear PLLA-*b*-PEO-*b*-PLLA and PDLA-*b*-PEO-*b*-PDLA formed a hydrogel as the polymer chain ends protruded out of the micelles and formed stereocomplexes with adjacent micelles, resulting in a physical network. However, no gelation occurred when mixing micelles formed from the analogous cyclic polymers due to the absence of chain ends, eliminating the possibility of stereocomplex formation under the investigated conditions. When a light-sensitive *o*-nitrobenzyl group was incorporated into the cyclic block copolymers, irradiation with UV light led to a transition from cyclic to linear, allowing for chain-end interaction and subsequent gelation of the mixture. These results reinforce the importance of polymer architecture in governing polymer properties, as the presence or absence of chain ends significantly alters the degree of polymer-polymer interactions such as chain entanglement.

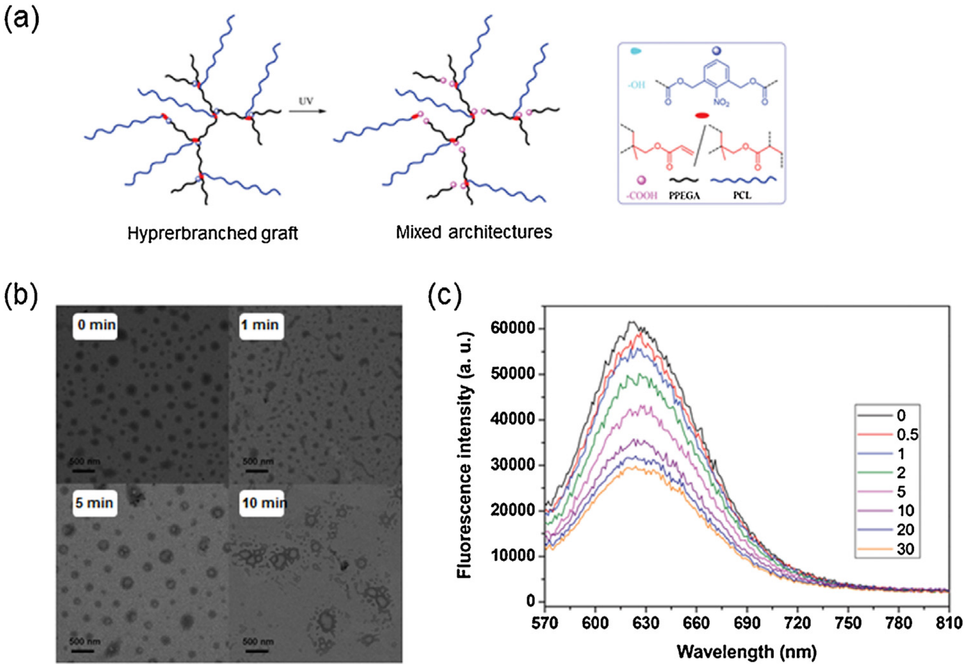


Fig. 12. (a) Light-triggered architecture transformation of hyperbranched graft copolymer to a mixture of linear and branched polymers; (b) Transmission electron micrographs of nano-objects formed by self-assembly of hyperbranched graft copolymer in water before and after UV irradiation for 1 min, 5 min, and 10 min; (c) Fluorescence emission spectra (λ_{exc} = 530 nm) of Nile red-loaded nanoparticles as a function of UV irradiation time. The decrease in fluorescence intensity indicated Nile red was released during UV irradiation [100], Copyright 2015. Adapted with permission from the Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

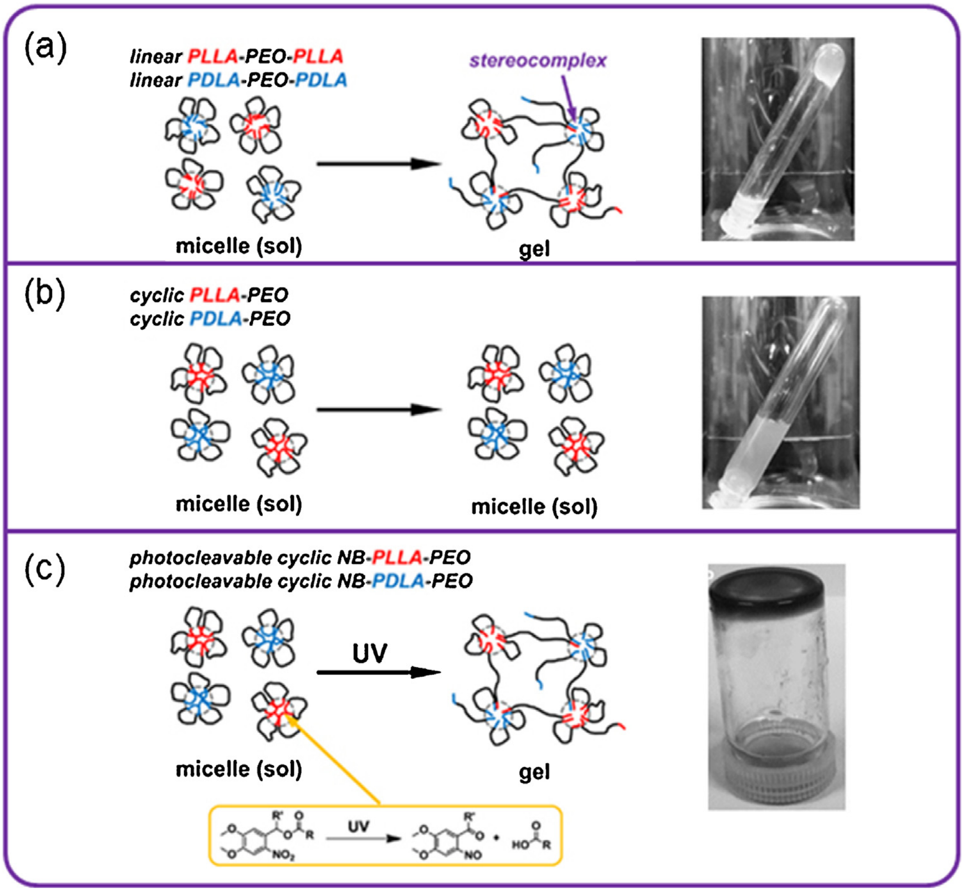


Fig. 13. Schematic illustrations of mixed micellar solutions of linear and cyclic PLA/PEO block copolymers. (a) Linear PLLA-*b*-PEO-*b*-PLLA and linear PDLA-*b*-PEO-*b*-PDLA form stereocomplexes between chain ends, leading to physical gelation; (b) cyclic PLLA-*b*-PEO and cyclic PDLA-*b*-PEO do not possess chain ends, eliminating the possibility for interaction between neighboring micelles; (c) photocleavable NB-PLLA-*b*-PEO and NB-PDLA-*b*-PEO results in a transition from cyclic to linear under UV irradiation and concomitant gelation [122], Copyright 2016. Reproduced with permission from the Nature Publishing Group.

4. Conclusion and future prospects

This review places focus on the scope of stimuli and synthetic strategies available for the preparation of architecture-transformable polymers. A range of dynamic bonds (reversible-covalent or supramolecular) have been exploited to enable architecture-transformable polymers to change their entire shape on exposure to specific stimuli. These macromolecular architecture transformations typically led to drastic changes in many solution and/or bulk properties, such as self-assembly behavior, chain entanglement, and thermal properties (e.g., T_g and T_m). Although many examples relied on a response to a single stimulus, we envision future progress in the design and synthesis of architecture-transformable polymers that respond to multiple stimuli. It may be interesting to introduce orthogonal dynamic bonds into the same architecture-transformable polymer to allow access to various pathways of shape change that could lead to completely different variations in properties [81]. To date, architecture-transformable polymers consisting of two different dynamic linkages were only able to change their topology once, upon the addition of one stimulus. When the second stimulus was applied to promote the cleavage of the other dynamic linkers, no further shape transformation was achieved. For example, Boyer and Davis demonstrated a dual-responsive core-crosslinked star polymer with acid-labile acetal bonds in the core [123]. Additionally, glutathione-sensitive disulfide linkers were employed to tether small molecular drugs on the surface of the core. The architectural transformation from star polymer to linear polymer was achieved under acidic conditions, which induced hydrolysis of the acetal crosslinks. However, a second topological transformation was absent while the addition of glutathione is capable of cleaving disulfide bonds, resulting in the release of small drugs. Another important consideration is achieving complete reversibility of topological transformations, which would allow efficient cycling of polymer properties.

Additionally, several challenges still remain in the viewpoints of both synthesis and applications. One challenge stems from the efficiency of architecture transformations. In a macromolecular system, it is usually difficult to separate a mixed set of polymers, especially those with similar molecular weights and solubility in common solvents [124,125]. Therefore, highly efficient architecture transformations mediated by robust chemistry (such as “click” and “unclick” reactions) are desired for clean reactions and ease of purification [126]. Moreover, modern polymer characterization techniques allow chemists to clearly discriminate between polymers with different architectures. For example, while traditional GPC analysis is only capable of providing limited information on hydrodynamic volume (apparent molecular weight) and polydispersity of the polymers, recent developments combining multi-angle light scattering detection with GPC have led to accurate determination of the absolute molecular weights of polymers, which can assist in recognition of the polymer shapes, especially highly compact structures such as hyperbranched polymers [31]. In addition, the combination of high performance liquid chromatography (HPLC) with GPC offers an opportunity to efficiently separate polymers in a two-dimensional manner based on differences in both hydrodynamic volumes and solvophilicity [89].

Furthermore, it is also noteworthy that most examples outlined in this review were performed in solution, potentially hindering the application of this process to useful materials. There is a significant need to explore these transformations in bulk. However, polymers with a high T_g may suffer from limited mobility, thereby reducing the availability of reactive groups along the polymer chains, resulting in low efficiency of new bond formation which may dictate the reassembly of chains. One possible strategy to overcome this hurdle would be applying a processing temperature that is higher than the T_g of investigated polymers to promote chain mobility. In addition, polymers with high degrees of crystallinity would exhibit poor light penetration, limiting their potential in photoresponsive architecture-transformable polymeric materials in bulk. Therefore, more rational design and study needs to be conducted to facilitate the transition of this concept from solution into bulk materials. Given the considerable progress of traditional stimuli-responsive polymeric materials in the field of modern manufacturing, biology, and medicine, we believe that the development of architecture-transformable polymers will not only expand the scope of stimuli-responsive polymers, but also open the door to an unprecedented class of adaptive materials with unique properties and applications.

Acknowledgements

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