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Solving fundamental concepts in supramolecular science with functionality-tolerant living polymerizations of self-assembling monomers and dendronized monomers

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Dedicated to Professor Nikos Hadjichristidis to honor his scientific and editorial contributions and his 80th birthday!

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ABSTRACT

The evolution and development of several examples of functionality-tolerant living polymerizations to the level of perfection that they could be employed to solve fundamental concepts in supramolecular science by living polymerization of self-assembling monomers and self-organizable dendronized monomers is briefly reviewed. The review focuses on the development of the living polymerization methodology with brief examples on how they impacted the field of self-assembly and self-organization. The first polymerization reaction discussed is the stereoselective polymerization of phenylacetylene and of other arylacetylenes to generate helical poly(arylacetylene) stereoisomers. The transition from functionality non-tolerant to functionality-tolerant stereoselective polymerizations and the evolution to functionality-tolerant living stereoselective polymerization of phenylacetylene is used as the main example of this brief review. This living polymerization methodology is followed by living polymerization of vinyl ethers, oxazolines, of group transfer polymerization, of cationic ring-opening polymerization of cyclic siloxanes combined with hydrosilylation, of ROMP of cylooxanorbornene. This brief review is concluded by a brief discussion of the capabilities of the above-mentioned living methodologies with living radical polymerizations. The numerous applications in the field of supramolecular science of these living methodologies are not reviewed. However, the reader is directed to numerous comprehensive review articles discussing these applications. The challenges that remain to be solved in all these functionality-tolerant living polymerizations are presented.

1. Introduction

In 1956 Michael Szwarc discovered living anionic polymerization of styrene initiated by single electron transfer from sodium naphthalene to styrene to form the styryl radical anion. The radical of this radical anion dimerizes to generate the dianion propagating the polymerization of styrene in two directions [1]. In the same year Szwarc laboratory demonstrated the synthesis of block copolymers by living anionic polymerization [2]. The story of this discovery, the inspiration for it and the relaxed definition of living polymerization was told by Szwarc in the first Highlight written at my invitation in the first issue of the Journal of Polymer Science: Part A: Polymer Chemistry who pioneered the publication of highlights, graphical abstracts and front covers in scientific publications in US [3]. Mechanistic investigations on the living anionic polymerization and of the single-electron transfer (SET) processes responsible for the initiation step were under investigation and debate for many years. Instead of joining mechanistic debates, Nikos Hadjichristidis embarked on the elaboration of methodologies for the construction of polymers with complex architecture by living anionic polymerization of conventional monomers. By designing complex architectures with the help of high-quality experiments performed in sealed glassware under high vacuum, combined with excellent characterization of the final products, Nikos became the most influential scientist involved in this field. There is no debate, as is the case in mechanistic studies, when the structural characterization of the final product is performed as Nikos always did. He expanded the arsenal of living anionic polymerization by combining living anionic with other living methodologies. Through design and synthesis of complex architectures Nikos provided models for commercial block copolymers, branched polyethylene, micellar structures, to name just a few. He also

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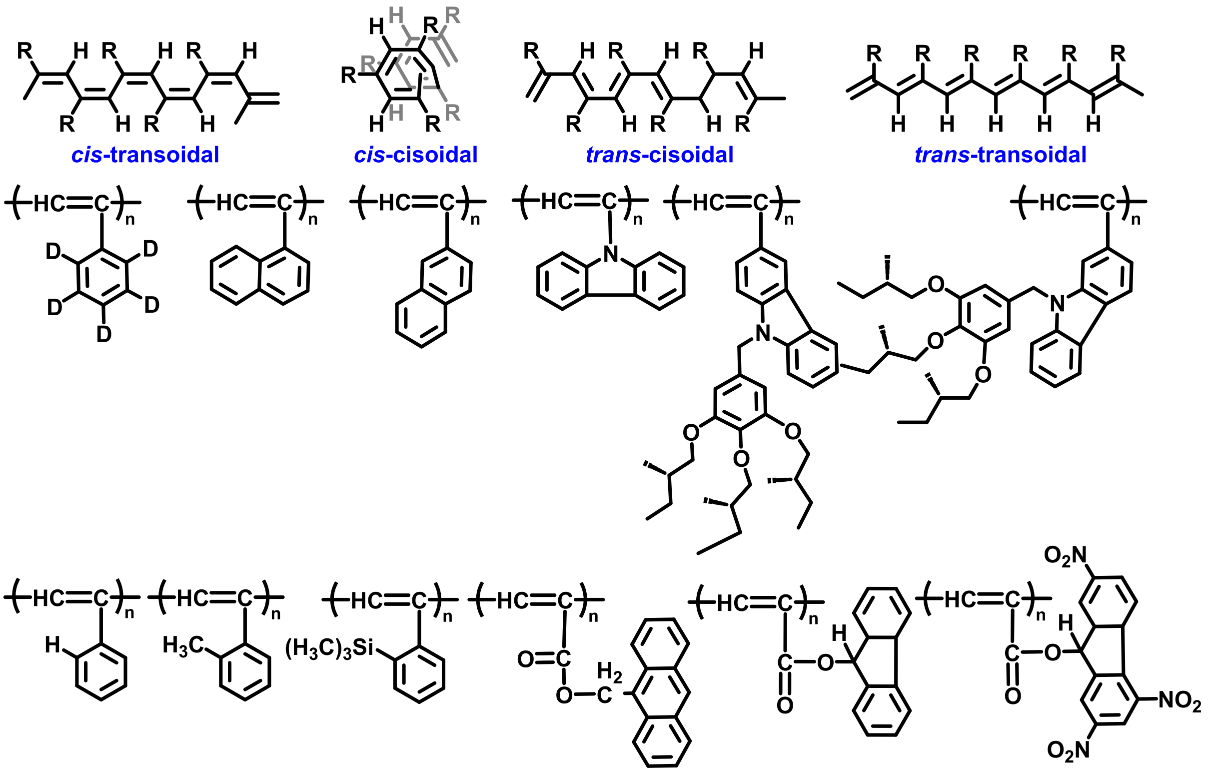
optimized the properties of commercial polymers and designed new polymers with well-defined properties designed by their perfect architecture. Nikos collaborated and continues to collaborate with the premier practitioners in polymer chemistry and polymer physics. Instead of enumerating his numerous landmark complex structures, techniques and methodologies I would rather cite some of his remarkable review and highlight articles, written at my invitation, on the methodology of living anionic polymerization and on complex architectures synthesized by this method since these landmark publications speak by themselves [4–7]. He is the very rare case of scientist who shares in great details the way he does all his experiments by not turning down to write invited papers and review/highlights describing the technique.

This paper is a combination of review/highlight article that discusses mostly the approach used by our laboratory to solve fundamental concepts in supramolecular science with the help of functionality-tolerant living polymerizations of self-assembling monomers including self-organizable dendronized monomers. Since self-assembling monomers and self-organizable dendronized monomers contain a large diversity of nucleophilic and electrophilic functional groups, very few living polymerization methodologies can be employed in these studies. Some of these living polymerizations have to be performed and employed at very low degrees of polymerization and at room temperature and some other at high temperatures and low degrees of polymerization. Justification for the selection of the method will be provided in each case. With the exception of ring opening metathesis polymerization (ROMP) [8] no living polymerization can compete with living anionic even if they tolerate a larger diversity of functionalities. The selection of living methodologies reported here, was also taking into account, the possibility of challenging Nikos to improve the method or to develop more competitive and less expensive procedures.

2. Synthesis of helical stereoisomers of poly(phenylacetylene)s and of poly(arylacetylene)s by stereoselective and living stereoselective polymerization. The *ortho*-substituent effect

Percec et al reported the stereoselective synthesis and characterization of all helical stereoisomers of polyphenylacetylene (PPA): *cis*-cisoidal, *cis*-transoidal, *trans*-cisoidal, and *trans*-transoidal [9]. The *cis*-cisoidal PPA is crystalline and insoluble and therefore, its structure was demonstrated by X-ray diffraction experiments combined with a calibration plot involving ^{1}H NMR and IR spectroscopies to determine its *cis*-content. ^{1}H NMR methods were elaborated for the characterization of the other stereoisomers of PPA and for the determination of the *cis*-content of the *cis*-transoidal stereoisomer. A combination of NMR and IR spectroscopy together with a calibration plot was elaborated for the calculation of the *cis*-content of both insoluble *cis*-cisoidal and soluble *cis*-transoidal stereoisomers. A new variant of a Ziegler-Natta catalyst was elaborated to synthesize the *cis*-cisoidal and *cis*-transoidal helical stereoisomers of PPA: $AlEt_3/Fe(dmg)_2.2Py$ where dmg stands for dimethylglyoxime, was the most most efficient. $(PPh_3)_2PdCl_2$ was employed for the synthesis of *trans*-cisoidal PPA. It was also discovered that thermal isomerization of the *cis*-cisoidal and *cis*-transoidal stereoisomers is accompanied by an intramolecular electrocyclization accompanied by aromatization and chain cleavage [9,10]. This thermal intramolecular cyclization accompanied by cis–trans isomerization can be induced also by the heat of polymerization when the polymerization reaction is highly exothermic or is performed at high temperature. The presence of oxygen can also be involved in this sequence of reactions although this issue is not completely elucidated [11–13].Therefore, electrocyclization should be considered very carrefuly when investigating stereoselective polymerizations of PA. Related combinations of methods were employed for the synthesis of helical stereoisomers of poly(pentadeuterophenylacetylene) [14], poly(α-ethynylnaphthalene) [15,16], poly(ß-ethynylnaphthalene) [17], poly(N-ethynylcarbazole) [18], poly(2-and 3-ethynyl-9-substituted carbazole)s (Scheme 1) [19]. Electron-acceptor and electron-donor aromatic propiolic esters were



Scheme 1. Helical stereoisomers of the poly(arylacetylene)s synthesized by Percec et al.

synthesized and polymerized by anionic polymerization but the stereochemistry of the resulting polymers was not elucidated [20] (Scheme 1). Two proceedings of plenary lectures and a review article discussed in more details these developments [21–23]. In 1974 Higashimura laboratory from Kyoto University together with his graduate student Masuda started ~~to~~ a systematic series of investigations on the polymerization of PA and of many other acetylenic monomers with WCl_6 and $MoCl_5$, other metal salts and combinations of these salts with reducing agents [24]. Review articles on these topics were published [25,26]. However, this laboratory was mostly interested in kinetic investigations and did not study the stereochemistry of the resulting PPA. In 1983 Percec investigated by a combination of ^{1}H- and ^{13}C NMR the structure of PPA synthesized by WCl_6 and $MoCl_5$ catalytic systems and demonstrated a stereoselective polymerization to *cis*-transoidal helical conformation [27–29]. A more refined methodology to determine the *cis*-content of PPA by expanding the method published in 1977 [9] was also elaborated in these publications. Our 1983 papers on the structural analysis PPA were contemporary with the elegant work of Katz from Columbia University who demonstrated, aided by our stereochemical analysis methods, the stereoselective polymerization of PA with metal carbenes [30] and metal carbynes [31,32]. In 1990 Kunzler and Percec demonstrated the living polymerization of *ortho*-aryl substituted acetylenes by $MoCl_5$ and WCl_6 based initiators demonstrating the *ortho*-phenyl substituent effect that suppresses the intramolecular electrocyclization [33]. The *ortho*-substituent effect was applied by Higashimura laboratory to provide the living metathesis polymerization of [o-(trifluoromethyl)phenyl]acetylene by Mo-based three-component catalysts [34], thus validating the concept of Kunzler and Percec.

Prior to the publication from 1977 that developed the methods to determine the *cis*-content of PPA [9]. Kern from Monsanto Company in US demonstrated the polymerization and oligomerization of PA with the Wilkinson catalyst, $RhCl[PPh_3]_3$, $RhCl_3/LiBH_4$ and $RhCl_3$ [35–37]. Although Kern recorded an X-ray diffractogram for the red-insoluble PPA he could not assign it, as Percec did, to the *cis*-cisoidal PPA since he did not have the combined NMR-IR method elaborated by Percec to quantitatively discriminate between *cis*-cisoidal and *trans*-cisoidal conformers together with their *cis*-content.

Starting in 1986 Anita Furlani together with Maria Vittoria Russo and their students from Sapienza University in Rome replaced the phosphine ligand of the Wilkinson catalyst used by Kern with the pi-ligand cyclooctadiene (COD) combined with a variety of N-based ligands. By screening libraries of Rh complexes Furlani-Russo laboratory discovered with the help of Percec's NMR method that $[Rh(COD)Cl]_2$ in methanol in the presence of NaOH dissociates the Rh complex yielding high *cis*-content *cis*-transoidal PPA in a very short reaction time at room temperature [38–40]. Free standing films of PPA were obtained in the presence of a Rh-imidazole catalysts [41]. These series of elegant experiments pioneered the stereoselective polymerization of PA and of other acetylenic monomers with Rh-based catalysts. In 1998 the same laboratory reported the stereoselective polymerization of PA and *p*-nitrophenylacetylene providing polymers with molecular weight distribution as narrow as 1.08 [42,43]. These and the previous experiments were an alarm clock to the entire community working in this field since narrow polydispersity functional helical PPA could be synthesized by functional groups-tolerant stereoselective Rh-catalysis. These results also indicated the potential of living stereoselective polymerization of PA by Rh-catalysis. The entire scientific community working in this field moved from Ziegler-Natta, WCl_6, $MoCl_5$ and other catalytic systems to Rh-catalysis since Rh tolerates a large diversity of functional groups during the stereoselective polymerization of PA and many other acetylenic monomers. In 1990 Tabata laboratory replaced the inorganic base NaOH used by Furlani together with $[Rh(COD)Cl]_2$ in methanol with the organic base NEt_3 and changed COD to NBD to generate $[Rh(NBD)Cl]_2$ that produced a very active catalytic system that provided long-lived propagating species from PA and from substituted PA during stereoselctive polymerization [44–47]. A comparison of the structure of substituted PPA synthesized by different catalytic systems including Ziegler-Natta, Rh, $MoCl_5$ and WCl_6 was also reported by Tabata laboratory [48]. Tabata laboratory demonstrated also stereoselective polymerization of propiolic esters with Rh-based catalysts [49]. Tabata laboratory employed their Rh-catalytic systems to the development of a large research program on helical polymers that is not the topic of this paper and therefore, it will not be discussed here. Stereoselective polymerization of PA was also accomplished in 1994 by Alper who employed $Rh^+(COD)BPh_4^-$ in the presence of Et_3SiH [50]. Stereoselective polymerization of PA with more complex ligands attached to Rh, stereoselective polymerization of PA in water as well as the polymerization of liquid crystal monomers were all accomplished [51–53].

Although symptoms of living stereoselective polymerizations with Rh catalysts were seen in many experiments mentioned above, the first living stereoselective Rh-based catalyst, $Rh(C\equiv CC_6H_5)(nbd)[P(C_6H_5)_3]_2$ in the presence of DMAP, for the polymerization of PA was reported by Noyori laboratory in 1994 [54]. In 1986 Noyori reported a more active Rh catalyst for the living stereoselective polymerization of PA, $[Rh(OCH_3)(NBD)]_2/P(C_6H_5)_3/DMAP$, [55]. Noyori laboratory also elaborated additional Rh catalysts with enhanced reactivity for living stereoselective polymerization of PA and compared their reactivity and mechanism of polymerization [56,57].

A Rh-catalyst was developed independently and simultaneously with the Noyori catalysts by Erica Farnetti together with M. Falcon, and N. Marsich from the University of Trieste. They demonstrated stereoselective living polymerization of phenylacetylene promoted by rhodium catalysts with bidentate phosphine ligands [58]. This catalayst involves the use of $[Rh(OCH_3)(NBD)]_2$ together with the bidentate phoshines dppe, dppp and dppb, rather than monodentate phosphines as Noyori laboratory used. $[Rh(OCH_3)(NBD)]_2$/dppb is an excellent catalyst providing very narrow polydispersity PPA with *cis*-transoidal helical conformation but with low initiator efficiency since it consists of a mixture of reactive and unreactive species. This simple, elegant but forgotten experiment deserves additional investigations. Masuda, who pioneered together with Higashimura the WCl_6 and $MoCl_5$-based catalysts discussed above for the stereoselective polymerization of PA, also developed Rh catalysts for the living stereoselective polymerization of PA [59–62].

The most recent developments in stereoselective living polymerization of phenylacetylene mediated by Rh were developed in Maeda laboratory who also reported the first end-functionalization of *cis*-transoidal PPA including its synthesis in water [63–66]. It is also interesting to mention that Maeda laboratory succeeded to develop simple methods for the synthesis of linear and cyclic poly(diphenylacetylene) after he revised the original mechanism proposed for the polymerization of diphenylacetylene with $WCl_6/Sn(Ph)_4$ [67,68].

Last but not least, we should mention the well-characterized Mo-alkylidene complexes of Schrock that mediate the living polymerization of (o-trimethylsilylphenyl)acetylene, of ethynylmetallocenes, the living cyclopolymerization of 1,6-heptadiyne derivatives and tantalum-carbene complexes that are effective for living polymerization of 2-butyne [69–73].

3. Self-organizable dendronized helical stereoisomers of PPA eliminate intramolecular electrocyclization accompanied by chain cleavage and generate molecular Machines

The Rh catalyst elaborated by Noyori was employed by our laboratory for the living stereoselective synthesis of *cis*-transoidal PPA dendronized with self-assembling dendrons [19,74–82]. This process allowed the development of a new concept at the interface between polymer science, organic chemistry, supramolecular chemistry, and nanotechnology. The helix-coil transition of PPA accompanied by intramolecular electrocyclization was replaced with an unprecedented and reversible thermally induced *cis*-cisoidal to *cis*-transoidal isomerization that provided a molecular machine interfaced with the real world for the first time by simple coating of the polymer into a helical dendritic jacket [83] (Fig. 1).

4. From living side-chain liquid crystalline poly(vinyl ether)s, poly(oxazoline)s and poly(siloxane)s to self-organizable dendronized polymers by living cationic polymerizations

In 1986 and 1987 our laboratory pioneered the synthesis of poly (vinyl ether)s, poly(propenyl ether)s and poly(oxazoline)s containing mesogenic side groups as new classes of side-chain liquid crystalline polymers [84,85]. Several years later our laboratory transformed these methodologies into the most successful living polymerizations employed in the molecular engineering of highly functional mesogenic vinyl ethers [86–94]. This methodology was inspired and improved from the living polymerization of vinyl ethers elaborated by O. Webster [95] (Fig. 2).

Percec was a consultant at the Central Research, Experimental Station of DuPont and was involved in the development of this technology. Group transfer polymerization (GTP) also discovered by Owen Webster was another functionality-tolerant living polymerization that was employed in these experiments [91,96–98] (Figs. 3 and 4). Living cationic polymerization of cyclic siloxanes was an additional functionality-tolerant polymerization, that was employed in a two-step process: the cationic polymerization/copolymerization that is relatively sensitive to functionalities, followed by hydrosilylation that tolerates a large diversity of functionalities. This methodology was employed to produce a new mechanism decoupling the motion of the main-chain from the side-groups by phase separation [93,94].

Cationic ring-opening polymerization of oxazolines was discovered simultaneously in four different laboratories [99–102]. It was subsequently elaborated into a living polymerization process [103] and more recently expanded to the preparation of high molecular weight polymers [104,105]. The functionality tolerance of this polymerization was demonstrated by Percec [106,107] and soon after it was employed in the synthesis of side-chain liquid crystal polymers [85]. The simplest method for the synthesis of oxazolines was also elaborated by our laboratory [108]. This brief discussion on the functionality-tolerant living polymerizations justifies the selection of living polymerization of vinyl ethers [109,110] and oxazolines [111–116] for the first examples of self-organizable dendronized polymers prepared by living polymerizations.

The discovery and direct visualization of A15 [117–123], and Sigma Frank-Kasper [124] and liquid quasi crystal (QLC) [125] phases was made by employing conventional organic reactions and radical polymerizations. However, the demonstration that all these phases can be accomplished within five monomer repeat units of a polyoxazoline could not have been accomplished without the living polymerization of oxazolines [126] (Fig. 5).

5. From self-organizable helical dendronized polymers by living ROMP to monodisperse polymers by self-interrupted living ROMP of dendronized monomers

Living ring opening metathesis polymerization (ROMP) is one of the most functionality-tolerant living polymerization known [115,127–132] and therefore, the early experiments on self-organizable helical dendronized polymers were accomplished by ROMP and even by conventional free radical polymerization experiments [133–137]. The most unusual feature of living ROMP mediated by the Grubbs Ru-catalyst is the extremely long stability of its active species. This facilitated the first

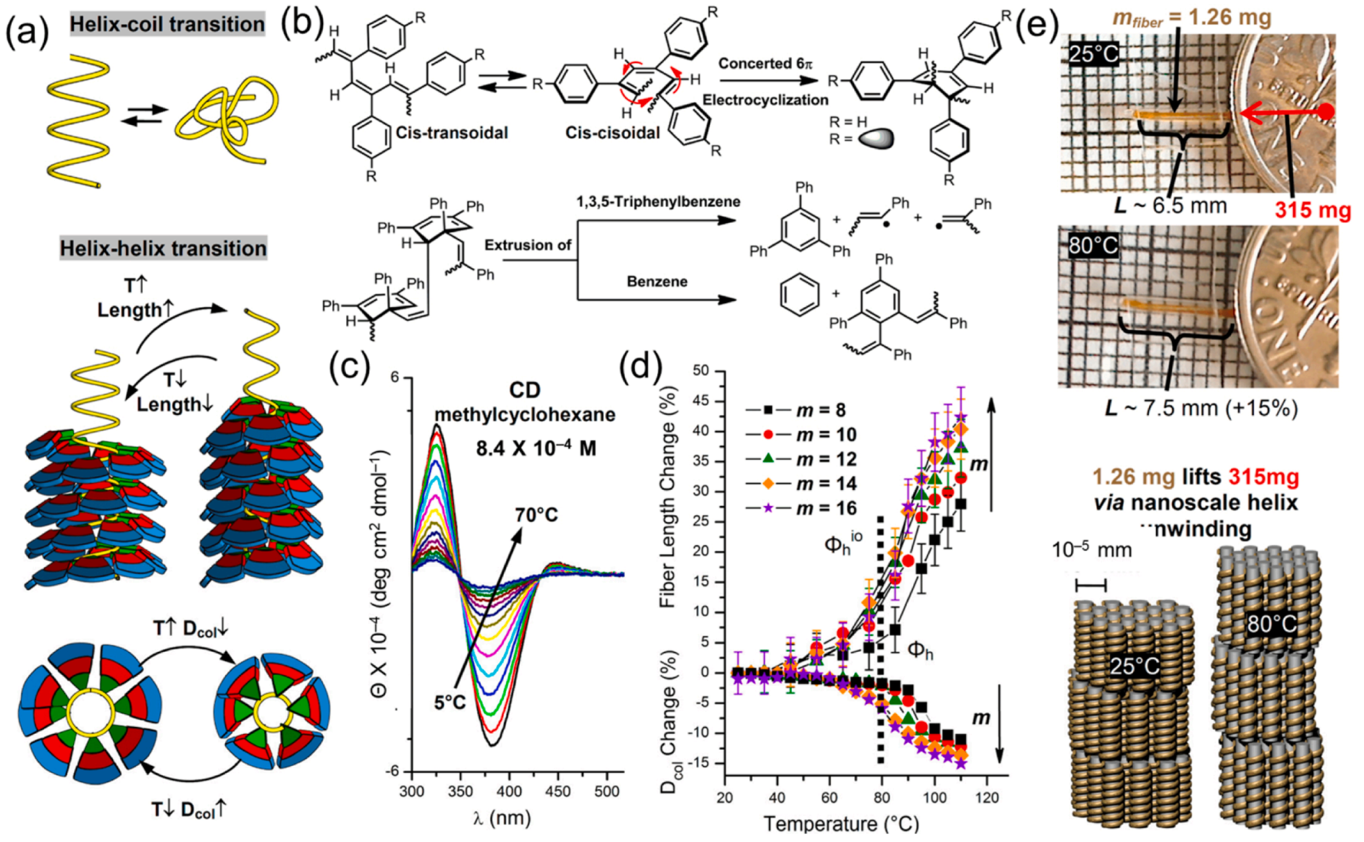


Fig. 1. Molecular machine self-organized from dendronized helical polyphenylacetylenes. Illustration of the helix–coil transition and its transformation into a helix–helix transition that mediates expansion and contraction of the helical structure with temperature (a); expanded images collected by a digital camera at 25 °C and at 80 °C of the oriented fiber (b); variable-temperature CD spectrum (c); comparison of the fiber length change from optical microscopy and column diameter from the fiber XRD for the library of the polyphenylacetylenes with different peripheral alkyl chain length in the dendron (m) (d). The Figure is adapted and modified from [74]. Copyright © 2008, American Chemical Society.

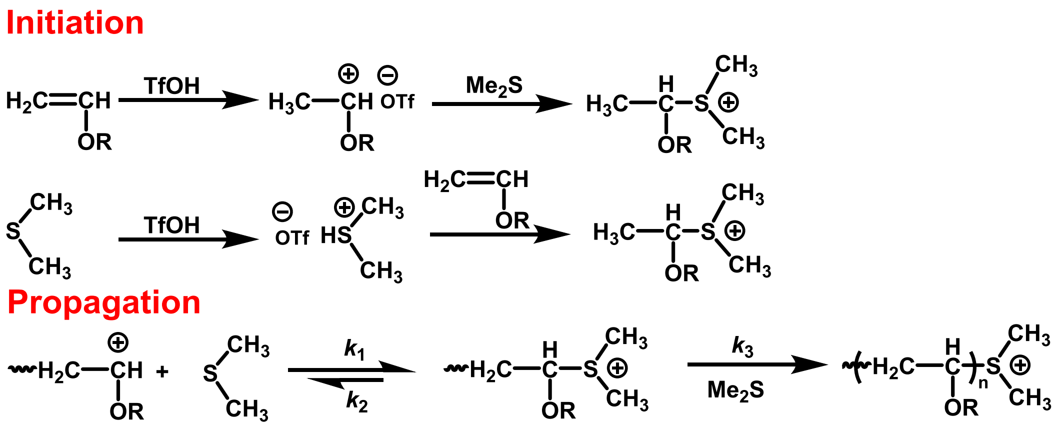


Fig. 2. Mechanism of living cationic polymerization of isobutyl vinyl ether. This figure was redrawn from reference 95.

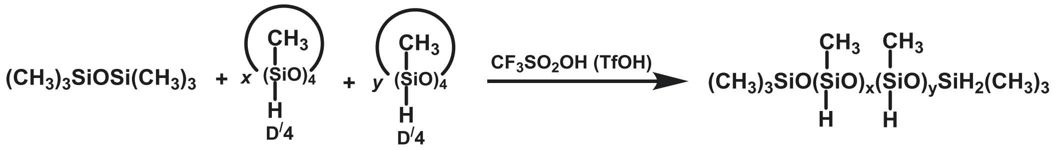


Fig. 3. Synthesis of poly(methylsiloxane-co-dimethylsiloxane)s. The Figure was redrawn from reference 93.

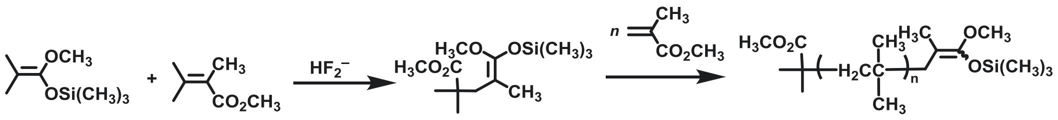


Fig. 4. Polymerization of acrylic monomers by GTP. The Figure was redrawn from reference 97.

synthesis of a monodisperse polymer by self-interrupted living ROMP of a dendronized monomer (Fig. 6) [138]. This experiment could not be accomplished yet with any other living polymerization methodology.

6. Can SET-LRP and ATRP compete with other FUNCTIONALITY-TOLERANt living polymerizations of self-organizable dendronized monomers?

A recent perspective from our laboratory discussed the historical development of different living radical polymerization methodologies and also provides solutions to resolve the incompatibility between single- electron transfer living radical polymerization (SET-LRP) in non-disproportionating solvents [139–154]. The closely related SET-LRP and ATRP differ mostly by the nature of solvent, disproportionating vs non-disproportionating, and Cu species, Cu(0) vs Cu(I), employed as catalyst in the polymerization. Although all living radical polymerizations are under continuous mechanistic investigations the question that we would like to address here is if they can compete with the functionality-tolerant living polymerizations already discussed and what are the most important problems that must be elucidated in order to provide additional developments of this methodology. We will refer particularly to SET-LRP. SET-LRP is the first method to provide LRP of acrylonitrile (AN), vinyl chloride (VC) and of acrylates at room temperature [146,147,155–217] even in air and in the presence of radical inhibitors [163–167]. It provides perfectly bifunctional polymers, lack of termination even at 100 % conversion, proceeds in mixtures of solvents exhibiting cooperative and synergistic solvent effect [168–176], and uses a simple Cu-wire or any other Cu-shape as a catalyst generating the simplest method for continuous industrial scale development from low molar mass up to very high molar mass polymers. SET-LRP can be also photoinduced [177]. The development of TEMNINI [178–182] and thio-bromo “click” [183–185] allowed for the first time the elaboration of methodologies for the synthesis of dendrimers from conventional monomers. However, as far as the main topic of this brief publication, due to solvent-intolerance which is equivalent with functionality-tolerance, only one helical structure of a self-organizable dendronized polymer was elucidated with the help of SET-LRP, an 8/4 helical structure of a dendronized polymer [186–190] (Fig. 7). Therefore, there is a long way to go until LRPs will compete with the other functionality-tolerant living polymerization methodologies discussed in this brief publication. We expect that solving fundamental problems such as the catalytic effect of solvent [191], and the mixed ligand effect [192,193] may provide the expected developments for LRPs.

7. Conclusion

Functionality-tolerant stereoselective living polymerization is the dream of polymer synthesis for all classes of monomers. Unfortunately, this dream came through only for the stereoselective living polymerization of phenylacetylene and its derivatives, many other arylacetylenes and substituted acetylenes. This brief review/highlight-like article tells the story of this successful discovery. It started with Ziegler-Nata stereoselective polymerization of PA and with the development of NMR combined with IR analysis methods for the determination of all helical isomers of PPA. It continued with $MoCl_5$ and WCl_6 based stereoselective systems, the *ortho*-phenyl substituent effect to generate living polymerizations of PPA and culminated with enantioselective polymerization of PA mediated by Rh-catalysts. Ultimately a large diversity of Rh-based initiators mediating stereoselective living polymerization of PA were developed and are already used every day. Since the backbone of

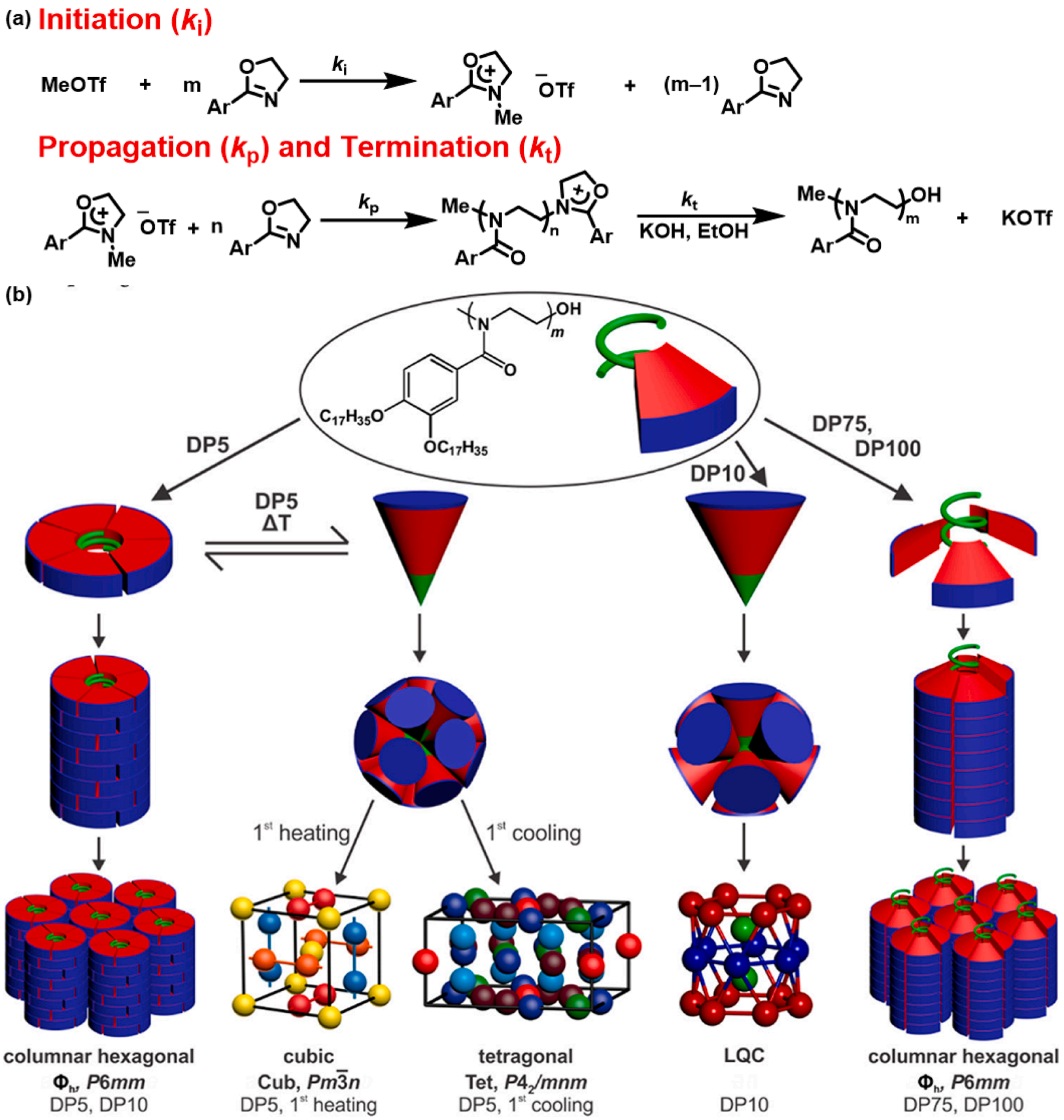


Fig. 5. (a) Living cationic ring opening polymerization of poly oxazolines; (b) Summary of periodic and quasiperiodic arrays self-organized from assemblies of poly [(3,4)17G1-Oxz]. Part (a) of the Figure is redrawn and part (b) was an adapted and modified from reference 126. Copyright © 2018, American Chemical Society.

the helical-PPA provides a chromophore for UV-combined with circular dichroism (CD) experiments, the stereoisomers of PPA provided access to numerous investigations related to helical chirality. Numerous review articles on applications, many written at my invitation are available [23,76,80,82,194–201] and therefore, applications were not discussed here. The Rh-based stereoselective living polymerization can generate polymers from very low molar mass up to very high molar mass. A warning to be considered is, as demonstrated by Percec et al in 1977, the heat of polymerization can induce the thermal-mediated intramolecular electrocyclization accompanied by cis–trans isomerization. Rh provides excellent pathways for functionality-tolerant stereoselective living polymerizations but it is extraordinarily expensive. What is needed to advance this field even father is what Percec laboratory did to metal-catalyzed cross-coupling reactions: replace the very expensive Pd with the very inexpensive but more reactive Ni and create synthetic strategies towards very stable but reactive and inexpensive catalysts [202–209]. Additional functionality-tolerant living polymerizations are the cationic polymerization and cyclopolymerization [210,211] of vinyl ethers and group transfer polymerization of acrylic monomers, both pioneered by Webster [95–98], the cationic ring-opening polymerization of oxazolines and Ru-mediated ROMP. The first three are ideal for the synthesis of low molar mass polymers either in solution at room temperature or in bulk at high temperature. All are excellent but limited in scope. ROMP is an excellent methodology but it is restricted to the structure of the monomers that can be used. Cationic ring-opening polymerization and copolymerization of cyclic siloxanes followed by hydrosilylation is also a useful method but it is very limited in scope. Unfortunately, we could use in one single case living anionic polymerization to low molar mass dendronized polymers to solve a conceptual problem on this topic [128]. We expect that this brief review/perspective will encourage other laboratories to pursue functionality-tolerant living and stereoselective living polymerization for all classes of monomers in order to bring an even larger bridge between polymer synthesis and supramolecular science [212–217]. A more detailed discussion on the terminology of living polymerization was recently published by our laboratory elsewhere [139] and the readers of this paper are recommended to consult it.

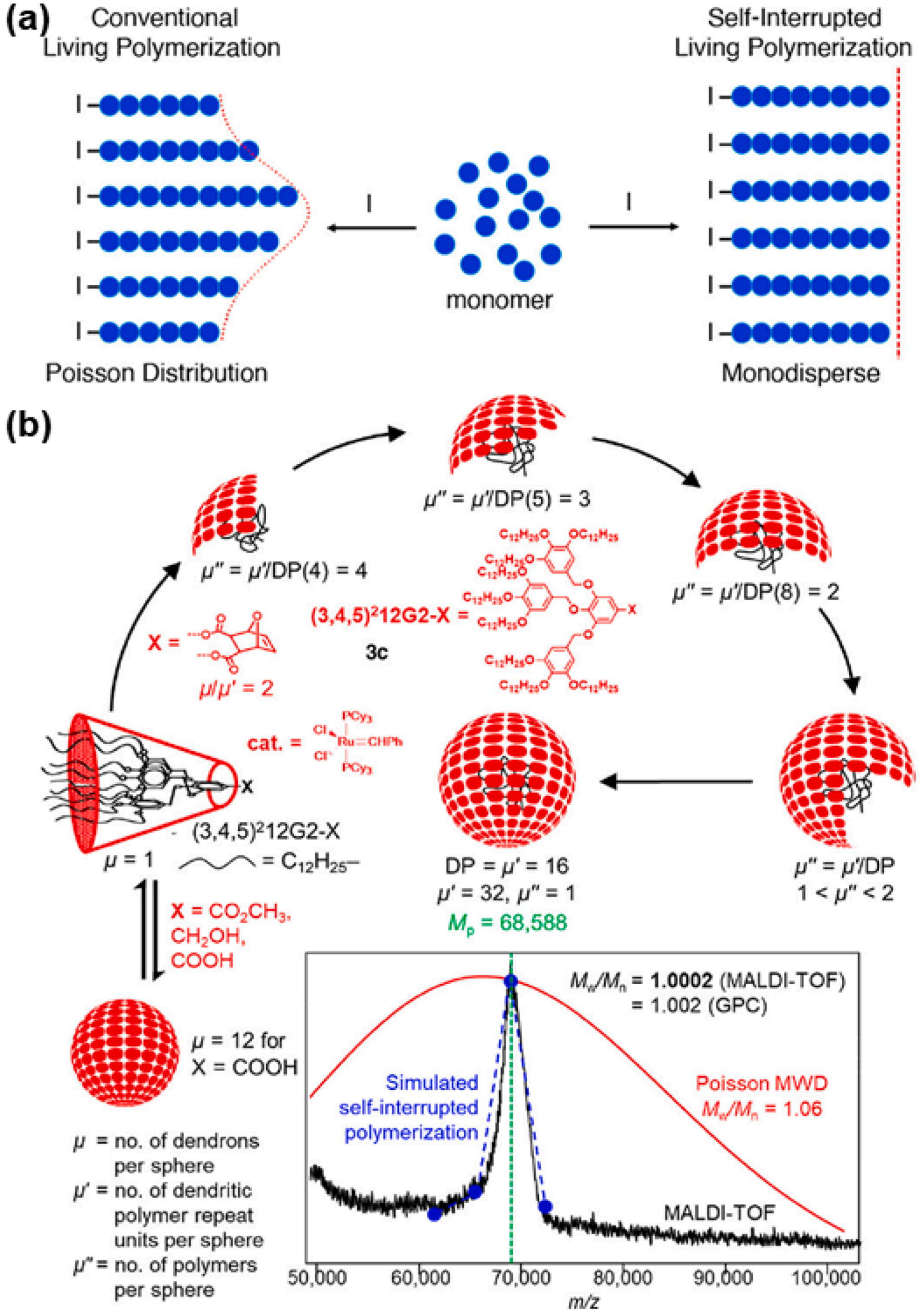


Fig. 6. (a) Distinguishing conventional living polymerization and self-interrupted living polymerization (SILP); (b) Mechanism of SILP. Polymer chains with DP < 16 and nonpolymerizable dendrons with ester, acid, or alcohol apex groups self-assemble into spheres. A sphere can be formed from a single chain with DP = 16, at which point the active polymer chain end is sequestered inside the sphere and polymerization ceases (center). Comparison of experimental (black), simulated (blue), and theoretical Poisson (red) MW distributions. Parts of the Figure were adapted and combined from reference 138. Copyright © 2020, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

CRediT authorship contribution statement

Virgil Percec: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **Dipankar Sahoo:** Software, Visualization, Writing – review & editing.

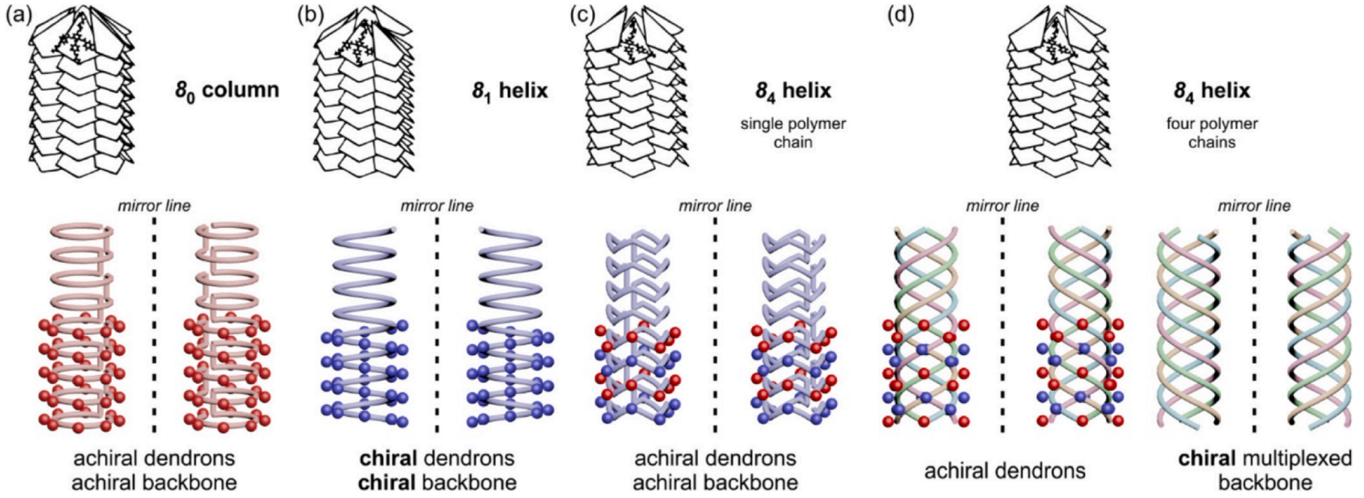


Fig. 7. Schematic representations of four models for the supramolecular columns of 12-4EO-PMA: (a) achiral nonhelical 8_0 column of stacked disks; (b) chiral 8_1-helical column; (c) achiral 8_4-helical column with a single polymer chain; (d) 8_4-helical column with achiral arrangement of dendrons and a chiral backbone multiplex of four polymer chains. In each schematic representation (bottom), the polymer backbone is shown with and without its jacketing dendrons. The Figure is adapted from reference 190. Copyright © 2017, American Chemical Society.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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