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Perfecting self-organization of covalent and supramolecular mega macromolecules *via* sequence-defined and monodisperse components

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ABSTRACT

Biological macromolecules such as nucleic acids and proteins are homochiral, display monodisperse chain length with mega, multimillion, molecular weight and encode functions by their precise sequence *via* self-organization. The functions of biological macromolecules are either independent on molecular weight or, like in the case of ribosome, are programmed by the self-organization of their mega molecular weight. In spite of the fact that Staudinger coined the name macromolecule 100 years ago, self-organizable synthetic covalent and supramolecular mega macromolecules exhibiting the symptoms of biological macromolecules started to emerge only recently. This personal perspective will discuss, with examples mostly from our laboratory, methodologies for the synthesis of self-organizable covalent and supramolecular mega macromolecules for which functions are encoded, programmed and perfected *via* homochiral, sequence-defined and monodisperse components. Methodologies to generate them together with historical developments will be briefly discussed.

1. Introduction

This year we celebrate the 100-years anniversary of the landmark publication of Hermann Staudinger that first draw the covalent structure of macromolecules [1] and subsequently defined it in words [1,2]. This anniversary was celebrated *via* several International Symposia organized during the Spring ACS Meeting 2020 from Philadelphia. One of us (VP) organized an International Symposium entitled “From Staudinger Macromolecules to the Genome of Macromolecules.” Since Staudinger was a highly regarded organic chemist, most of the plenary lecturers at this symposium were given by organic chemists including two Nobel Prize laureates. The opening lecture given by VP was entitled “From Berzelius to Staudinger through Polymers and Macromolecules.” Several years ago, one of us (VP) edited a two-volume book that celebrated the 60 years anniversary of the 1953 Nobel Prize of Hermann Staudinger “for his discoveries in the field of macromolecular chemistry” [3,4]. The preface to this two-volumes book [5] and a manuscript from this book [6] provide additional details on Staudinger concept and professional career. While editing this book I learned about Staudinger’s life more than he would have liked anybody to know about him except for himself. My connection with the Hermann Staudinger House that hosts the Institute of Macromolecular Chemistry from the University of Freiburg, Germany was presented by invitation in a recent publication from a special volume dedicated to Staudinger with the occasion of the 100 anniversary of his paper that coined the name macromolecule [7] and in an invited lecture given on September 29, 2020 at the Royal Swedish Academy of Engineering Sciences IVA. This lecture was presented, submitted to publication, and published after this manuscript was submitted to publication [8]. References [5–8] give more details on references [1,2] and subsequent publications of Staudinger defining covalent macromolecules and also tell the story that almost took me back from US to Freiburg on the Staudinger chair. This explains the number of many volumes, symposia and publications that I dedicated to Staudinger. A number of other remarkable, comprehensive but short publications that refer to Staudinger life and accomplishments are also available [9–15]. These publications can introduce anybody interested in learning as much as possible about Staudinger and his work and therefore it will not be repeated here. The first review article in the field of polymerization published by Carothers in 1931 [16] and the classic first polymer chemistry textbook published by Flory in 1953 [17] must be on the desk of everybody reading this paper. While Flory received a Nobel Prize in 1974, in my opinion, Carothers, would have received a Nobel Prize maybe even before Staudinger if he would not have committed suicide on April 29, 1937 in Philadelphia (he was 41 years old at that time), one

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Table 1
Covalent linear mega homopolymers prepared by various polymerization techniques.

Mega homopolymer[a]	Polymerization technique	Solvent	T (°C)	M_n[b] (g/mol)	M_w/M_n	Conv. (%)	Laboratory (year)	Ref.
PMMA	RAFT under high pressure (5 kbar)	toluene	65	1.25×10^{6}[c]	1.03	99	J. Penelle (2004)	56
PDMAEMA	ATRP	MeOH/water (10/1, v/v)	50	1.10×10^{6}	1.26	85	L.H. Gan (2006)	57
PMA	SET-LRP	DMSO	25	1.42×10^{6}	1.15	70	V. Percec (2006)	58
PBMA	Reverse ATRP in miniemulsion	water	60	9.89×10^{5}	1.24	83	M.F. Cunningham (2007)	59
PMA	SET-LRP	EtOH/water (95/5, v/v)	25	8.00×10^{5}	1.15	80	V. Percec (2008)	60
Poly oxanorbornene	ROMP	1,2-dichloroethane	100	1.23×10^{6}	1.38	97	N. G. Lemcoff (2009)	61
PS	AGET ATRP under high pressure (6 kbar)	anisole/DMF (31/6, v/v)	22	1.20×10^{6}	1.64	55	P. Kwiatkowski (2011)	62
PHEMA	SET-LRP	DMSO	25	1.01×10^{6}	1.49	56	V. Percec (2013)	63
PHEA	SET-LRP	TFE with 30% DMSO	50	9.13×10^{5}	1.21	67	V. Percec (2013)	64
PAM	RAFT/MADIX	water	10	1.27×10^{6}	1.32	100	M. Destarac (2014)	65
PDMA	RAFT/MADIX	water	20	1.04×10^{6}	1.06	100	M. Destarac (2014)	65
PMA	PET-RAFT	DMSO	rt	2.18×10^{6}	1.08	98	C. Boyer (2014)	66
PA	ICAR ATRP under high pressure (6 kbar)	DMSO	60	1.03×10^{6}[d]	–	73	X. Cheng (2016)	67
PSM-PS	Cu(0)-RDRP	DMSO	100	1.6×10^{6}	1.39	N/A	J. Rzayev (2016)	68
PDMA	photo-RAFT	water	rt	8.57×10^{6}[c]	1.17	89	B.S. Sumerlin (2017)	69
Poly norbornene	ROMP	benzene	25	2.05×10^{6}	1.12	N/A	K. Nomura (2017)	70
PMMA	Frustrated Lewis Pair-LP	toluene	rt	1.93×10^{6}	1.10	92	Y. Zhang (2018)	71
PNFHMA	Chain-Transfer-Light LP	DMSO	rt	3.05×10^{6}	1.12	99	M. Chen (2019)	72

[a] PMMA: poly(methyl methacrylate), PDMAEMA: poly[2-(dimethylamino)ethyl methacrylate], PMA: poly(methyl acrylate), PBMA: poly(butyl methacrylate), PS: polystyrene, PHEMA: poly(2-hydroxyethyl methacrylate), PHEA: poly(2-hydroxyethyl acrylate), PAM; poly(acrylamide), PDMA: poly(N,N-dimethyl acrylamide), PA: polyacrylonitrile, PNFHMA: poly(nonafluorohexyl methacrylate), PSM: poly(solketal methacrylate).

[b] Number-average molecular weight determined by GPC.

[c] Number-average molecular weights determined by GPC equipped with MALS detector.

[d] Viscosity-average molecular weight value determined by the Mark–Houwink equation.

year before the commercialization of Nylon fibers from the polymers he discovered at DuPont. In 1953, when Staudinger received the Nobel Prize (Staudinger was 72 years old at that time), Carothers would have been only 57 years old. This perspective is part of the expanded and updated invited lecture entitled "From Frank-Kasper Phases to Early Events of Life" given by VP during the USA-Israel Joint Symposium "Polymeric Material from Synthesis to Applications" organized also during the spring ACS meeting in Philadelphia in 2020 and dedicated to the 100s anniversary of the Staudinger paper [1] that coined the name macromolecule. Since mega covalent and supramolecular macromolecules as well as the self-organization concept emerged after Staudinger days, they will be both introduced in the independent subchapter 2.

2. Definitions and nomenclature. Mega macromolecules and self-organization

Mega is a prefix in the metric system of units denoting a factor of one million. It originated when the corresponding Ancient Greek word was Romanized. To my knowledge Mega was connected for the first time to macromolecules or polymers by Elias in his beautiful book *Mega Molecules* [18]. Since all mega molecules are in fact natural and synthetic macromolecules, we decided in this personalized perspective, that relies mostly on research from our laboratory, to use the word mega macromolecules when referring to multimillion covalent and supramolecular synthetic macromolecules. The decision on the specific selection of which macromolecules will be discussed in this perspective was based on their ability to self-organize and through their self-organization to create functions. Most of the functions selected here generate new pathways and mechanisms for the synthesis of covalent and supramolecular macromolecules, create motion in organized macromolecular systems, select stereochemistry and even provide an extraordinary acceleration of their own process of self-organization. Water channels and membranes, ionic and electronic conductors mediated by self-organization will also be discussed very briefly. Self-organization is encountered in all complex systems [19,20] such as biology [21–23] social and political organizations, technological systems, internet and the highways, financial systems, many physical and chemical systems. The simplest definition of self-organization is "*order for free*" or "*spontaneous order*" In the simplest words "*self-organization is a process in which overall order arises from local interactions between parts of an initially disordered system*" [19,24–31]. Some of the most important features of self-organization are self-control, self-repair, adaptability and emergence [19]. Due to the very general and limited scope of this perspective we will not discuss similarities between equilibrium and far from equilibrium self-organization. It is sufficient to mention that any equilibrium self-organized system proceeds through many far from equilibrium states during the first order phase transition from order to disorder. Numerous Frank-Kasper phases that will be discussed are far from equilibrium. Micellar assemblies are equilibrium while closely related vesicles are far from equilibrium. For the non-expert, we believe that it is sufficient to provide the example of one of the most common and simple self-organized system that is "*the pattern of wind-blown ripples on the surface of a sand dune*" [23]. Self-organization in low molar mass and macromolecular systems was pioneered by low molar mass and macromolecular lyotropic and thermotropic liquid crystals [25] including the use of living polymerizations for their engineering [32], by biological membrane mimics [25,27,31], by the discovery and ultrafast development of the new field of supramolecular chemistry [24,26,28,29,33–38] and by many other remarkable contributors to this field [39–55] and many other whom we apologize to for not mentioning their names.

2.1. Covalent linear mega macromolecules

Surprisingly, there are relatively few reports on the accessible and simple synthesis of linear mega macromolecules even based on non-self-assembling monomers that are or can be functionalized (Table 1) [56–72]. Some of them required quite specialized high-pressure reaction set-ups for their synthesis [56,62,63] and are less interesting. The photo-RAFT synthesis of mega poly(N,N-dimethylacrylamide) (Mn = 8,570,000; Mw/Mn = 1.17) in water reported by Sumerlin laboratory in 2017 is remarkable [69].

Single-electron transfer living radical polymerization (SET-LRP) was the method used in our laboratory to generate mega linear poly

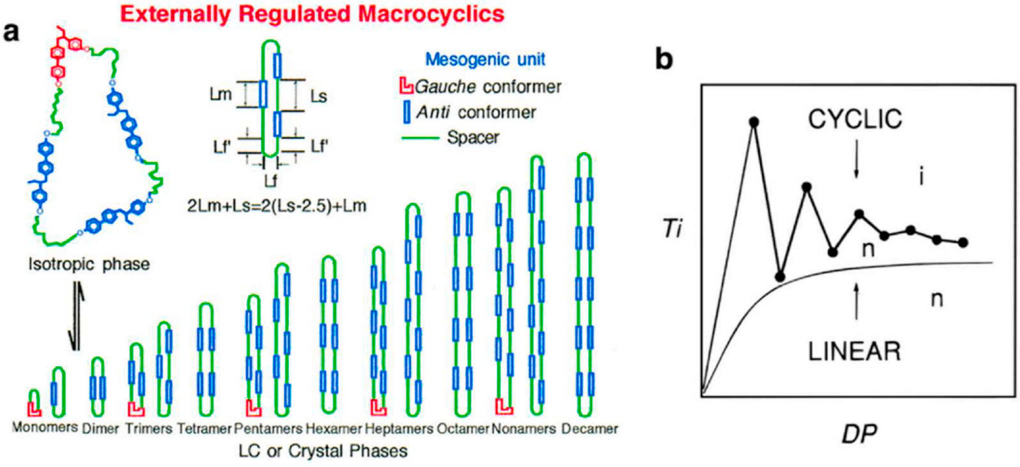

Fig. 1. (a) Externally regulated macrocyclics; (b) Experimental dependence of the isotropization temperature (T_i) of cyclic ($L_s < L_m$) and linear LC monodisperse polymers on DP (T_i and DP are in arbitrary units). Reproduced with permission from Refs. [91,94]. Copyright 1997 and 2000, American Chemical Society.

(acrylate)s and poly(methactylate)s under very mild conditions at room temperature [58,60,63,64]. Thus, in 2006 a poly(methyl acrylate) of Mn = 1,420,000 with Mw/Mn = 1.15 was obtained by SET-LRP in DMSO at room temperature [58]. At high conversion this polymerization self-organizes a biphasic system containing the perfectly colorless and transparent polymer together with very little DMSO solvent and monomer in one phase and the catalyst, ligand and most of the remaining solvent in the second phase [58]. In 2013, poly (2-hydroxyethyl methacrylate) of Mn = 1,017,900 with Mw/Mn = 1.49 was also reported by SET-LRP [63], poly(2-ethylhexyl acrylate) of Mn = 913,100 and Mw/Mn = 1.20 was reported in 2014 [64], while a bifunctional poly(methyl acrylate) with Mn = 800,000 and Mw/Mn = 1.20 was reported in 2008 [60]. To give a simple example, by scanning through most of the living polymerization methodologies from Table 1 we discovered that only ROMP was efficient for the development of Self-Interrupted Living Polymerization (SILP) that recently produced the first monodisperse polymers by chain reactions rather than by iterative methods (see subchapter 7.5). Therefore, we encourage more activity to be dedicated to the synthesis of mega macromolecules by methodologies that also tolerate a large diversity of functional groups. This will help the development of self-organizable monodisperse mega macromolecules.

2.1.1. From self-generated biphasic to programmed biphasic SET-LRP

The biphasic system observed during the SET-LRP of methyl acrylate in DMSO at room temperature [58] was induced by the very high solubility of Cu(I)X/ligand and Cu(II)X_2/ligand in DMSO in the absence of monomer and polymer and by the higher solubility of the polymer in DMSO and monomer that does not contain Cu(I)X and Cu(II)X_2 species and ligand [58]. When methyl acrylate was replaced with *n*-butyl acrylate this biphasic system was observed at lower degrees of

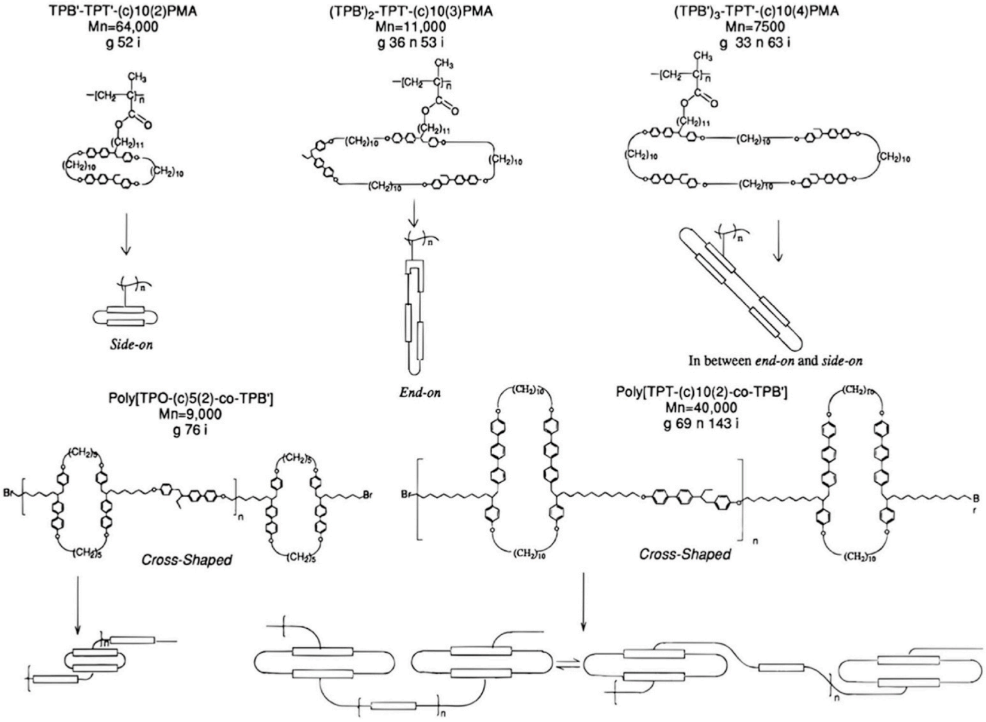

Fig. 2. Mechanism and the structural models which explain the formation of the LC phases and the phase behavior of side chain LC polymers and main chain LC polymers. Reproduced with permission from Refs. [93]. Copyright 1996, American Chemical Society.

polymerization than for the case of poly(methyl acrylate). Haddleton laboratory investigated the SET-LRP of *n*-butyl acrylate in DMSO and named it "*self-generated biphasic*" SET-LRP [73]. Perfect chain end functionality polymers free of Cu species were obtained by the *self-generated biphasic* SET-LRP [58,73]. Inspired by the self-generated SET-LRP system Percec laboratory elaborated a large diversity of "*programmed biphasic*" SET-LRP systems in which an even better solvent for Cu catalyst, water, generates biphasic systems with many combinations of organic solvents including water soluble solvents and monomers that are not miscible with water containing Cu species and ligand [74–80]. The self-generated and programmed biphasic SET-LRP systems provide a simple example in which the selective partitioning of monomer, polymer, catalysts, ligand and solvent in two different phases provides an extremely efficient and economic SET-LRP process by self-organization in which activation and deactivation of the growing chain occurs at the interface of the two phases. No purification of the resulting polymer is required. This self-organization is dependent on the nature of the solvents, monomer, their concentrations and occurs at a certain monomer conversion or it can be programmed to start even at zero-conversion [74–80].

2.2. Covalent cyclic mega DNA and liquid crystals

The classic cyclic biological compounds are phospholipids [81–83] and DNA [84–86]. Linear phospholipids self-organize biological human membranes that are stable at room temperature and above but not at very high temperature while archaebacterial extremophiles survive at high temperatures since their membranes are based on cyclic phospholipids [81–83]. Inspired by the cyclic phospholipids of the membranes of archaebacterial extremophiles our laboratory synthesized monodisperse macrocyclic main chain polyether liquid crystal (LC) oligomers based on conformational isomerism and compared their structures and phase transitions with those of the corresponding monodisperse linear homologous compounds. This comparison demonstrated that isotropization phase transitions of the cyclic LCs are higher than those of the corresponding linear compounds, invalidating a hypothesis advanced in 1888, that linear rather than cyclic are the most favorable topology for the self-organization of LC phases [87]. The explanation for this unexpected result known by cell membranes biologists but not by synthetic LC experts relies on the fact that cyclic LCs fold into more rigid rods than the corresponding linear components (Fig. 1) [88–94].

Self-organizable main-chain and side-chain liquid crystal polymers containing cyclic mesogenic groups that fold into supramolecular rods were also elaborated [93] (Fig. 2).Cyclic DNA is widely spread in biology, exists as catenanes and knots [84–86] and may have inspired Stoddart [36] and Sauvage [38] to assemble their synthetic homologues into molecular machines. There are quite a number of books on cyclic polymers that do not self-organize. They will not ne enumerated here.

2.3. Covalent and supramolecular branched-dendritic mega macromolecules

A TERminator Multifunctional INItiator (TERMINI) methodology was elaborated to generate closed to mega dendritic poly(methyl methacrylate) [95,96]. This method applies to the synthesis of dendrimers from any commercial monomers. Its expansion *via* thio-bromo click led to the synthesis of poly(acrylate) dendrimers also from commercial monomers [97,98]. Supramolecular dendrimers were elaborated by numerous elegant methods developed by Lehn [99–101] and other laboratories [44]. Phase transfer catalyzed polyetherification of properly designed AB_2 monomers based on conformational isomerism allowed the design of branched liquid crystal polyethers able to self-organize liquid crystal phases [92,102–104] and through this accelerated process to select the building blocks required to construct the first and only willow-like liquid crystal dendrimers by iterative methods [103]. Unexpectedly, these liquid crystal dendrimers display lower melt viscosity and shorter switching times in display applications than conventional liquid crystals.

2.4. Self-organizable mega dendronized macromolecules: columnar and spherical

Conventional radical polymerization of self-assembling dendronized monomers in self-assembled state generated a methodology to produce up to 3,500,000 molar mass self-organizable polymers forming columnar hexagonal arrays, in only 5 min reaction time [105–107]. Lower molar mass dendronized polymers made by conventional radical polymerization in dilute solution produced spherical self-organizable polymers that generate Frank-Kasper phases [105,107]. More details of this polymerization process and on the self-organization in Frank-Kasper phases will be presented in subchapter 2.4.1.

2.4.1. Frank-Kasper phases in soft matter. From supramolecular dendrimers and self-organizable dendronized polymers to block copolymers, surfactants, giant molecules and DNA

The discovery of Frank-Kasper phases and quasicrystals, that were known in metals and metal alloys, in supramolecular dendrimers and self-organizable dendronized polymers started in 1997 [107,109–111]. Investigation of many rational libraries of self-assembling dendrons and dendrimers [112–128] generated a table of supramolecular nano-assemblies that was elaborated in 2009 [128]. This table of supramolecular nano-assemblies inspired similar tables of nano-assemblies for proteins [129,130]. Frank-Kasper phases were in the meantime discovered in block copolymers, surfactants, giant molecules and DNA nanoparticles [131–146] and created a large new field of research in self-organized soft condensed matter that is only briefly mentioned here. Large efforts in theoretical, computation, simulation [147–150] were also initiated by the discovery of Frank-Kasper phases.

2.4.2. Spherical monodisperse supramolecular mega macromolecules and their Frank-Kasper Phases

770 monodisperse self-assembling dendrons, with the short name (4-3,4-3,5)BpPr12G2-CO_2CH_3, of molar mass 2239 (362 atoms/dendron), prepared by iterative synthesis, self-organized monodisperse supramolecular spheres of molar mass 1,724,030 (278, 740 atoms/sphere). These supramolecular monodisperse spheres self-organize into Pm3n or Frank-Kasper A15 periodic arrays (containing 2,229, 920 atoms and 13,792,240 M mass per unit cell or lattice [128]. These supramolecular spheres and their A15 phase are self-organized from conical dendrons and are in the range of the molar mass of the ribosome.

2.4.3. Homochiral spherical monodisperse supramolecular mega macromolecules

482 chiral conical dendrons of (R)-(4-3,4-3,4)BpPr12G2-CONHsecBu containing 372 atoms/molecule of 2280 M mass self-assemble into monodisperse chiral spheres of 1,098,960 M mass generated from 9179, 304 atoms/sphere [151]. These chiral monodisperse spheres self-organize a Pm3n or Frank-Kasper A15 phase containing 1,434,432 atoms per lattice or unit cell with a molar mass of 8,791,680/unit cell.

3. Methodologies for the analysis of self-organized structures

3.1. The transplant of helical diffraction theory and of Watson-Crick structure determination methodology from biological macromolecules to synthetic supramolecular macromolecules

The transplant of helical diffraction theory from biological macromolecules to supramolecular macromolecules provided access to the detailed structural analysis of columnar supramolecular helical polymers with the same level of precision as that of biological macromolecules such as proteins and DNA [152] and facilitated the development of

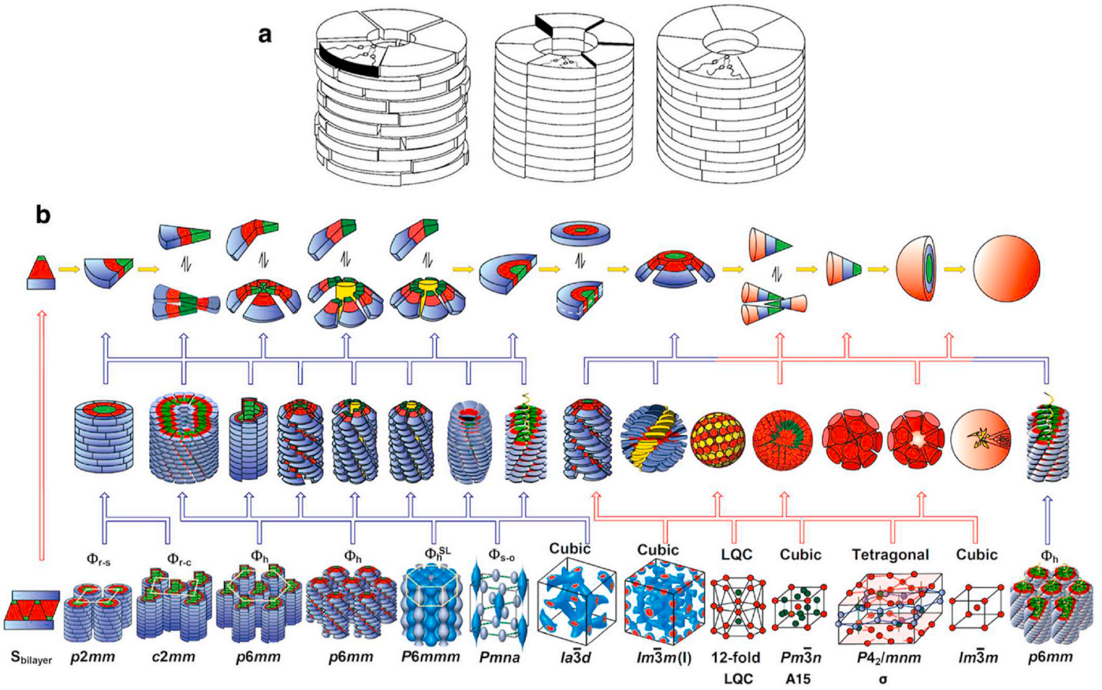

Fig. 3. (a) Self-assembly and self-organization of dendrimers and dendronized polymers in supramolecular dendrimers or polymers. Their structure during late 1980s to early 1990s. (b) Structural and retrostructural analysis of supramolecular dendrimers or supramolecular polymers. As of mid 1990s to early 2000. Reproduced with permission from Refs. [19]. Copyright 2011, Wiley-VCH Verlag GmbH &Co. KGaA.

many previously unknown columnar and spherical assemblies. Briefly we have developed a methodology of structural and retrostructural analysis based on the DNA structural analysis method elaborated by Watson and Crick [19,30]. A combination of DSC, XRD, TEM, electron diffraction, UV, CD, experimental density and helical diffraction theory is used to build molecular models that are optimized until they reconstruct the oriented-fiber X-ray diffractogram of the columnar assemblies or the X-ray diffractogram of the spherical assemblies. A detailed explanation of this concept is presented in several review articles [19, 30] and it will not be repeated here.

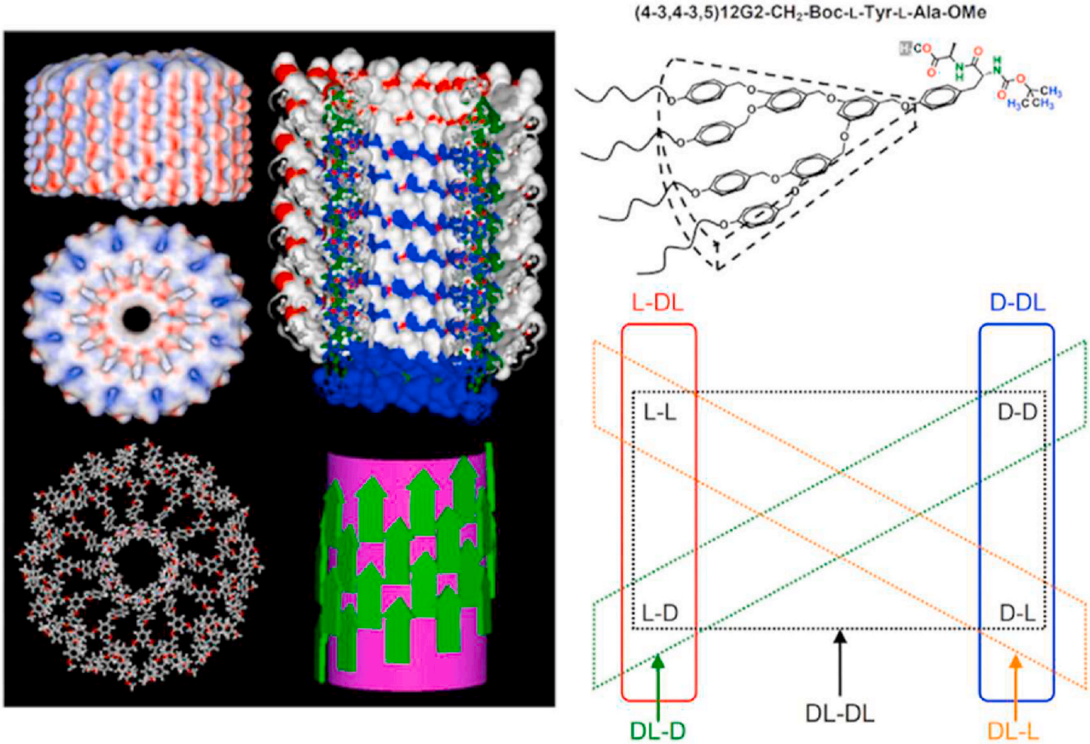

Fig. 4. Self-assembly of constitutional and conformational isomeric dendritic dipeptides into homochiral helical Aquaporin-like channels *via* the stereochemistry of the dendritic dipeptide. Reproduced with permission from Ref. [201]. Copyright 2011, Wiley-VCH Verlag GmbH &Co. KGaA.

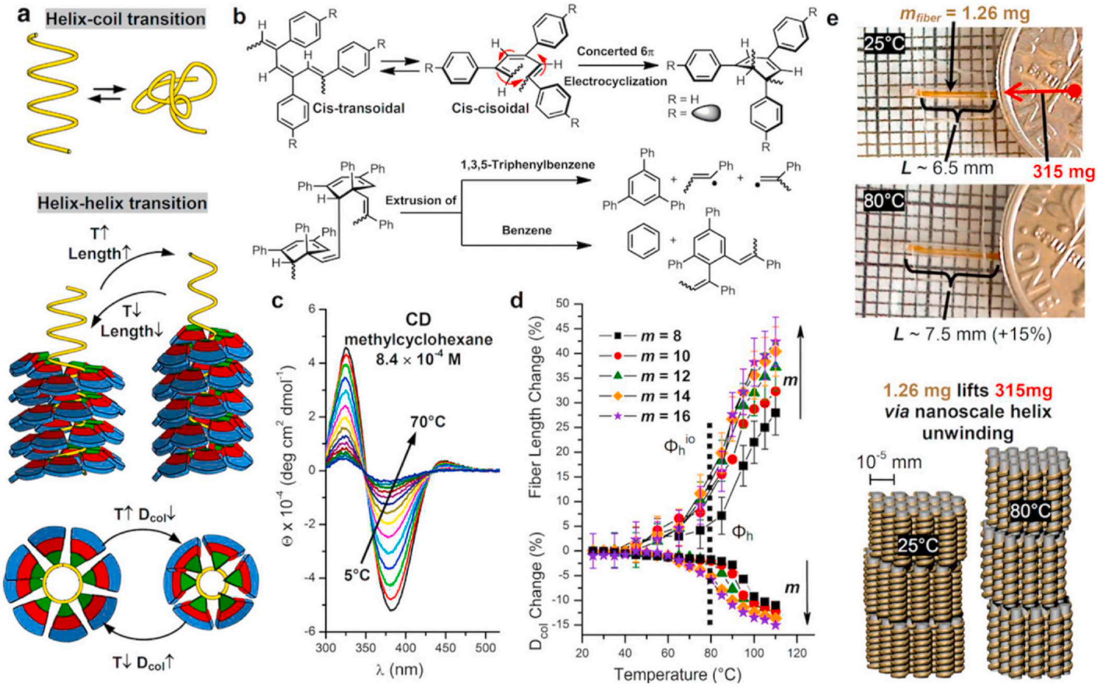

Fig. 5. Intramolecular electrocyclization followed by chain cleavage of *cis*-transoidal and *cis*-cisoidal stereoisomers of PPA is eliminated by dendronizing PPA (a). The helix-coil transition accompanied by electrocyclization (b) was eliminated and replaced by an unprecedented helix-helix *cis*-cisoidal to *cis*-transoidal transition that provides a molecular machine (c, d, e). Reproduced with permission from Refs. [7]. Copyright 2020, Wiley-VCH Verlag GmbH &Co. KGaA.

4. The early days of the self-organization of columnar supramolecular macromolecules

In the late 1980s self-assembling dendrons were employed to self-organize columnar supramolecular polymers by a combination of H-bonding, ionic interactions, conventional and living polymerizations [153–161]. The first experiments comparing the strength of noncovalent supramolecular and covalent polymer backbones were performed at this time [19,30]. Their detailed supramolecular structures were analyzed by X-ray diffraction experiments [162–166] to produce the first self-organized ionic conductors with high mobility of their charge carriers. Quite a number of review articles were published also at the same time [19,30,167–170]. The co-assembly process for supramolecular polymers was also elaborated at the same time (Fig. 3) [171–173]. However, the order of these self-organized assemblies was for many years not competitive with the order of biological assemblies and therefore high-resolution structural analysis was not accessible until in the last several years.

4.1. *The early days that combined living polymerization with supramolecular chemistry to self-organize complex condensed matter*

The living polymerization of vinyl ethers, the living cationic ring opening polymerization of cyclic imino ethers (ROP), ring-opening metathesis polymerization (ROMP), the living cationic polymerization of cyclic siloxanes and their living anionic polymerization were shown to be very powerful when combined with self-assembly to self-organize complex soft condensed matter [29,173–181]. These polymerization methodologies were employed in the field of self-organization at the same time other groups [25] were using only conventional polymerizations.

4.2. *Some comments on self-assembly and self-organization: fluorous phase*

H-bonding [19], ionic and many other supramolecular interactions [19,30] were conventionally employed in self-organization by our and many other laboratories. However, the investigation of the role of fluorous phase in self-organization and supramolecular polymerization by our laboratory generated a new concept to stabilize supramolecular assemblies, insulate them from moisture and oxygen in order to protect their active components and also reduce the molar mass of supramolecular building blocks required for self-organization to mini-building blocks [182–190] Ultimately fluorous phase provided access to one of the simplest methodologies to enhance charge carries mobility of organic electronic components and protect the electronic components from moisture [19,30,186].

5. Aquaporin-like porous supramolecular polymers

The self-organization of dendritic dipeptides into porous supramolecular macromolecules facilitated the development of synthetic water channels and of membranes for water purification *via* aquaporin-mimics [191–194]. The (4-3,4-3,4)12G2-CH_2-Boc-L-Tyr-L-Ala-OMe constitutional isomer of the self-assembling building block from Fig. 4 self-organizes hollow spherical supramolecular dendrimers forming an A15 Frank-Kasper phase. The aquaporin-like porous supramolecular polymers [191–194] act as very selective water channels [194] and inspired similar concepts in other laboratories [195–199]. Once the elucidation of the mechanism of self-organization of both constitutional isomeric dendritic dipeptides became available, they provided access to the study of the role of all stereochemical permutations of the dendritic dipeptides on supramolecular polymerization and on their order in the self-organized state (Fig. 4) that will be discussed in subchapter 5.1.

5.1. *Why are biological systems homochiral?*

In order to address this question all stereochemical permutations of dendritic dipeptides starting from the enantiomerically pure homochiral, to heterochiral and racemic were investigated in supramolecular polymerization process of (4-3,4-3,5)12G2-CH_2-Boc-L-Tyr-L-Ala-OMe (Fig. 4) [200,201]. A combination of X-ray analysis of the structures of

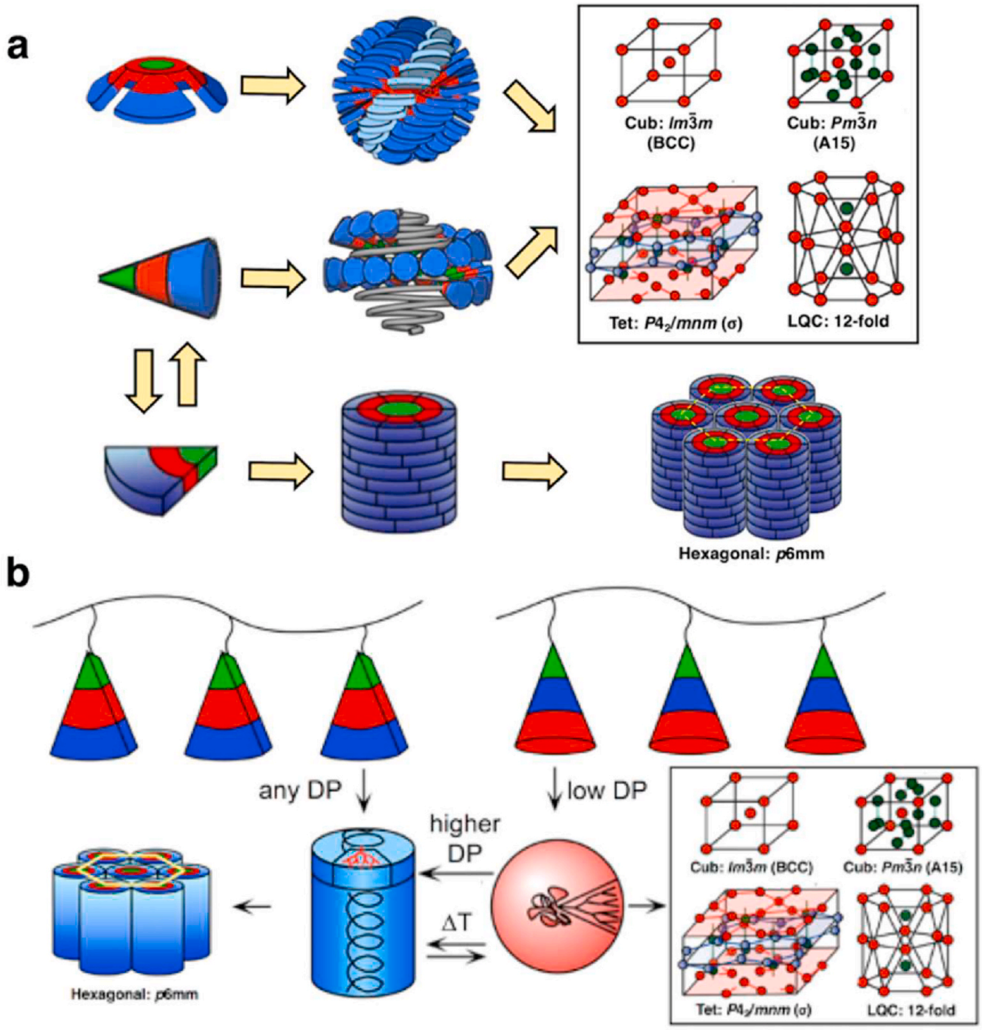

Fig. 6. (a) Self-organization of conical and crown-like conformations of dendrimers into chiral spheres and their BCC, A15, σ and liquid quasicrystal (LQC) assemblies, and tappered conformations of dendrimers into hexagonal columns. (b) Self-organization dendronized polymers into chiral spheres and their BCC, A15, σ and LQC assemblies. Reproduced with permission from Ref. [7]. Only Frank-Kasper phases produced from identical size spheres are shown. Copyright 2020, Wiley-VCH Verlag GmbH &Co. KGaA, and from Refs. [223]. Copyright 2008, American Chemical Society.

the resulting supramolecular polymers combined with their mechanism of supramolecular polymerization in solution demonstrated that the order of the resulting polymer decreases from homochiral to heterochiral and to racemic when it forms only a disordered micellar like-structure rather than a highly crystalline order as in the case of the homochiral assembly [200,201]. This correlation of order with stereochemical purity and its decrease from homochiral to heterochiral and to racemic provides one explanation on why biology selected homochiral building blocks for its creation and not heterochiral or racemic. It must be stressed that in this self-organization process produces strongly H-bonded structures that are closed in their strength to a covalent bond and therefore, their components cannot deracemize. These results also explain why the majority rules and the sergeant and soldiers concepts are not used in biology [201]. Briefly, while the handedness of a helical structure would be selected by these two concepts, the order of the biological assembly will decrease at the transition from homochiral to heterochiral and to racemic even in the case of the same handedness of their helix when the handedness will be selected by these two concepts [201]. When deracemization is possible, as it will be discussed in subchapter 8.1., a different mechanism of self-organization applies.

6. From helical stereochemically-defined Poly(phenylacetylene) (PPA) to molecular machines *via* living polymerization and self-organization

The driving force behind the discovery of the helical stereoisomers of PPA was discussed in a recent paper from 2020 [7]. The *cis*-stereoisomers of PPA produced one of the most investigated helical polymer [202–214]. The combination of living polymerization, *cis*-, *trans*--stereoisomerism combined with self-organization generated one of the richest tools available today to produce new concepts in organic chemistry, polymer chemistry, supramolecular assemblies, membranes for separation processes including separation of enantiomers and molecular machines [215–225] (Fig. 5). Fig. 5 illustrates how a *cis*--dendronized poly(phenyl acetylene) changes the irreversible *cis-trans* thermal isomerization accompanied by intramolecular electrocyclization and chain cleavage at the helix-coil transition of the parent polymer into an unprecedented thermal reversible *cis*-cisoidal to *cis*--transoidal helix-helix transition. This helix-helix transition produced a new concept in molecular machines [222–225]. New concepts in this area appear every other day even so many years after the original discovery [217].

7. From chiral columnar polydisperse to chiral spherical monodisperse supramolecular polymers

7.1. From columnar supramolecular polymers to monodisperse spherical supramolecular macromolecules

By analogy with biological macromolecules, monodisperse quasi-equivalent self-assembling dendrons prepared by iterative synthesis, have been discovered to self-organize into monodisperse spherical

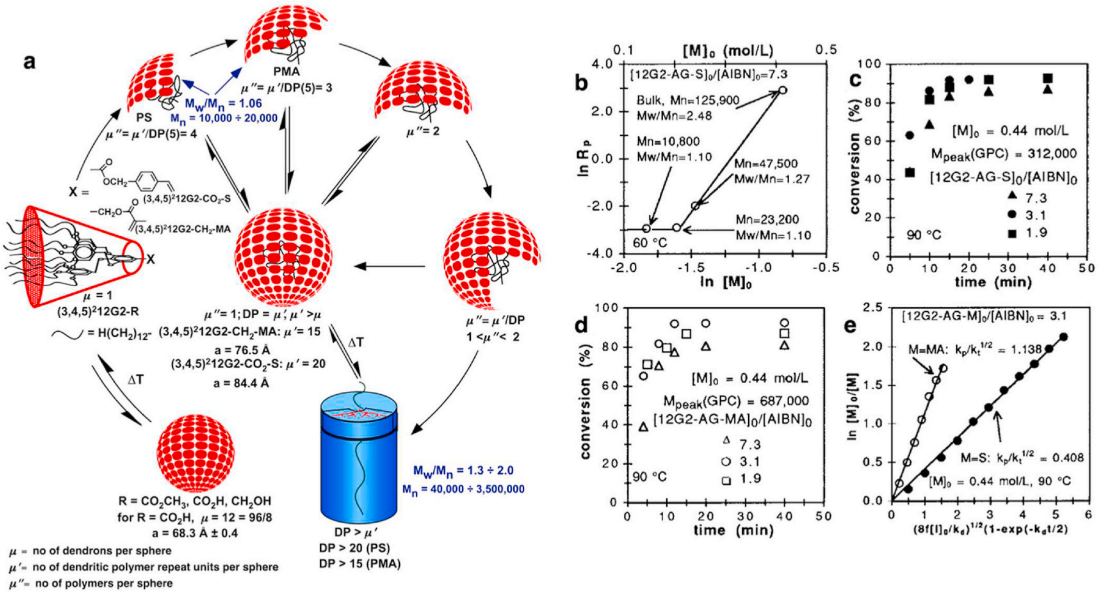

Fig. 7. (a) Conventional radical polymerizations of conical dendronized monomers and the structure and shape of the resulting polymers. (a–d) Radical polymerizations of $(3,4,5)^2$12G2-CO_2-S. Dependence of ln Rp on ln $[M]_0$ for the polymerization of $(3,4,5)^2$12G2-CO_2-S (in benzene and bulk) (a); conversion in time for the bulk ($[M]_0$) 0.44 mol/L) polymerization of $(3,4,5)^2$12G2-CO_2-S (b) and of $(3,4,5)^2$12G2-CH_2-MA(c) and determination of the kp/kt1/2 for the polymerization of $(3,4,5)^2$12G2-CO_2-S (b) and $(3,4,5)^2$12G2-CH_2-MA (O) (d). Reproduced with permission from Ref. [7]. Copyright 2020, Wiley-VCH Verlag GmbH &Co. KGaA, and Reproduced with permission from Refs. [105]. Copyright 1997, American Chemical Society.

supramolecular polymers (Fig. 6) [108,109]. Scanning through rationally designed libraries of conformational isomeric self-assembling building blocks led to the discovery of Pm3n or A15 Frank-Kasper phase [107–109,112–128], tetragonal or σ Frank-Kasper phase [110] and liquid quasicrystal (LQC) assemblies [111]. This has been shown to be a general concept in organized soft matter [111–131]. All spherical assemblies are monodisperse and chiral. Additional Frank-Kasper phases self-organized from at least two different size spheres such as C14, C15 and Z phases [135,138,143] are not shown. First order phase transitions from chiral *polydisperse* columnar supramolecular polymers to *monodisperse* chiral spherical supramolecular macromolecules have been discovered [118–128] (Fig. 6).

7.2. Self-interrupted iterative synthesis (SIIS) of dendrons and dendrimers

Our laboratory discovered both the convergent self-interrupted iterative synthesis of self-assembling dendrons [226] and the divergent self-interrupted synthesis of dendrimers [227]. The reduced reactivity as the generation number increases during divergent synthesis of dendrimers was predicted by deGennes [228] and observed by Tomalia [229]. However, complete self-interruption of the convergent or divergent iterative syntheses of dendrimers at a certain generation number was neither predicted not observed until our laboratory discovered both of them [226,227].

7.3. From self-interrupted convergent and divergent iterative synthesis (SIIS) to self-interrupted polymerization (SIP)

A self-interrupted iterative organic synthesis (SIIS) is an unproductive concept for the field of organic synthesis. However, a self-interrupted conventional radical or other traditional polymerization (SIP) is expected to produce a new concept for the synthesis of polymers with narrow molecular weight distribution by a living-like polymerization. This concept was indeed observed when polymerizable functional groups such as methacrylate or styrene were attached to quasi-equivalent self-assembling dendrons and their conventional radical polymerization was investigated and elucidated (Fig. 7) [105,107]. At low concentration in dilute ideal solution an unprecedented living-like radical polymerization by SIP producing polymers with narrow molecular weight distribution was observed (Fig. 7) [105,107]. At high concentration in self-assembled state high molecular weight polymers with broader polydispersity were obtained by a self-accelerated polymerization (SAP) process in self-assembled state (Fig. 7a and b).

7.4. Self-accelerated polymerization (SAP) in self-assembled state

The reverse of SIP is to perform the same polymerization in the self-assembled state or even in bulk melt state when the polymerizable group of the monomer produces a very high concentration in a supramolecular reactor. In this case up to 3,500,000 molar mass polymers could be obtained in only 5 min reaction time by SAP with conventional polymerizable groups such as styrene and methacrylate and radical initiators (Fig. 7) [105–107]. It is important to stress that 5 min is the required time to assemble a Schlenk tube and take the first sample during the polymerization process. Most probably, this polymerization is spontaneous. This is a concentration dependent polymerization process (Fig. 7).

7.5. Monodisperse polymers by self-interrupted living polymerization (SILP)

In all polymerization reactions, including chain and step, the reactivity of growing species is independent of chain length [17]. A decrease in reactivity with the increase of chain length is expected to provide monodisperse macromolecules if the reactivity of all chains becomes zero at a certain chain length. This concept was recently employed to generate for the first time monodisperse macromolecules by a self-interrupted ROMP living chain polymerization (SILP) (Fig. 8) [230,231]. This concept was born after the detection of the shape change of the self-organized polymer during the polymerization could be observed by kinetic experiments [94]. We would like to mention that many of the living polymerization methodologies reported in Table 1 for the synthesis of mega macromolecules were tested for this SILP process. We found only ROMP to be suitable so far for it. SILP *vs* shape change of the polymer during the living polymerization process is strongly dependent on the concentration of the reaction mixture and on the stability of the

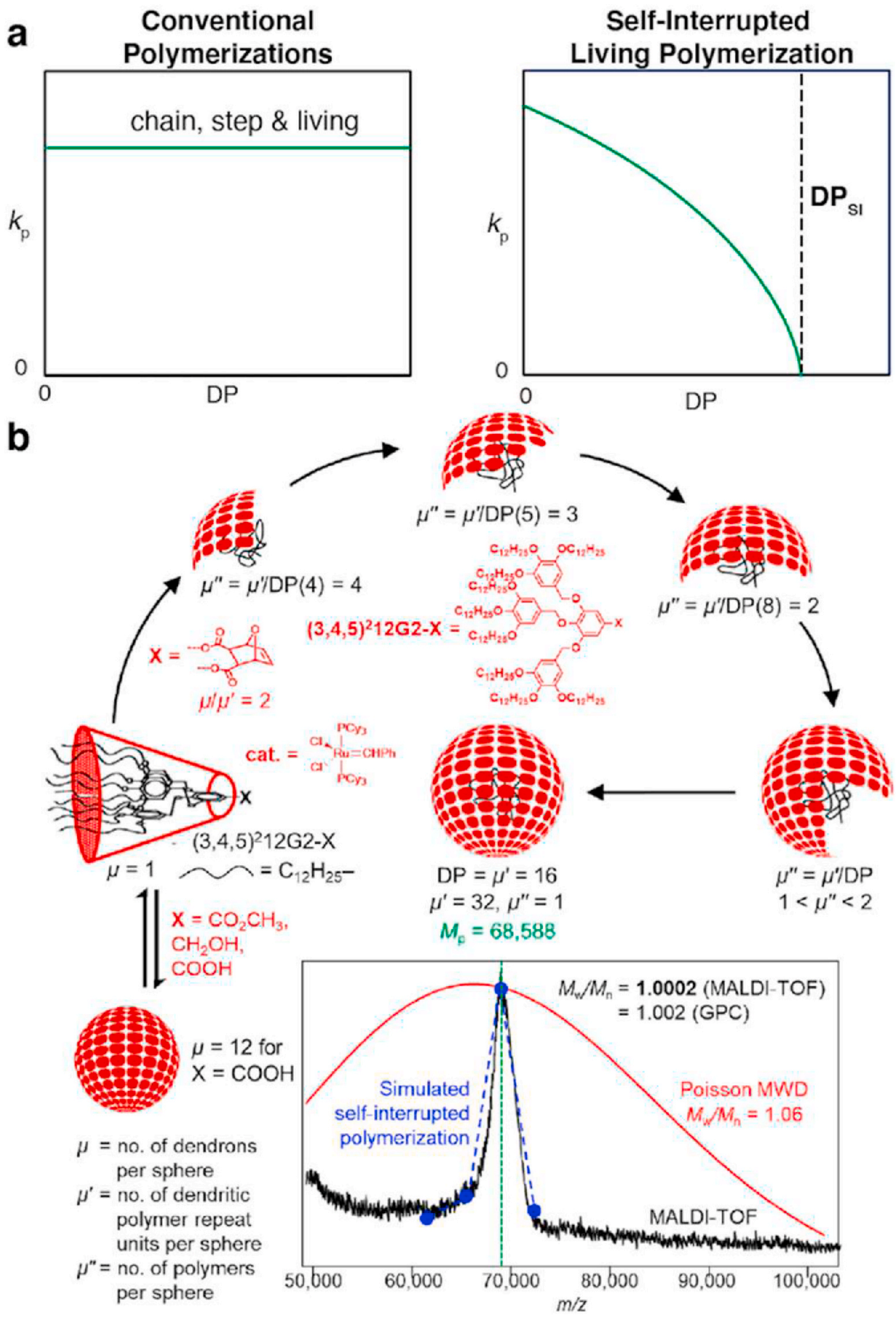

Fig. 8. (a) Comparison of conventional chain, step, and living polymerizations with SILP, k_p vs DP. DP_{SI} denotes the degree of polymerization at which polymerization self-interrupts. (b) Mechanism of SILP (top). Polymer chains with DP < 16 and non-polymerizable dendrons with ester, acid, or alcohol apex groups self-assemble into monodisperse 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 (bottom). Reproduced with permission from Ref. [230]. Copyright 2020, American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

supramolecular assembly and polymer resulting during this process.

7.6. Narrow molecular weight distribution supramolecular polymer assemblies with defined molar mass by self-organization of amphiphilic Janus dendrimers (JDs) and amphiphilic Janus glycodendrimers (JGDs)

Mimics of cell membranes, vesicles, are generated by self-assembly of amphiphilic Janus dendrimers (JD) and Janus glycodendrimers (JGD) including sequence-defined JGD by very simple injection of their ethanol or THF solution in water or in buffer [232]. It must be mentioned that vesicles are far from equilibrium self-organized systems while micellar systems are equilibrium assemblies. Narrow polydispersity and well-defined molar masses can be accomplished by this injection process (Fig. 9) [31,232–235]. A mechanism explaining this concept was elaborated [234]. Although the reason for almost monodisperse structures is not yet clear the current level of understanding of the mechanism provides an almost living-like supramolecular polymerization methodology in which the molar mass of the resulting assemblies can be predicted [234]. Self-assembly of phospholipids [236] and of block-copolymers [237] do not produce narrow molecular weight distribution vesicles even by injection or any other method of self-organization. It is very important to mention that sequence-defined

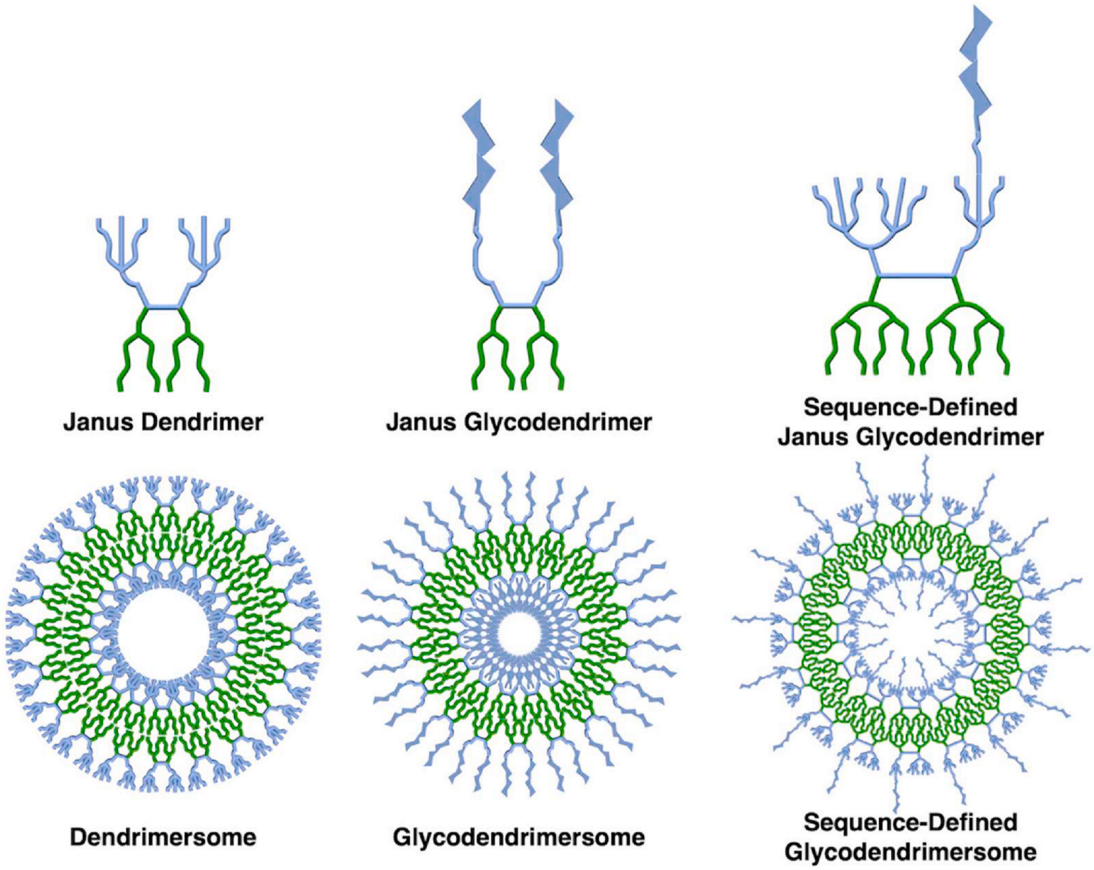

Fig. 9. Illustration of Janus dendrimers, dendrimersomes, Janus glycodendrimers, glycodendrimersomes, sequence-defined Janus dendrimers, and sequence-defined glycodendrimersomes [31,232–235].

Janus dendrimers and glycodendrimers provide by self-organization a morphology on their surface that enhances the reactivity of carbohydrates towards interaction with sugar binding proteins knows as lectins and galectins at lower rather than higher concentration [238–241]. It is also very important to mention here that the mechanical properties of dendrimersomes and their interaction with bacteria can mediate endocytosis *via* a related mechanism close to that of natural cells [242].

8. Supramolecular polymerization accompanied by deracemization

8.1. Isotactic or homochiral dynamic macromolecules by deracemization of an atactic or racemic dynamic supramolecular polymer: The hat-shaped model

This concept is illustrated in Fig. 10 [243]. A mixture of racemic hat-like-shape forming columnar hexagonal assemblies is similar to an atactic polymer (Fig. 10a) and therefore, it produces a disordered supramolecular polymer as discussed in subchapter 5.1. If this polymer is self-organized in a columnar hexagonal periodic array, a spontaneous deracemization occurs in the crystal state upon annealing to create a highly crystalline isotactic-homochiral supramolecular polymer. The driving force for this concept is generated by the fact that the hexagonal unit cell is produced from 4 quarters of supramolecular columns or a single column (Fig. 10b). Therefore, single-handed helical columns are required for helical columnar crystallization and therefore, minimization of the free energy of the system is generated by crystallization *via* deracemization. This is a new concept in supramolecular polymerization that does not exist in covalent stereospecific polymerization.

8.2. The cogwheel helical model of self-organization and supramolecular polymerization

All supramolecular polymers and assemblies discovered since the 1980s display sufficiently high 2D or 3D order to be investigated by X-ray diffraction, including by helical diffraction theory [152]. However, none of them exhibited the degree of order observed by XRD in highly ordered biological macromolecules. This situation changed in 2016 [244] when our laboratory discovered the cogwheel helical model of self-organization and supramolecular polymerization that provided an even higher degree of crystalline order than observed in the most ordered biological macromolecules. This self-organization process is accompanied by deracemization to generate a low order crystalline helical columnar assembly followed by an extremely high helical crystal order. The high order was discovered by accident during X-ray diffraction experiments that required long time exposure and therefore, annealing at different temperatures. Briefly this transition can be detected only by heating and cooling with 1 °C/min and annealing for long times at a certain temperature. The question that came to our mind was very simple. The cogwheel crystal structure may not be structurally perfect enough to form with very fast rate as happened in the case of biological macromolecules. Can a sequence-defined primary structure provide the perfect tertiary structure required to form the precise cogwheel crystal with high rate? This idea was encouraged by the use of a combination of sequence-defined and monodisperse component to discover that macrocyclic liquid crystals and not linear are the optimum topology to create liquid crystals [90,91,245–252] including the discovery of a biaxial nematic liquid crystal [250] and by the discovery *via* conformational isomerism that dendritic LC molecules display faster dynamics than the corresponding linear topologies [102–104,249–252]

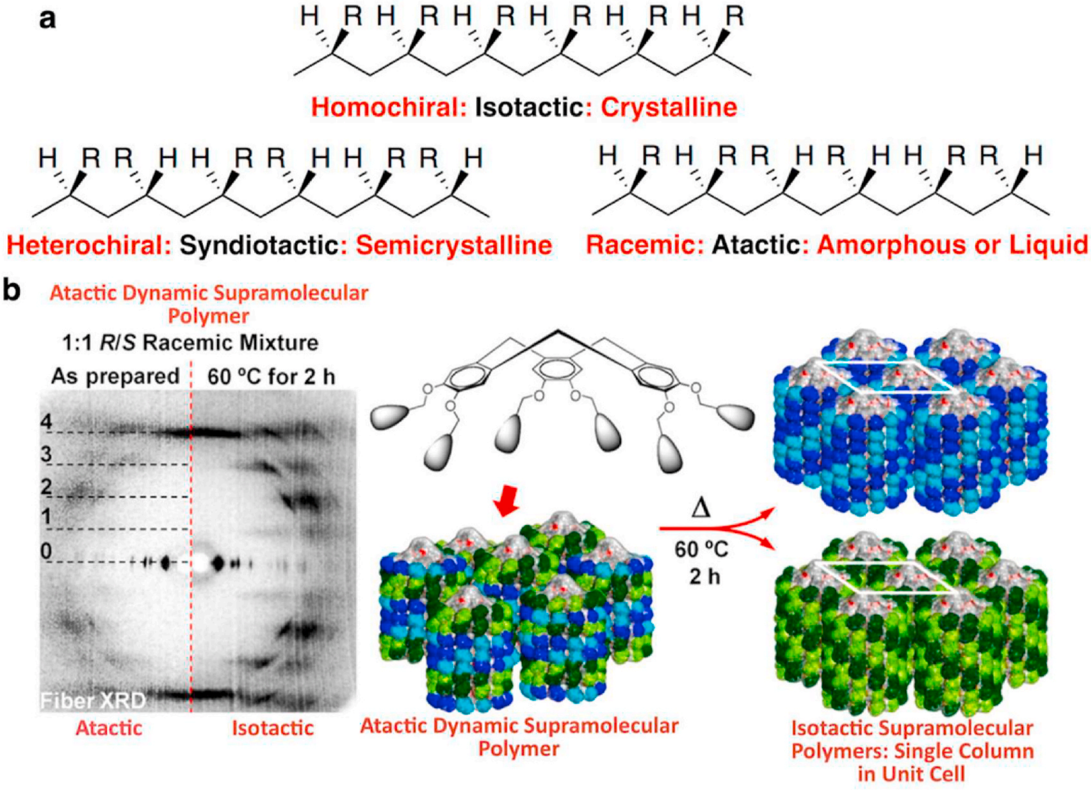

Fig. 10. (a) The macromolecular chemist and organic chemist definitions used for stereospecific polymers (b) Isotactic (homochiral) supramolecular polymers by stereo-sequence rearrangement of dynamic atactic (racemic) polymers in crystal state. Reproduced with permission from Ref. [7]. Copyright 2020, Wiley-VCH Verlag GmbH &Co. KGaA.

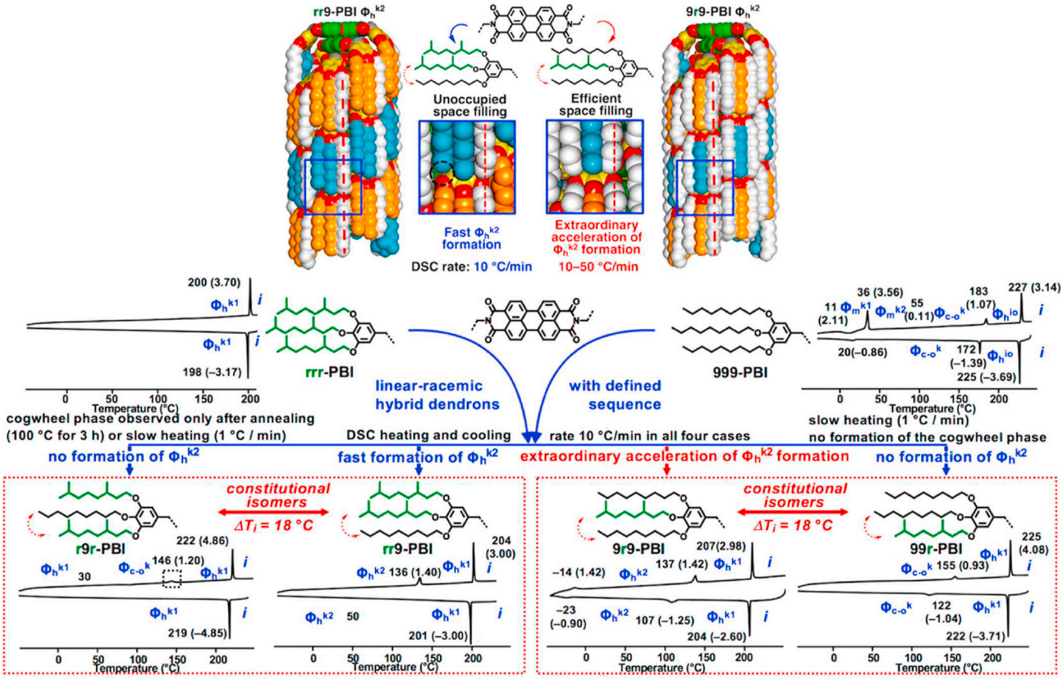

Fig. 11. The cogwheel helical high order crystal self-organized from the ideal sequence is shown on top-right with the perfect tertiary structure of the column (top). DSC traces of PBIs with sequence-defined hybrid **r**/*n*-nonyl dendrons recorded upon second heating and first cooling at 10 °C/min. Phases determined by fiber XRD, transition temperatures (in °C), and associated enthalpy changes (in parentheses, in kcal/mol) are indicated (bottom). Reproduced with permission from Ref. [254]. Copyright 2020, American Chemical Society.

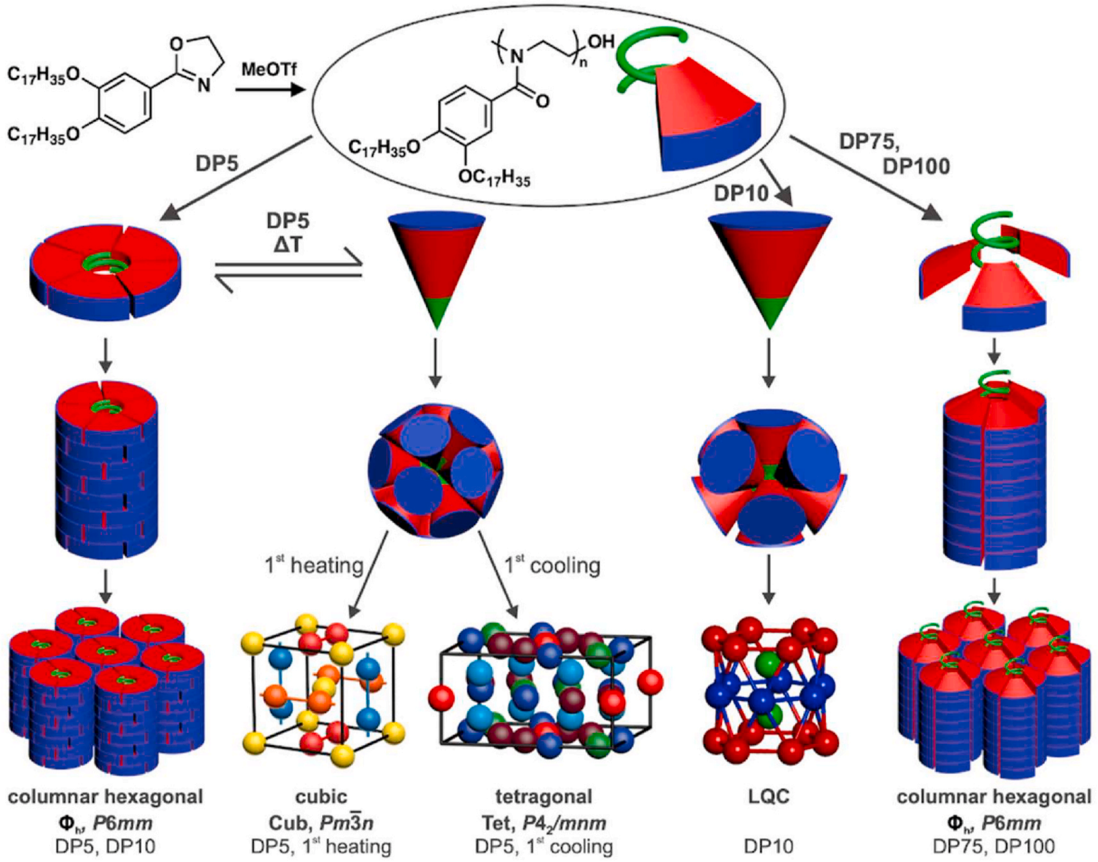

Fig. 12. Polymerization of dendronized poly(2-oxazoline) and summary of periodic and quasiperiodic arrays self-organized from assemblies of poly[(3,4)17G1-Oxz]. Reproduced with permission from Ref. [260]. Copyright 2018, American Chemical Society.

(see subchapters 2.2 and 2.3).

8.2.1. *Extraordinary acceleration of cogwheel helical self-organization by the sequence encoding the tertiary structure*

The first series of experiments were encouraging [253] since they provided a sequence that could detect the cogwheel self-organization at 10 °C/min only on heating and not on cooling but could not predict the outcome of the second series of experiments. The second series of experiments discovered the sequence that would encode the cogwheel helical self-organization and crystallization with the highest rate available in the conventional instrumentation such as DSC and X-ray machines (50 °C/min) [254] (Fig. 11).

9. Constructing self-assembling building blocks for supramolecular polymerization and self-organization *via* living oligomerization

All the experiments described so far were generated with self-assembling building blocks, some of them mediating a similar/different supramolecular assembly *via* additional supramolecular or covalent backbones. An additional unrelated methodology is to employ mini-building blocks like minidendrons that upon living oligomerization will generate building block that undergo supramolecular polymerization and self-organization. A classic example is provided by cyclic imino ethers (2-oxazolines) that can produce self-assembling building block *via* living cationic ring opening polymerization (ROP) even when are substituted with minidendrons or other functional groups [255–260]. The power of this strategy is demonstrated by the experiment illustrated in Fig. 12 [260]. It is expected that this ROP can be monitored in situ to generate highly order assemblies within record time [261,262]. Monodisperse spheres are self-organized in this case from narrow molecular weight distribution polymers. How can polydispersity be tolerated during the self-organization of monodisperse spheres? This is a very fundamental question for the entire field of polymer self-organization. It is not the goal of this perspective to discuss this issue in great details here, but we feel that we must at least address the similarities and differences between monodisperse self-assembling dendrons and narrow molecular weight distribution self-organizable polymers in a qualitative manner. This will be briefly done in subchapter 9.1.

9.1. *Limitations of narrow molecular weight distribution vs monodisperse building blocks in self-organization*

The spherical supramolecular polymers illustrated in Fig. 12 are monodisperse even if they are generated from narrow molecular weight distribution building blocks produced by living ROP of dendronized 2-oxazolines [260]. Since a living polymerization provides a Poisson molecular weight distribution with a maximum 1–3% chains of the desirable length (Fig. 13a), the as generated self-organized system contains a mixture of molecular weights and therefore assemblies (Fig. 13b). Is the de-mixing based on chain length occurring to generate the monodisperse spheres (Fig. 12)? This is one of the most fundamental questions of both supramolecular and macromolecular science that must be addressed and must be answered.

10. Instead of conclusions

Research from other laboratories on supramolecular polymers was also reviewed this year and therefore was not discussed here [48]. Last but not least, if a Nobel Prize would not have given in 1987 to Donald J. Cram [35], together with Jean Marie Lehn [24] and Charles J. Pedersen [34] "*for their development and the use of molecules with structure-specific*

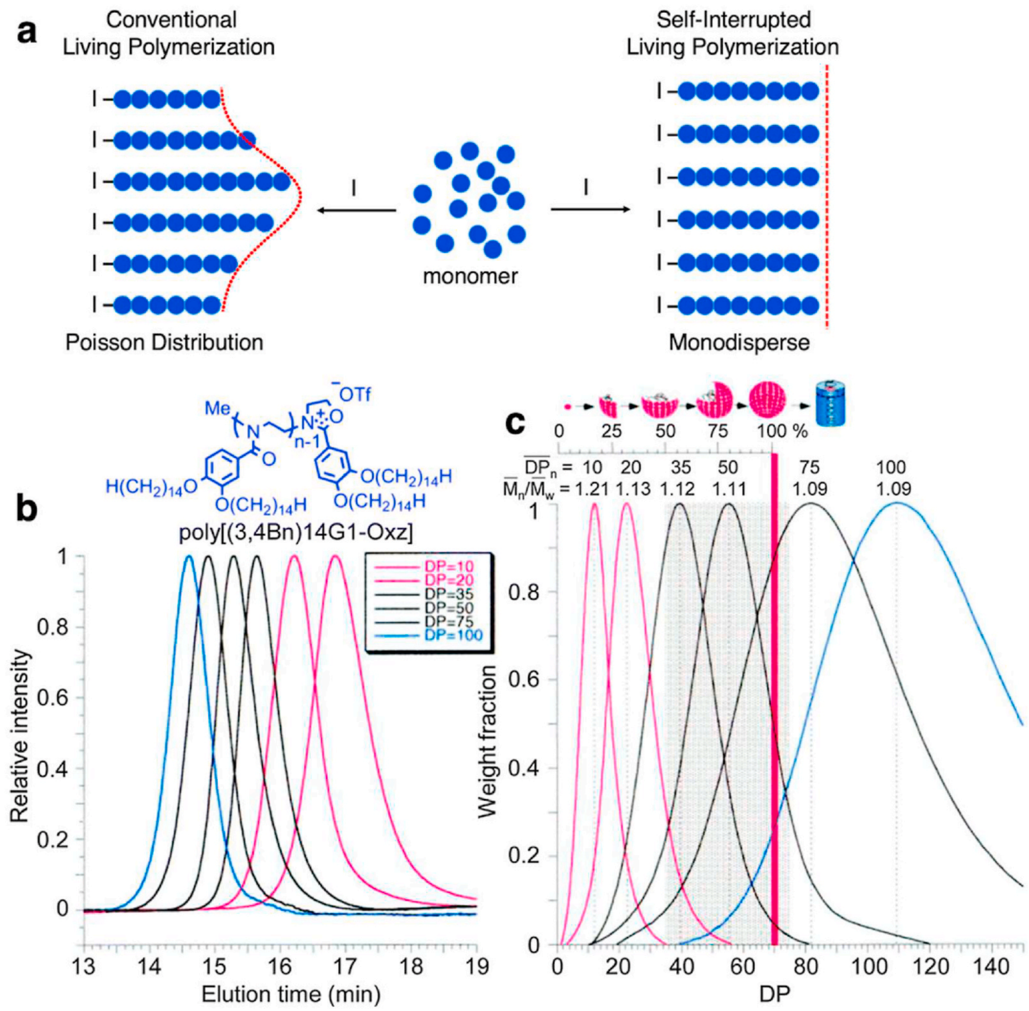

Fig. 13. (a) Comparison between conventional living polymerization with Poisson distribution and self-interrupted living polymerization (SILP) with monodisperse distribution. (b,c) Dependence of shape of supramolecules self-assembled by the dendronized polymer poly[(3,4Bn)14G1-Oxz] on its degree of polymerization (DP) observed during the living cationic ROP of its monomer. Selected GPC traces for poly[(3,4Bn)14G1-Oxz] (a), and its weight fraction as a function of the theoretical DP = $[M]_0/[I]_0$ (b). Reproduced with permission from Refs. [230]. Copyright 2020, American Chemical Society, and from Refs. [30]. Copyright 2015, Royal Society of Chemistry.

interactions of high selectivity", known today as supramolecular chemistry, I wonder if inspiration for some of the work reported here would have been so powerful. A recent elegant example from E.L.Thomas laboratory on how improved perfection of self-organized matter contributes to the elucidation of the determination of the structure of supramolecular assemblies is available [263]. Numerous reviews on the development of helical assemblies with the help of helical PPA are also available [202–214]. A new methodology to design unprecedented supramolecular columnar arrangements by the supramolecular orientational memory (SOM) effect was recently discovered and will be summarized in a different publication [264–266]. The most fundamental question that we have at the end of this perspective is the following. Will soft condensed matter end up displaying the perfect high order that was required during the discovery and commercialization of the field-effect transistor? The transistor was discovered at Bell Labs in Murray Hill, New Jersey in 1947 by William Shockley, John Bardeen and Walter Brattain who received the Nobel Prize for Physics in 1956 [267–269]. The original transistor produced in 1951 was made from Germanium. However, it took until mid 1960s to produce the Silicon based single crystal transistor that is used by all of us today. It all relied on improving the perfection of inorganic single crystals that are assembled from few to several atoms per unit cell only. The difference between inorganic and organic supramolecular materials is that the organic rely, as discussed earlier in this article, on mega numbers of atom per unit cell. However biological mega macromolecules are also of the size of the synthetic macromolecules and they exhibit the same level of high order as the inorganic matter generated from a small number of metal atoms. Therefore, we believe that perfecting the order, dynamics and rate of self-organization of highly ordered supramolecular polymer materials by some of the methods discussed in this perspective including monodisperse, homochiral and sequence-defined that are widely used in biology will provide access to unprecedented organic materials and functions similar to those generated from few metal atoms or from biological macromolecules. At this point this is only a dream, but so was the dream of covalent macromolecules of Hermann Staudinger from 100 years ago.

Declaration of competing interest

Acknowledgements

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References

[1] H. Staudinger, Über polymerisation, Ber. Dtsch. Chem. Ges. 53 (1920) 1073–1085, https://doi.org/10.1002/cber.19200530627.

[2] H. Staudinger, J. Fritschi, Über isopren und kautschuk. 5. Mitteilung. Über die hydrierung des kautschuks und über seine konstitution, Helv. Chim. Acta 5 (1922) 785–806, https://doi.org/10.1002/hlca.19220050517.

[3] V. Percec (Ed.), Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize I, Adv. Polym. Sci. 261, Springer International Publishing, 2013.

[4] V. Percec (Ed.), Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize II, Adv. Polym. Sci. 262, Springer International Publishing, 2013.

[5] V. Percec, Preface, in: V. Percec (Ed.), Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize I, Adv. Polym. Sci. 261, Springer International Publishing, Cham, 2013 xi–xiii.

[6] V. Percec, From synthetic macromolecules to biological-like complex systems, in: V. Percec (Ed.), Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize I, Adv. Polym. Sci. 261, Springer International Publishing, Cham, 2013, pp. 173–197.

[7] V. Percec, Merging macromolecular and supramolecular chemistry into bioinspired synthesis of complex systems, Isr. J. Chem. 60 (2020) 48–66, https://doi.org/10.1002/ijch.202000004.

[8] V. Percec, Q. Xiao, The legacy of Hermann Staudinger: covalently linked macromolecules, Inside Chem. 6 (2020) 2855–2861, https://doi.org/10.1016/j.chempr.2020.10.007.

[9] H. Morawetz, Polymers: the Origins and Growth of a Science, Wiley, Chichester, England, 1985.

[10] H.F. Mark, Polymers in the 1920's, in: B. Rånby (Ed.), Physical Chemistry of Colloids and Macromolecules. The Svedberg Symposium, Blackwell Scientific Publications, Oxford, England, 1986, pp. 5–8.

[11] S. Brohult, Svedberg as a scientist, in: B. Rånby (Ed.), Physical Chemistry of Colloids and Macromolecules. The Svedberg Symposium, Blackwell Scientific Publications, Oxford, England, 1986, pp. 9–13.

[12] B. Rånby, Svedberg — Discoverer of the Protein Macromolecules, vol. 98, Macromolecular Symposia, 1995, pp. 1227–1245, https://doi.org/10.1002/masy.199509801113.

[13] H. Morawetz, A few comments on early polymer studies, Macromol. Symp. 98 (1995) 1163–1171, https://doi.org/10.1002/masy.199509801105.

[14] R. Mülhaupt, Hermann Staudinger and the origin of macromolecular chemistry, Angew. Chem. Int. Ed. 43 (2004) 1054–1063, https://doi.org/10.1002/anie.200330070.

[15] H. Ringsdorf, Hermann Staudinger and the future of polymer research Jubilees—beloved occasions for cultural piety, Angew. Chem. Int. Ed. 43 (2004) 1064–1076, https://doi.org/10.1002/anie.200330071.

[16] W.H. Carothers, Polymerization, Chem. Rev. 8 (1931) 353–426, https://doi.org/10.1021/cr60031a001.

[17] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca and London, 1953.

[18] H.-G. Elias, Mega Molecules: Tales of Adhesives, Bread, Diamonds, Eggs, Fibers, Foams, Gelatin, Leather, Meat, Plastics, Resists, Rubber, … and Cabbages and Kings, Springer-Verlag, Berlin and Heidelberg, Germany, 1987.

[19] B.M. Rosen, C.J. Wilson, D.A. Wilson, M. Peterca, M.R. Imam, V. Percec, Dendron-mediated self-assembly, disassembly, and self-organization of complex systems, Chem. Rev. 109 (2009) 6275–6540, https://doi.org/10.1021/cr900157q.

[20] J.M. Ottino, Engineering complex systems, Nature 427 (2004), https://doi.org/10.1038/427399a, 399–399.

[21] S. Kauffman, At Home in the Universe: the Search for the Laws of Self-Organization and Complexity, Oxford University Press, 1996.

[22] S.A. Kauffman, The Origins of Order: Self-Organization and Selection in Evolution, Oxford University Press, 1993.

[23] S. Camazine, J.-L. Deneubourg, N.R. Franks, J. Sneyd, G. Theraula, E. Bonabeau, Self-Organization in Biological Systems, Princeton University Press, 2020.

[24] J.-M. Lehn, Supramolecular chemistry—scope and perspectives molecules, supermolecules, and molecular devices (Nobel Lecture), Angew Chem. Int. Ed. Engl. 27 (1988) 89–112, https://doi.org/10.1002/anie.198800891.

[25] H. Ringsdorf, B. Schlarb, J. Venzmer, Molecular architecture and function of polymeric oriented systems: models for the study of organization, surface recognition, and dynamics of biomembranes, Angew Chem. Int. Ed. Engl. 27 (1988) 113–158, https://doi.org/10.1002/anie.198801131.

[26] J.-M. Lehn, Perspectives in supramolecular chemistry—from molecular recognition towards molecular information processing and self-organization, Angew Chem. Int. Ed. Engl. 29 (1990) 1304–1319, https://doi.org/10.1002/anie.199013041.

[27] T. Kunitake, Synthetic bilayer membranes: molecular design, self-organization, and application, Angew Chem. Int. Ed. Engl. 31 (1992) 709–726, https://doi.org/10.1002/anie.199207091.

[28] J.-M. Lehn, Toward self-organization and complex matter, Science 295 (2002) 2400–2403, https://doi.org/10.1126/science.1071063.

[29] J.-M. Lehn, Toward complex matter: supramolecular chemistry and self-organization, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 4763–4768, https://doi.org/10.1073/pnas.072065599.

[30] H.-J. Sun, S. Zhang, V. Percec, From structure to function *via* complex supramolecular dendrimer systems, Chem. Soc. Rev. 44 (2015) 3900–3923, https://doi.org/10.1039/C4CS00249K.

[31] S.E. Sherman, Q. Xiao, V. Percec, Mimicking complex biological membranes and their programmable glycan ligands with dendrimersomes and glycodendrimersomes, Chem. Rev. 117 (2017) 6538–6631, https://doi.org/10.1021/acs.chemrev.7b00097.

[32] V. Percec, D. Tomazos, Molecular engineering of side-chain liquid-crystalline polymers by living cationic polymerization, Adv. Mater. 4 (1992) 548–561, https://doi.org/10.1002/adma.19920040905.

[33] J.-M. Lehn, Dynamers: from supramolecular polymers to adaptive dynamic polymers, in: V. Percec (Ed.), Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize I, Adv. Polym. Sci. 261, Springer International Publishing, Cham, 2013, pp. 155–172.

[34] C.J. Pedersen, The discovery of crown ethers (Noble Lecture), Angew Chem. Int. Ed. Engl. 27 (1988) 1021–1027, https://doi.org/10.1002/anie.198810211.

[35] D.J. Cram, The design of molecular hosts, Angew Chem. Int. Ed. Engl. 27 (1988) 1009–1020, https://doi.org/10.1002/anie.198810093.

[36] J.F. Stoddart, Mechanically interlocked molecules (MIMs)—molecular shuttles, switches, and machines (Nobel Lecture), Angew. Chem. Int. Ed. 56 (2017) 11094–11125, https://doi.org/10.1002/anie.201703216.

[37] B.L. Feringa, The art of building small: from molecular switches to motors (Nobel Lecture), Angew. Chem. Int. Ed. 56 (2017) 11060–11078, https://doi.org/10.1002/anie.201702979.

[38] J.-P. Sauvage, From chemical topology to molecular machines (Nobel Lecture), Angew. Chem. Int. Ed. 56 (2017) 11080–11093, https://doi.org/10.1002/anie.201702992.

[39] B. Linton, A.D. Hamilton, Formation of artificial receptors by metal-templated self-assembly, Chem. Rev. 97 (1997) 1669–1680, https://doi.org/10.1021/cr960375w.

[40] D. Ajami, J. Rebek, More chemistry in small spaces, Acc. Chem. Res. 46 (2013) 990–999, https://doi.org/10.1021/ar300038r.

[41] T.R. Cook, P.J. Stang, Recent developments in the preparation and chemistry of metallacycles and metallacages via coordination, Chem. Rev. 115 (2015) 7001–7045, https://doi.org/10.1021/cr5005666.

[42] J.K. Klosterman, Y. Yamauchi, M. Fujita, Engineering discrete stacks of aromatic molecules, Chem. Soc. Rev. 38 (2009) 1714–1725, https://doi.org/10.1039/B901261N.

[43] Y.-S. Chen, E. Solel, Y.-F. Huang, C.-L. Wang, T.-H. Tu, E. Keinan, Y.-T. Chan, Chemical mimicry of viral capsid self-assembly via corannulene-based pentatopic tectons, Nat. Commun. 10 (2019) 3443, https://doi.org/10.1038/s41467-019-11457-6.

[44] F. Grimm, K. Hartnagel, F. Wessendorf, A. Hirsch, Supramolecular self-assembly of dendrimers containing orthogonal binding motifs, Chem. Commun. (2009) 1331–1333, https://doi.org/10.1039/B822043C.

[45] A.D. Schlüter, J.P. Rabe, Dendronized polymers: synthesis, characterization, assembly at interfaces, and manipulation, Angew. Chem., Int. Ed. Engl. 39 (2000) 864–883, https://doi.org/10.1002/(sici)1521-3773(20000303)39:5<864::aid-anie864>3.0.co;2-e.

[46] O. Ikkala, G. ten Brinke, Functional materials based on self-assembly of polymeric supramolecules, Science 295 (2002) 2407–2409, https://doi.org/10.1126/science.1067794.

[47] S. Datta, Y. Kato, S. Higashiharaguchi, K. Aratsu, A. Isobe, T. Saito, D.D. Prabhu, Y. Kitamoto, M.J. Hollamby, A.J. Smith, R. Dalgliesh, N. Mahmoudi, L. Pesce, C. Perego, G.M. Pavan, S. Yagai, Self-assembled poly-catenanes from supramolecular toroidal building blocks, Nature 583 (2020) 400–405, https://doi.org/10.1038/s41586-020-2445-z.

[48] T. Aida, E.W. Meijer, Supramolecular polymers – we've come full circle, Isr. J. Chem. 60 (2020) 33–47, https://doi.org/10.1002/ijch.201900165.

[49] P.K. Hashim, J. Bergueiro, E.W. Meijer, T. Aida, Supramolecular polymerization: a conceptual expansion for innovative materials, Prog. Polym. Sci. 105 (2020) 101250, https://doi.org/10.1016/j.progpolymsci.2020.101250.

[50] S.F.M. van Dongen, H.-P.M. de Hoog, R.J.R.W. Peters, M. Nallani, R.J.M. Nolte, J.C.M. van Hest, Biohybrid polymer capsules, Chem. Rev. 109 (2009) 6212–6274, https://doi.org/10.1021/cr900072y.

[51] Y. Tu, F. Peng, A. Adawy, Y. Men, L.K.E.A. Abdelmohsen, D.A. Wilson, Mimicking the cell: bio-inspired functions of supramolecular assemblies, Chem. Rev. 116 (2016) 2023–2078, https://doi.org/10.1021/acs.chemrev.5b00344.

[52] Y. Lim, K.-S. Moon, M. Lee, Recent advances in functional supramolecular nanostructures assembled from bioactive building blocks, Chem. Soc. Rev. 38 (2009) 925–934, https://doi.org/10.1039/b809741k.

[53] E. Krieg, M.M.C. Bastings, P. Besenius, B. Rybtchinski, Supramolecular polymers in aqueous media, Chem. Rev. 116 (2016) 2414–2477, https://doi.org/10.1021/acs.chemrev.5b00369.

[54] F. Würthner, C.R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, Perylene bisimide dye assemblies as archetype functional supramolecular materials, Chem. Rev. 116 (2016) 962–1052, https://doi.org/10.1021/acs.chemrev.5b00188.

[55] B.N.S. Thota, L.H. Urner, R. Haag, Supramolecular architectures of dendritic amphiphiles in water, Chem. Rev. 116 (2016) 2079–2102, https://doi.org/10.1021/acs.chemrev.5b00417.

[56] J. Rzayev, J. Penelle, HP-RAFT, A free-radical polymerization technique for obtaining living polymers of ultrahigh molecular weights, Angew. Chem. Int. Ed. 43 (2004) 1691–1694, https://doi.org/10.1002/anie.200353025.

[57] B.W. Mao, L.H. Gan, Y.Y. Gan, Ultra high molar mass poly[2-(dimethylamino) ethyl methacrylate] *via* atom transfer radical polymerization, Polymer 47 (2006) 3017–3020, https://doi.org/10.1016/j.polymer.2006.03.021.

[58] V. Percec, T. Guliashvili, J.S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M.J. Monteiro, S. Sahoo, Ultrafast synthesis of ultrahigh molar mass polymers by metal-catalyzed living radical polymerization of acrylates, methacrylates, and vinyl chloride mediated by SET at 25 °C, J. Am. Chem. Soc. 128 (2006) 14156–14165, https://doi.org/10.1021/ja065484z.

[59] R.W. Simms, M.F. Cunningham, High molecular weight poly(butyl methacrylate) by reverse atom transfer radical polymerization in miniemulsion initiated by a redox system, Macromolecules 40 (2007) 860–866, https://doi.org/10.1021/ma061899t.

[60] G. Lligadas, V. Percec, Ultrafast SET-LRP of methyl acrylate at 25 °C in alcohols, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 2745–2754, https://doi.org/10.1002/pola.22607.

[61] C.E. Diesendruck, Y. Vidavsky, A. Ben-Asuly, N.G. Lemcoff, A latent s-chelated ruthenium benzylidene initiator for ring-opening metathesis polymerization, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 4209–4213, https://doi.org/10.1002/pola.23476.

[62] L. Mueller, W. Jakubowski, K. Matyjaszewski, J. Pietrasik, P. Kwiatkowski, W. Chaladaj, J. Jurczak, Synthesis of high molecular weight polystyrene using AGET ATRP under high pressure, Eur. Polym. J. 47 (2011) 730–734, https://doi.org/10.1016/j.eurpolymj.2010.10.006.

[63] N.H. Nguyen, X. Leng, V. Percec, Synthesis of ultrahigh molar mass poly(2-hydroxyethyl methacrylate) by single-electron transfer living radical polymerization, Polym. Chem. 4 (2013) 2760–2766, https://doi.org/10.1039/C3PY00224A.

[64] S.R. Samanta, V. Percec, Synthesis of high molar mass poly(n-butyl acrylate) and poly(2-ethylhexyl acrylate) by SET-LRP in mixtures of fluorinated alcohols with DMSO, Polym. Chem. 5 (2013) 169–174, https://doi.org/10.1039/C3PY01008B.

[65] E. Read, A. Guinaudeau, D.J. Wilson, A. Cadix, F. Violleau, M. Destarac, Low temperature RAFT/MADIX gel polymerisation: access to controlled ultra-high molar mass polyacrylamides, Polym. Chem. 5 (2014) 2202–2207, https://doi.org/10.1039/C3PY01750H.

[66] J. Xu, K. Jung, A. Atme, S. Shanmugam, C. Boyer, A robust and versatile photoinduced living polymerization of conjugated and unconjugated monomers and its oxygen tolerance, J. Am. Chem. Soc. 136 (2014) 5508–5519, https://doi.org/10.1021/ja501745g.

[67] Z. Huang, J. Chen, L. Zhang, Z. Cheng, X. Zhu, ICAR ATRP of acrylonitrile under ambient and high pressure, Polymers 8 (2016) 59–68, https://doi.org/10.3390/polym8030059.

[68] J.K.D. Mapas, T. Thomay, A.N. Cartwright, J. Ilavsky, J. Rzayev, Ultrahigh molecular weight linear block copolymers: rapid access by reversible-deactivation radical polymerization and self-assembly into large domain nanostructures, Macromolecules 49 (2016) 3733–3738, https://doi.org/10.1021/acs.macromol.6b00863.

[69] R.N. Carmean, T.E. Becker, M.B. Sims, B.S. Sumerlin, Ultra-high molecular weights *via* aqueous reversible-deactivation radical polymerization, Inside Chem. 2 (2017) 93–101, https://doi.org/10.1016/j.chempr.2016.12.007.

[70] S. Chaimongkolkunasin, X. Hou, K. Nomura, Ring opening metathesis polymerization of norbornene and tetracyclododecene with cyclooctene by using (arylimido)vanadium(V)–alkylidene catalyst, J. Polym. Sci., Part A: Polym. Chem. 55 (2017) 3067–3074, https://doi.org/10.1002/pola.28622.

[71] Y. Bai, J. He, Y. Zhang, Ultra-high-molecular-weight polymers produced by the immortal phosphine-based catalyst system, Angew. Chem. Int. Ed. 57 (2018) 17230–17234, https://doi.org/10.1002/anie.201811946.

[72] H. Gong, Y. Gu, Y. Zhao, Q. Quan, S. Han, M. Chen, Precise synthesis of ultra-high-molecular-weight fluoropolymers enabled by chain-transfer-agent differentiation under visible-light irradiation, Angew. Chem. Int. Ed. 59 (2020) 919–927, https://doi.org/10.1002/anie.201912698.

[73] C. Boyer, A. Atme, C. Waldron, A. Anastasaki, P. Wilson, P.B. Zetterlund, D. Haddleton, M.R. Whittaker, Copper(0)-mediated radical polymerisation in a self-generating biphasic system, Polym. Chem. 4 (2012) 106–112, https://doi.org/10.1039/C2PY20560B.

[74] G. Lligadas, S. Grama, V. Percec, Recent developments in the synthesis of biomacromolecules and their conjugates by single electron transfer–living radical polymerization, Biomacromolecules 18 (2017) 1039–1063, https://doi.org/10.1021/acs.biomac.7b00197.

[75] G. Lligadas, S. Grama, V. Percec, Single-electron transfer living radical polymerization platform to practice, develop, and invent, Biomacromolecules 18 (2017) 2981–3008, https://doi.org/10.1021/acs.biomac.7b01131.

[76] A. Moreno, S. Grama, T. Liu, M. Galià, G. Lligadas, V. Percec, SET-LRP mediated by TREN in biphasic water–organic solvent mixtures provides the most economical and efficient process, Polym. Chem. 8 (2017) 7559–7574, https://doi.org/10.1039/C7PY01841J.

[77] A. Moreno, M. Galià, G. Lligadas, V. Percec, SET-LRP in Biphasic mixtures of the nondisproportionating solvent hexafluoroisopropanol with water, Biomacromolecules 19 (2018) 4480–4491, https://doi.org/10.1021/acs.biomac.8b01381.

[78] A. Moreno, T. Liu, M. Galià, G. Lligadas, V. Percec, Acrylate-macromonomers and telechelics of PBA by merging biphasic SET-LRP of BA, chain extension with MA and biphasic esterification, Polym. Chem. 9 (2018) 1961–1971, https://doi.org/10.1039/C8PY00156A.

[79] A. Moreno, T. Liu, L. Ding, I. Buzzacchera, M. Galià, M. Möller, C.J. Wilson, G. Lligadas, V. Percec, SET-LRP in biphasic mixtures of fluorinated alcohols with water, Polym. Chem. 9 (2018) 2313–2327, https://doi.org/10.1039/C8PY00062J.

[80] X. Feng, D.S. Maurya, N. Bensabeh, A. Moreno, T. Oh, Y. Luo, J. Lejnieks, M. Galià, Y. Miura, M.J. Monteiro, G. Lligadas, V. Percec, Replacing Cu(II)Br$_2$ with Me$_6$-TREN in biphasic Cu(0)/TREN catalyzed SET-LRP eeveals the mixed-ligand effect, Biomacromolecules 21 (2020) 250–261, https://doi.org/10.1021/acs.biomac.9b01282.

[81] S.J. Singer, G.L. Nicolson, The fluid mosaic model of the structure of cell membranes, Science 175 (1972) 720–731, https://doi.org/10.1126/science.175.4023.720.

[82] K. Yamauchi, M. Kinoshita, Highly stable lipid membranes from archaebacterial extremophiles, Prog. Polym. Sci. 18 (1993) 763–804, https://doi.org/10.1016/0079-6700(93)90008-Z.

[83] G. di Prisco (Ed.), Life under Extreme Conditions: Biochemical Adaptation, Springer-Verlag, Berlin Heidelberg, 1991, https://doi.org/10.1007/978-3-642-76056-3.

[84] S.A. Wasserman, N.R. Cozzarelli, Biochemical topology: applications to DNA recombination and replication, Science 232 (1986) 951–960, https://doi.org/10.1126/science.3010458.

[85] M.A. Krasnow, A. Stasiak, S.J. Spengler, F. Dean, T. Koller, N.R. Cozzarelli, Determination of the absolute handedness of knots and catenanes of DNA, Nature 304 (1983) 559–560, https://doi.org/10.1038/304559a0.

[86] S.A. Wasserman, J.M. Dungan, N.R. Cozzarelli, Discovery of a predicted DNA knot substantiates a model for site-specific recombination, Science 229 (1985) 171–174, https://doi.org/10.1126/science.2990045.

[87] F. Reinitzer, Beiträge zur Knntniss des Cholesterins, Monatsh. Chem. 9 (1888) 421–441, https://doi.org/10.1007/BF01516710.

[88] V. Percec, Liquid crystals 100 years later. What are the new concepts used in the design of molecular, macromolecular and supramolecular liquid crystals? Macromol. Symp. 117 (1997) 267–273, https://doi.org/10.1002/masy.19971170130.

[89] V. Percec, M. Kawasumi, P.L. Rinaldi, V.E. Litman, Synthesis and characterization of cyclic liquid crystalline oligomers based on 1-(4-hydroxy-4'-biphenylyl)-2-(4-hydroxyphenyl)butane and 1,10-dibromodecane, Macromolecules 25 (1992) 3851–3861, https://doi.org/10.1021/ma00041a005.

[90] V. Percec, M. Kawasumi, Similarities and differences between the mesomorphic behaviour of oligomeric macrocyclics and of linear high relative molecular mass polyethers based on 1-(4′-hydroxybiphenyl-4-yl)-2-(4-hydroxyphenyl)butane and flexible spacers, J. Chem. Soc., Perkin Trans. 1 (1993) 1319–1334, https://doi.org/10.1039/P19930001319.

[91] V. Percec, P.J. Turkaly, A.D. Asandei, Macrocyclization overrides the polymer effect in the stabilization of liquid crystalline (LC) phases with a novel odd−even alternation. A demonstration with LC crown Ethers, Macromolecules 30 (1997) 943–952, https://doi.org/10.1021/ma9614813.

[92] V. Percec, Molecular design of novel liquid crystalline polymers with complex architecture: macrocyclics and dendrimers, Pure Appl. Chem. 67 (1995) 2031–2038, https://doi.org/10.1351/pac199567122031.

[93] V. Percec, A.D. Asandei, P. Chu, Design of side chain and main chain liquid crystalline polymers containing supramolecular quasi-rigid-rodlike mesogens obtained from collapsed main chain macrocyclics, Macromolecules 29 (1996) 3736–3750, https://doi.org/10.1021/ma951891b.

[94] V. Percec, M.N. Holerca, Detecting the shape change of complex macromolecules during their synthesis with the aid of kinetics. A new lesson from biology, Biomacromolecules 1 (2000) 6–16, https://doi.org/10.1021/bm005507g.

[95] V. Percec, B. Barboiu, C. Grigoras, T.K. Bera, Universal iterative strategy for the divergent synthesis of dendritic macromolecules from conventional monomers by a combination of living radical polymerization and irreversible TERminator Multifunctional INItiator (TERMINI), J. Am. Chem. Soc. 125 (2003) 6503–6516, https://doi.org/10.1021/ja034746j.

[96] V. Percec, C. Grigoras, H.-J. Kim, Toward self-assembling dendritic macromolecules from conventional monomers by a combination of living radical polymerization and irreversible terminator multifunctional initiator, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 505–513, https://doi.org/10.1002/pola.11014.

[97] B.M. Rosen, G. Lligadas, C. Hahn, V. Percec, Synthesis of dendrimers through divergent iterative thio-bromo "Click" chemistry, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 3931–3939, https://doi.org/10.1002/pola.23519.

[98] B.M. Rosen, G. Lligadas, C. Hahn, V. Percec, Synthesis of dendritic macromolecules through divergent iterative thio-bromo "Click" chemistry and SET-LRP, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 3940–3948, https://doi.org/10.1002/pola.23518.

[99] J.-M. Lehn, Supramolecular polymer chemistry—scope and perspectives, Polym. Int. 51 (2002) 825–839, https://doi.org/10.1002/pi.852.

[100] V. Berl, M. Schmutz, M.J. Krische, R.G. Khoury, J.-M. Lehn, Supramolecular polymers generated from heterocomplementary monomers linked through multiple hydrogen-bonding arrays—formation, characterization, and properties, Chem. Eur J. 8 (2002) 1227–1244, https://doi.org/10.1002/1521-3765(20020301)8:5<1227::AID-CHEM1227>3.0.CO;2-0.

[101] J.-M. Lehn, Dynamers: dynamic molecular and supramolecular polymers, Prog. Polym. Sci. 30 (2005) 814–831, https://doi.org/10.1016/j.progpolymsci.2005.06.002.

[102] V. Percec, M. Kawasumi, Synthesis and characterization of a thermotropic nematic liquid crystalline dendrimeric polymer, Macromolecules 25 (1992) 3843–3850, https://doi.org/10.1021/ma00041a004.

[103] V. Percec, P. Chu, G. Ungar, J. Zhou, Rational design of the first nonspherical dendrimer which displays calamitic nematic and smectic thermotropic liquid crystalline phases, J. Am. Chem. Soc. 117 (1995) 11441–11454, https://doi.org/10.1021/ja00151a008.

[104] V. Percec, P. Chu, M. Kawasumi, Toward "willowlike" thermotropic dendrimers, Macromolecules 27 (1994) 4441–4453, https://doi.org/10.1021/ma00094a005.

[105] V. Percec, C.-H. Ahn, B. Barboiu, Self-encapsulation, acceleration and control in the radical polymerization of monodendritic monomers *via* self-assembly, J. Am. Chem. Soc. 119 (1997) 12978–12979, https://doi.org/10.1021/ja9727878.

[106] V. Percec, C.-H. Ahn, W.-D. Cho, A.M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S.A. Prokhorova, S.S. Sheiko, S.Z.D. Cheng, A. Zhang, G. Ungar, D.J.P. Yeardley, Visualizable cylindrical macromolecules with controlled stiffness from backbones containing libraries of self-assembling dendritic side groups, J. Am. Chem. Soc. 120 (1998) 8619–8631, https://doi.org/10.1021/ja981211v.

[107] V. Percec, C.-H. Ahn, G. Ungar, D.J.P. Yeardley, M. Möller, S.S. Sheiko, Controlling polymer shape through the self-assembly of dendritic side-groups, Nature 391 (1998) 161–164, https://doi.org/10.1038/34384.

[108] V.S.K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, Rational design of the first spherical supramolecular dendrimers self-organized in a novel thermotropic cubic liquid-crystalline phase and the determination of their Shape by X-ray analysis, J. Am. Chem. Soc. 119 (1997) 1539–1555, https://doi.org/10.1021/ja963295i.

[109] S.D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V.S. K. Balagurusamy, Direct visualization of individual cylindrical and spherical supramolecular dendrimers, Science 278 (1997) 449–452, https://doi.org/10.1126/science.278.5337.449.

[110] G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, Giant supramolecular liquid crystal lattice, Science 299 (2003) 1208–1211, https://doi.org/10.1126/science.1078849.

[111] X. Zeng, G. Ungar, Y. Liu, V. Percec, A.E. Dulcey, J.K. Hobbs, Supramolecular dendritic liquid quasicrystals, Nature 428 (2004) 157–160.

[112] V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, R. Graf, H.W. Spiess, V.S. K. Balagurusamy, P.A. Heiney, Self-assembly of dendronized triphenylenes into helical pyramidal columns and chiral spheres, J. Am. Chem. Soc. 131 (2009) 7662–7677, https://doi.org/10.1021/ja8094944.

[113] V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, R. Graf, H.W. Spiess, V.S. K. Balagurusamy, P.A. Heiney, Self-assembly of dendronized triphenylenes into helical pyramidal columns and chiral spheres, J. Am. Chem. Soc. 131 (2009) 7662–7677, https://doi.org/10.1021/ja8094944.

[114] V. Percec, W.-D. Cho, P.E. Mosier, G. Ungar, D.J.P. Yeardley, Structural analysis of cylindrical and spherical supramolecular dendrimers quantifies the concept of monodendron shape control by generation number, J. Am. Chem. Soc. 120 (1998) 11061–11070, https://doi.org/10.1021/ja9819007.

[115] V. Percec, W.-D. Cho, G. Ungar, Increasing the diameter of cylindrical and spherical supramolecular dendrimers by decreasing the solid angle of their monodendrons *via* periphery functionalization, J. Am. Chem. Soc. 122 (2000) 10273–10281, https://doi.org/10.1021/ja0024643.

[116] V. Percec, W.-D. Cho, G. Ungar, D.J.P. Yeardley, Synthesis and structural analysis of two constitutional isomeric libraries of AB$_2$-based monodendrons and supramolecular dendrimers, J. Am. Chem. Soc. 123 (2001) 1302–1315, https://doi.org/10.1021/ja0037771.

[117] V. Percec, C.M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V.S.K. Balagurusamy, P.A. Heiney, Designing libraries of first generation AB$_3$ and AB$_2$ self-assembling dendrons *via* the primary structure generated from combinations of $(AB)_y-AB_3$ and $(AB)_y-AB_2$ building blocks, J. Am. Chem. Soc. 126 (2004) 6078–6094, https://doi.org/10.1021/ja049846j.

[118] V. Percec, M. Peterca, M.J. Sienkowska, M.A. Ilies, E. Aqad, J. Smidrkal, P. A. Heiney, Synthesis and retrostructural analysis of libraries of AB$_3$ and constitutional isomeric AB$_2$ phenylpropyl ether-based supramolecular dendrimers, J. Am. Chem. Soc. 128 (2006) 3324–3334, https://doi.org/10.1021/ja060062a.

[119] V. Percec, B.C. Won, M. Peterca, P.A. Heiney, Expanding the structural diversity of self-assembling dendrons and supramolecular dendrimers *via* complex building blocks, J. Am. Chem. Soc. 129 (2007) 11265–11278, https://doi.org/10.1021/ja073714j.

[120] V. Percec, M. Peterca, A.E. Dulcey, M.R. Imam, S.D. Hudson, S. Nummelin, P. Adelman, P.A. Heiney, Hollow spherical supramolecular dendrimers, J. Am. Chem. Soc. 130 (2008) 13079–13094, https://doi.org/10.1021/ja8034703.

[121] M. Peterca, M.R. Imam, P. Leowanawat, B.M. Rosen, D.A. Wilson, C.J. Wilson, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, Self-assembly of hybrid dendrons into doubly segregated supramolecular polyhedral columns and vesicles, J. Am. Chem. Soc. 132 (2010) 11288–11305, https://doi.org/10.1021/ja104432d.

[122] V. Percec, M. Peterca, Y. Tsuda, B.M. Rosen, S. Uchida, M.R. Imam, G. Ungar, P. A. Heiney, Elucidating the structure of the Pm3n cubic phase of supramolecular dendrimers through the modification of their aliphatic to aromatic volume ratio, Chem. Eur J. 15 (2009) 8994–9004, https://doi.org/10.1002/chem.200901324.

[123] V. Percec, J. Smidrkal, M. Peterca, C.M. Mitchell, S. Nummelin, A.E. Dulcey, M. J. Sienkowska, P.A. Heiney, Self-assembly of hybrid dendrons with complex primary structure into functional helical pores, Chem. Eur J. 13 (2007) 3989–4007, https://doi.org/10.1002/chem.200601582.

[124] G. Ungar, V. Percec, M.N. Holerca, G. Johansson, J.A. Heck, Heat-shrinking spherical and columnar supramolecular dendrimers: their interconversion and dependence of their shape on molecular taper angle, Chem. Eur J. 6 (2000) 1258–1266, https://doi.org/10.1002/(SICI)1521-3765(20000403)6:7<1258::AID-CHEM1258>3.0.CO;2-O.

[125] V. Percec, M.N. Holerca, S. Uchida, W.-D. Cho, G. Ungar, Y. Lee, D.J.P. Yeardley, Exploring and expanding the three-dimensional structural diversity of supramolecular dendrimers with the aid of libraries of alkali metals of their AB$_3$ minidendritic carboxylates, Chem. Eur J. 8 (2002) 1106–1117, https://doi.org/10.1002/1521-3765(20020301)8:5<1106::AID-CHEM1106>3.0.CO;2-G.

[126] V. Percec, M.N. Holerca, S. Nummelin, J.J. Morrison, M. Glodde, J. Smidrkal, M. Peterca, B.M. Rosen, S. Uchida, V.S.K. Balagurusamy, M.J. Sienkowska, P. A. Heiney, Exploring and expanding the structural diversity of self-assembling dendrons through combinations of AB, constitutional isomeric AB$_2$, and AB$_3$ biphenyl-4-methyl ether building blocks, Chem. Eur J. 12 (2006) 6216–6241, https://doi.org/10.1002/chem.200600178.

[127] G. Ungar, V. Percec, X. Zeng, P. Leowanawat, Liquid quasicrystals, Isr. J. Chem. 51 (2011) 1206–1215, https://doi.org/10.1002/ijch.201100151.

[128] B.M. Rosen, D.A. Wilson, C.J. Wilson, M. Peterca, B.C. Won, C. Huang, L.R. Lipski, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, Predicting the structure of supramolecular dendrimers *via* the analysis of libraries of AB$_3$ and constitutional isomeric AB$_2$ biphenylpropyl ether self-assembling dendrons, J. Am. Chem. Soc. 131 (2009) 17500–17521, https://doi.org/10.1021/ja907882n.

[129] D.A. Tomalia, S.N. Khanna, A Systematic framework and nanoperiodic concept for unifying nanoscience: hard/soft nanoelements, superatoms, meta-atoms, new emerging properties, periodic property patterns, and predictive Mendeleev-like nanoperiodic tables, Chem. Rev. 116 (2016) 2705–2774, https://doi.org/10.1021/acs.chemrev.5b00367.

[130] S.E. Ahnert, J.A. Marsh, H. Hernández, C.V. Robinson, S.A. Teichmann, Principles of assembly reveal a periodic table of protein complexes, Science 350 (2015), https://doi.org/10.1126/science.aaa2245.

[131] M. Peterca, V. Percec, Recasting metal alloy phases with block copolymers, Science 330 (2010) 333–334, https://doi.org/10.1126/science.1196698.

[132] Z. Su, M. Huang, S.Z.D. Cheng, Complex self-assembled lattices from simple polymer blends, Proc. Natl. Acad. Sci. U.S.A. 117 (2020) 19618–19620, https://doi.org/10.1073/pnas.2013590117.

[133] M. Huang, C.-H. Hsu, J. Wang, S. Mei, X. Dong, Y. Li, M. Li, H. Liu, W. Zhang, T. Aida, W.-B. Zhang, K. Yue, S.Z.D. Cheng, Selective assemblies of giant tetrahedra *via* precisely controlled positional interactions, Science 348 (2015) 424–428, https://doi.org/10.1126/science.aaa2421.

[134] K. Yue, M. Huang, R.L. Marson, J. He, J. Huang, Z. Zhou, J. Wang, C. Liu, X. Yan, K. Wu, Z. Guo, H. Liu, W. Zhang, P. Ni, C. Wesdemiotis, W.-B. Zhang, S.C. Glotzer, S.Z.D. Cheng, Geometry induced sequence of nanoscale Frank–Kasper and quasicrystal mesophases in giant surfactants, Proc. Natl. Acad. Sci. U.S.A. 113 (2016) 14195–14200, https://doi.org/10.1073/pnas.1609422113.

[135] Z. Su, C.-H. Hsu, Z. Gong, X. Feng, J. Huang, R. Zhang, Y. Wang, J. Mao, C. Wesdemiotis, T. Li, S. Seifert, W. Zhang, T. Aida, M. Huang, S.Z.D. Cheng, Identification of a Frank–Kasper Z phase from shape amphiphile self-assembly, Nat. Chem. 11 (2019) 899–905, https://doi.org/10.1038/s41557-019-0330-x.

[136] X. Feng, R. Zhang, Y. Li, Y. Hong, D. Guo, K. Lang, K.-Y. Wu, M. Huang, J. Mao, C. Wesdemiotis, Y. Nishiyama, W. Zhang, W. Zhang, T. Miyoshi, T. Li, S.Z. D. Cheng, Hierarchical self-organization of AB$_n$ dendron-like molecules into a supramolecular lattice sequence, ACS Cent. Sci. 3 (2017) 860–867, https://doi.org/10.1021/acscentsci.7b00188.

[137] Y. Sun, R. Tan, Z. Ma, Z. Gan, G. Li, D. Zhou, Y. Shao, W.-B. Zhang, R. Zhang, X.-H. Dong, Discrete block copolymers with diverse architectures: resolving complex spherical phases with one monomer resolution, ACS Cent. Sci. 6 (2020) 1386–1393, https://doi.org/10.1021/acscentsci.0c00798.

[138] Y. Liu, T. Liu, X. Yan, Q.-Y. Guo, J. Wang, R. Zhang, S. Zhang, Z. Su, J. Huang, G.-X. Liu, W. Zhang, W. Zhang, T. Aida, K. Yue, M. Huang, S.Z.D. Cheng, Mesoatom alloys via self-sorting approach of giant molecules blends, Giant 4 (2020) 100031, https://doi.org/10.1016/j.giant.2020.100031.

[139] J. Huang, Z. Su, M. Huang, R. Zhang, J. Wang, X. Feng, R. Zhang, R. Zhang, W. Shan, X.-Y. Yan, Q.-Y. Guo, T. Liu, Y. Liu, Y. Cui, X. Li, A.-C. Shi, S.Z.D. Cheng, Spherical supramolecular structures constructed via chemically symmetric perylene bisimides: beyond columnar assembly, Angew. Chem. Int. Ed. 59 (2020) 18563–18571, https://doi.org/10.1002/anie.201914889.

[140] Z. Su, J. Huang, W. Shan, X.-Y. Yan, R. Zhang, T. Liu, Y. Liu, Q.-Y. Guo, F. Bian, X. Miao, M. Huang, S.Z.D. Cheng, Constituent isomerism-induced quasicrystal and Frank–Kasper σ superlattices based on nanosized shape amphiphiles, CCS Chem 2 (2020) 1434–1444, https://doi.org/10.31635/ccschem.020.202000338.

[141] S. Lee, M.J. Bluemle, F.S. Bates, Discovery of a Frank-Kasper σ phase in sphere-forming block copolymer melts, Science 330 (2010) 349–353, https://doi.org/10.1126/science.1195552.

[142] T.M. Gillard, S. Lee, F.S. Bates, Dodecagonal quasicrystalline order in a diblock copolymer melt, Proc. Natl. Acad. Sci. U.S.A. 113 (2016) 5167–5172, https://doi.org/10.1073/pnas.1601692113.

[143] K. Kim, M.W. Schulze, A. Arora, R.M. Lewis, M.A. Hillmyer, K.D. Dorfman, F. S. Bates, Thermal processing of diblock copolymer melts mimics metallurgy, Science 356 (2017) 520–523, https://doi.org/10.1126/science.aam7212.

[144] M. Girard, S. Wang, J.S. Du, A. Das, Z. Huang, V.P. Dravid, B. Lee, C.A. Mirkin, M. O. de la Cruz, Particle analogs of electrons in colloidal crystals, Science 364 (2019) 1174–1178, https://doi.org/10.1126/science.aaw8237.

[145] K.K. Lachmayr, C.M. Wentz, L.R. Sita, An exceptionally stable and scalable sugar–polyolefin Frank–Kasper A15 phase, Angew. Chem. Int. Ed. 59 (2020) 1521–1526, https://doi.org/10.1002/anie.201912648.

[146] K.K. Lachmayr, L.R. Sita, Small-molecule modulation of soft-matter Frank-Kasper phases: a method for adding function to form, Angew. Chem. Int. Ed. 59 (2020) 3563–3567, https://doi.org/10.1002/anie.201915416.

[147] Y. Li, S.-T. Lin, W.A. Goddard, Efficiency of various lattices from hard ball to soft ball: Theoretical study of thermodynamic properties of dendrimer liquid crystal from atomistic simulation, J. Am. Chem. Soc. 126 (2004) 1872–1885, https://doi.org/10.1021/ja038617e.

[148] P. Ziherl, R.D. Kamien, From lumps to lattices: crystallized clusters made simple, J. Phys. Chem. B 115 (2011) 7200–7205, https://doi.org/10.1021/jp109330p.

[149] C.R. Iacovella, A.S. Keys, S.C. Glotzer, Self-assembly of soft-matter quasicrystals and their approximants, Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 20935–20940, https://doi.org/10.1073/pnas.1019763108.

[150] A.-C. Shi, First reaction: mesoatom alloys via self-sorting approach of giant molecules blends, Giant 4 (2020) 100032, https://doi.org/10.1016/j.giant.2020.100032.

[151] D.A. Wilson, K.A. Andreopoulou, M. Peterca, P. Leowanawat, D. Sahoo, B. E. Partridge, Q. Xiao, N. Huang, P.A. Heiney, V. Percec, Supramolecular spheres self-assembled from conical dendrons are chiral, J. Am. Chem. Soc. 141 (2019) 6162–6166, https://doi.org/10.1021/jacs.9b02206.

[152] M. Peterca, V. Percec, M.R. Imam, P. Leowanawat, K. Morimitsu, P.A. Heiney, Molecular structure of helical supramolecular dendrimers, J. Am. Chem. Soc. 130 (2008) 14840–14852, https://doi.org/10.1021/ja806524m.

[153] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties. 1. Synthesis and characterization of 4-(11-undecan-1-yloxy)-4’-[3,4,5-tri(para-normal-dodecan-1-yloxybenzylox y) benzoate]biphenyl side groups, J. Polym. Sci., Part A: Polym. Chem. 29 (1991) 591–597, https://doi.org/10.1002/pola.1991.080290416.

[154] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties. 2. Synthesis and characterization of poly(2-[3,4,5-tri[p-(n-dodecan-1-yloxy)benzyloxy]benzoate]-7-[p-11-undec an-1-yloxy) benzoate]naphthalene]methyl siloxane), Polym. Bull. 24 (1990) 255–262, https://doi.org/10.1007/BF00306572.

[155] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties. 4. Side-chain liquid-crystalline polymethylsiloxanes containing hemiphasmidic mesogens based on 4-[3,4,5-tri-(alkan-1-yloxy)benzoate]biphenyl groups, Polym. Bull. 25 (1991) 431–438, https://doi.org/10.1007/BF00310233.

[156] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties .3. Synthesis and characterization of polymethylsiloxanes and copolymethyl-siloxanes based on 4-[3,4,5-tri(p-N-dodecan-1-yloxybenzyloxy)benzoate]-4’-(p-allyloxybenzoa te)biphenyl and 4-[3,4,5-tri(p-N-dodecan-1-yloxy-benzyloxy)benzoate]-4’-(p-allyloxybenzo ate) thiodiphenyl side groups, Polym. Bull. 25 (1991) 55–62.

[157] V. Percec, G. Johansson, J. Heck, G. Ungarb, S.V. Battyb, Molecular recognition directed self-assembly of supramolecular cylindrical channel-like architectures from 6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecen-2-ylmethyl 3,4,5-tris(p-dodecyloxybenzyloxy)benzoate, J. Chem. Soc., Perkin Trans. 1 (1993) 1411–1420, https://doi.org/10.1039/P19930001411.

[158] V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell, G. Ungar, Self-assembly of taper-shaped monoesters of oligo(ethylene oxide) with 3,4,5-tris(p-dodecyloxybenzyloxy)benzoic acid and of their polymethacrylates into tubular supramolecular architectures displaying a columnar mesophase, J. Chem. Soc., Perkin Trans. 1 (1993) 2799–2811, https://doi.org/10.1039/P19930002799.

[159] V. Percec, J.A. Heck, D. Tomazos, G. Ungar, The influence of the complexation of sodium and lithium triflate on the self-assembly of tubular-supramolecular architectures displaying a columnar mesophase based on taper-shaped monoesters of oligoethylene oxide with 3,4,5-tris[p-(n-dodecan-1-yloxy)benzyloxy]benzoic acid and of their polymethacrylates, J. Chem. Soc., Perkin Trans. 2 (1993) 2381–2388, https://doi.org/10.1039/P29930002381.

[160] V. Percec, D. Tomazos, J. Heck, H. Blackwell, G. Ungar, Self-assembly of taper-shaped monoesters of oligo(ethylene oxide) with 3,4,5-tris(n-dodecan-1-yloxy) benzoic acid and of their polymethacrylates into tubular supramolecular architectures displaying a columnar hexagonal mesophase, J. Chem. Soc., Perkin Trans. 2 (1994) 31–44, https://doi.org/10.1039/P29940000031.

[161] G. Ungar, V. Percec, M.N. Holerca, G. Johansson, J.A. Heck, Heat-shrinking spherical and columnar supramolecular dendrimers: their interconversion and dependence of their shape on molecular taper angle, Chem. Eur J. 6 (2000) 1258–1266, https://doi.org/10.1002/(SICI)1521-3765(20000403)6:7<1258::AID-CHEM1258>3.0.CO;2-O.

[162] Y.K. Kwon, S.N. Chvalun, J. Blackwell, V. Percec, J.A. Heck, Effect of temperature on the supramolecular tubular structure in oriented fibers of a poly(methacrylate) with tapered side groups, Macromolecules 28 (1995) 1552–1558, https://doi.org/10.1021/ma00109a029.

[163] Y.K. Kwon, S. Chvalun, A.-I. Schneider, J. Blackwell, V. Percec, J.A. Heck, Supramolecular tubular structures of a polymethacrylate with tapered side groups in aligned hexagonal phases, Macromolecules 27 (1994) 6129–6132, https://doi.org/10.1021/ma00099a029.

[164] V. Percec, J. Heck, M. Lee, G. Ungar, A. Alvarez-Castillo, Poly{2-vinyloxyethyl 3,4,5-tris[4-(n-dodecanyloxy)benzyloxy]benzoate}: a self-assembled supramolecular polymer similar to tobacco mosaic virus, J. Mater. Chem. 2 (1992) 1033–1039, https://doi.org/10.1039/JM9920201033.

[165] G. Ungar, D. Abramic, V. Percec, J.A. Heck, Self-assembly of twin tapered bisamides into supramolecular columns exhibiting hexagonal columnar mesophases. Structural evidence for a microsegregated model of the supramolecular column, Liq. Cryst. 21 (1996) 73–86, https://doi.org/10.1080/02678299608033797.

[166] V. Percec, M. Lee, J. Heck, H.E. Blackwell, G. Ungar, A. Alvarez-Castillo, Re-entrant isotropic phase in a supramolecular disc-like oligomer of 4-[3,4,5-tris(n-dodecanyloxy)benzoyloxy]-4′-[(2-vinyloxy)ethoxy]biphenyl, J. Mater. Chem. 2 (1992) 931–938, https://doi.org/10.1039/JM9920200931.

[167] V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi, G. Ungar, Molecular-recognition-directed self-assembly of supramolecular polymers, J. Macromol. Sci. Pure Appl. Chem. A31 (1994) 1031–1070, https://doi.org/10.1080/10601329409349776.

[168] V. Percec, J. Heck, G. Johansson, D. Tomazos, G. Ungar, Towards tobacco mosaic virus-like self-assembled supramolecular architectures, Macromol. Symp. 77 (1994) 237–265, https://doi.org/10.1002/masy.19940770127.

[169] V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi, P. Chu, G. Ungar, Molecular recognition directed self-assembly of supramolecular architectures, J. Macromol. Sci. Pure Appl. Chem. A31 (1994) 1719–1758, https://doi.org/10.1080/10601329408545879.

[170] Y. Kwon, C. Danko, S. Chvalun, J. Blackwell, J. Heck, V. Percec, Comparison of the supramolecular structures formed by a polymethacrylate with a highly tapered side-chain and its monomeric precursor, Macromol. Symp. 87 (1994) 103–114, https://doi.org/10.1002/masy.19940870113.

[171] D. Tomazos, G. Out, J. Heck, G. Johansson, V. Percec, M. Moller, Isomorphism within the hexagonal columnar mesophase of molecular and macromolecular self-assembled and co-assembled columns containing tapered groups, Liq. Cryst. 16 (1994) 509–527, https://doi.org/10.1080/02678299408029175.

[172] S.N. Chvalun, J. Blackwell, J.D. Cho, Y.K. Kwon, V. Percec, J.A. Heck, X-ray analysis of the internal rearrangement of the self-assembling columnar structure formed by a highly tapered molecule, Polymer 39 (1998) 4515–4522, https://doi.org/10.1016/S0032-3861(97)10131-8.

[173] J. Li, J. Heck, V. Percec, C. Rosenblatt, J. Collura, M. Fisch, Optical studies of supramolecular tubular structures generated by taper-shaped side-groups in the columnar hexagonal phase, J. Phys. II 4 (1994) 1813–1822, https://doi.org/10.1051/jp2:1994234.

[174] J.M. Rodriguez-Parada, V. Percec, Poly(vinyl ether)s and poly(propenyl ether)s containing mesogenic groups: a new class of side-chain liquid-crystalline polymers, J. Polym. Sci., Part A: Polym. Chem. 24 (1986) 1363–1378, https://doi.org/10.1002/pola.1986.080240619.

[175] V. Percec, A.D.S. Gomes, M. Lee, Molecular engineering of liquid crystal polymers by living polymerization. XI. Synthesis and characterization of poly 11-[(4-cyano-4′-trans-α-cyanostilbene) oxy] undecanyl vinyl ether, J. Polym. Sci., Part A: Polym. Chem. 29 (1991) 1615–1622, https://doi.org/10.1002/pola.1991.080291111.

[176] V. Percec, M. Lee, Molecular engineering of liquid crystal polymers by living polymerization. XXIII. Synthesis and characterization of AB block copolymers dased on ω-[(4-cyano-4′ -biphenyl)-oxy]alkyl vinyl ether, 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether, and 2-(4-blphenyloxy)ethyl vinyl ether with 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether, J. Macromol. Sci. Pure Appl. Chem. 29 (1992) 723–740, https://doi.org/10.1080/10601329208054112.

[177] V. Percec, B. Hahn, Liquid crystalline polymers containing heterocycloalkanediyl groups as mesogens. 7. Molecular weight and composition effects on the phase transitions of poly(methylsiloxane)s and poly(methylsiloxane-co-dimethylsiloxane)s containing 2-[4-(2(S)-methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane side groups, Macromolecules 22 (1989) 1588–1599, https://doi.org/10.1021/ma00194a014.

[178] V. Percec, D. Schlueter, J.C. Ronda, G. Johansson, G. Ungar, J.P. Zhou, Tubular architectures from polymers with tapered dide groups. Assembly of side groups *via* a rigid helical chain conformation and flexible helical chain conformation induced *via* assembly of side groups, Macromolecules 29 (1996) 1464–1472, https://doi.org/10.1021/ma951244k.

[179] V. Percec, D. Schlueter, Mechanistic Investigations on the formation of supramolecular cylindrical shaped oligomers and polymers by living ring opening metathesis polymerization of a 7-oxanorbornene monomer substituted with two tapered monodendrons, Macromolecules 30 (1997) 5783–5790, https://doi.org/10.1021/ma970157k.

[180] V. Percec, D. Schlueter, G. Ungar, S.Z.D. Cheng, A. Zhang, Hierarchical control of internal superstructure, diameter, and stability of supramolecular and macromolecular columns generated from tapered monodendritic building blocks, Macromolecules 31 (1998) 1745–1762, https://doi.org/10.1021/ma971459p.

[181] J.M. Rodriguez-Parada, V. Percec, Synthesis and characterization of liquid crystalline poly(N-acylethyleneimine)s, J. Polym. Sci., Part A: Polym. Chem. 25 (1987) 2269–2279, https://doi.org/10.1002/pola.1987.080250823.

[182] V. Percec, D. Schlueter, Y.K. Kwon, J. Blackwell, M. Moeller, P.J. Slangen, Dramatic stabilization of a hexagonal columnar mesophase generated from supramolecular and macromolecular columns by the semifluorination of the alkyl groups of their tapered building blocks, Macromolecules 28 (1995) 8807–8818, https://doi.org/10.1021/ma00130a013.

[183] V. Percec, G. Johansson, G. Ungar, J. Zhou, Fluorophobic effect induces the self-assembly of semifluorinated tapered monodendrons containing crown Eehers into supramolecular columnar dendrimers which exhibit a homeotropic hexagonal columnar liquid crystalline phase, J. Am. Chem. Soc. 118 (1996) 9855–9866, https://doi.org/10.1021/ja9615738.

[184] G. Johansson, V. Percec, G. Ungar, J.P. Zhou, Fluorophobic effect in the self-assembly of polymers and model compounds containing tapered groups into supramolecular columns, Macromolecules 29 (1996) 646–660, https://doi.org/10.1021/ma9511558.

[185] G. Johansson, V. Percec, G. Ungar, K. Smith, Fluorophobic effect generates a systematic approach to the synthesis of the simplest class of rodlike liquid crystals containing a single benzene unit, Chem. Mater. 9 (1997) 164–175, https://doi.org/10.1021/cm960267q.

[186] V. Percec, M. Glodde, T.K. Bera, Y. Miura, I. Shiyanovskaya, K.D. Singer, V.S. K. Balagurusamy, P.A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S.D. Hudson, H. Duan, Self-organization of supramolecular helical dendrimers into complex electronic materials, Nature 419 (2002) 384–387, https://doi.org/10.1038/nature01072.

[187] V. Percec, M. Glodde, G. Johansson, V.S.K. Balagurusamy, P.A. Heiney, Transformation of a spherical supramolecular dendrimer into a pyramidal columnar supramolecular dendrimer mediated by the fluorophobic effect, Angew. Chem. Int. Ed. 42 (2003) 4338–4342, https://doi.org/10.1002/anie.200351804.

[188] V. Percec, M.R. Imam, T.K. Bera, V.S.K. Balagurusamy, M. Peterca, P.A. Heiney, Self-assembly of semifluorinated Janus-dendritic benzamides into bilayered pyramidal columns, Angew. Chem. Int. Ed. 44 (2005) 4739–4745, https://doi.org/10.1002/anie.200501254.

[189] V. Percec, M. Glodde, M. Peterca, A. Rapp, I. Schnell, H.W. Spiess, T.K. Bera, Y. Miura, V.S.K. Balagurusamy, E. Aqad, P.A. Heiney, Self-assembly of semifluorinated dendrons attached to electron-donor groups mediates their π-stacking *via* a helical pyramidal column, Chem. Eur J. 12 (2006) 6298–6314, https://doi.org/10.1002/chem.200501195.

[190] V. Percec, E. Aqad, M. Peterca, M.R. Imam, M. Glodde, T.K. Bera, Y. Miura, V.S.K. Balagurusamy, P.C. Ewbank, F. Würthner, P.A. Heiney, Self-assembly of semifluorinated minidendrons attached to electron-acceptor groups into pyramidal columns, Chem. Eur J. 13 (2007) 3330–3345, https://doi.org/10.1002/chem.200600901.

[191] V. Percec, A.E. Dulcey, V.S.K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S.D. Hudson, P.A. Heiney, H. Duan, S.N. Magonov, S.A. Vinogradov, Self-assembly of amphiphilic dendritic dipeptides into helical pores, Nature 430 (2004) 764–768, https://doi.org/10.1038/nature02770.

[192] V. Percec, A.E. Dulcey, M. Peterca, M. Ilies, M.J. Sienkowska, P.A. Heiney, Programming the internal structure and stability of helical pores self-assembled from dendritic dipeptides *via* the protective groups of the peptide, J. Am. Chem. Soc. 127 (2005) 17902–17909, https://doi.org/10.1021/ja056313h.

[193] V. Percec, A.E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, M.J. Sienkowska, P.A. Heiney, Principles of self-assembly of helical pores from dendritic dipeptides, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 2518–2523, https://doi.org/10.1073/pnas.0509676103.

[194] M.S. Kaucher, M. Peterca, A.E. Dulcey, A.J. Kim, S.A. Vinogradov, D.A. Hammer, P.A. Heiney, V. Percec, Selective transport of water mediated by porous dendritic dipeptides, J. Am. Chem. Soc. 129 (2007) 11698–11699, https://doi.org/10.1021/ja076066c.

[195] M. Barboiu, Artificial water channels, Angew. Chem. Int. Ed. 51 (2012) 11674–11676, https://doi.org/10.1002/anie.201205819.

[196] M. Barboiu, A. Gilles, From natural to bioassisted and biomimetic artificial water channel systems, Acc. Chem. Res. 46 (2013) 2814–2823, https://doi.org/10.1021/ar400025e.

[197] M. Barboiu, Artificial water channels – incipient innovative developments, Chem. Commun. 52 (2016) 5657–5665, https://doi.org/10.1039/C6CC01724J.

[198] I. Kocsis, M. Sorci, H. Vanselous, S. Murail, S.E. Sanders, E. Licsandru, Y.-M. Legrand, A. van der Lee, M. Baaden, P.B. Petersen, G. Belfort, M. Barboiu, Oriented chiral water wires in artificial transmembrane channels, Sci. Adv. 4 (2018), https://doi.org/10.1126/sciadv.aao5603 eaao5603.

[199] Z. Sun, I. Kocsis, Y. Li, Y.-M. Legrand, M. Barboiu, Imidazole derivatives as artificial water channel building-blocks: structural design influence on water permeability, Faraday Discuss 209 (2018) 113–124, https://doi.org/10.1039/C8FD00024G.

[200] B.M. Rosen, M. Peterca, K. Morimitsu, A.E. Dulcey, P. Leowanawat, A.-M. Resmerita, M.R. Imam, V. Percec, Programming the supramolecular helical polymerization of dendritic dipeptides *via* the stereochemical information of the dipeptide, J. Am. Chem. Soc. 133 (2011) 5135–5151, https://doi.org/10.1021/ja200280h.

[201] V. Percec, P. Leowanawat, Why are biological systems homochiral? Isr. J. Chem. 51 (2011) 1107–1117.

[202] T. Nakano, Y. Okamoto, Synthetic helical polymers: conformation and function, Chem. Rev. 101 (2001) 4013–4038, https://doi.org/10.1021/cr0000978.

[203] J.J.L.M. Cornelissen, A.E. Rowan, R.J.M. Nolte, N.A.J.M. Sommerdijk, Chiral architectures from macromolecular building blocks, Chem. Rev. 101 (2001) 4039–4070, https://doi.org/10.1021/cr990126i.

[204] J.M. Seco, E. Quiñoá, R. Riguera, The assignment of absolute configuration by NMR, Chem. Rev. 104 (2004) 17–118, https://doi.org/10.1021/cr000665j.

[205] M.G. Mayershofer, O. Nuyken, Living polymerization of substituted acetylenes, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 5723–5747, https://doi.org/10.1002/pola.20993.

[206] J.G. Rudick, V. Percec, Helical chirality in dendronized polyarylacetylenes, New J. Chem. 31 (2007) 1083–1096, https://doi.org/10.1039/B616449H.

[207] J.G. Rudick, V. Percec, Nanomechanical function made possible by suppressing structural transformations of polyarylacetylenes, Macromol. Chem. Phys. 209 (2008) 1759–1768, https://doi.org/10.1002/macp.200800271.

[208] J. Liu, J.W.Y. Lam, B.Z. Tang, Acetylenic polymers: syntheses, structures, and functions, Chem. Rev. 109 (2009) 5799–5867, https://doi.org/10.1021/cr900149d.

[209] E. Yashima, K. Maeda, Y. Furusho, Single- and double-stranded helical polymers: synthesis, structures, and functions, Acc. Chem. Res. 41 (2008) 1166–1180, https://doi.org/10.1021/ar800091w.

[210] E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai, Helical polymers: synthesis, structures, and functions, Chem. Rev. 109 (2009) 6102–6211, https://doi.org/10.1021/cr900162q.

[211] J. Kumaki, S. Sakurai, E. Yashima, Visualization of synthetic helical polymers by high-resolution atomic force microscopy, Chem. Soc. Rev. 38 (2009) 737–746, https://doi.org/10.1039/B718433F.

[212] T. Ikai, Y. Okamoto, Structure control of polysaccharide derivatives for efficient separation of enantiomers by chromatography, Chem. Rev. 109 (2009) 6077–6101, https://doi.org/10.1021/cr8005558.

[213] J. Shen, Y. Okamoto, Efficient separation of enantiomers using stereoregular chiral polymers, Chem. Rev. 116 (2016) 1094–1138, https://doi.org/10.1021/acs.chemrev.5b00317.

[214] E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, Supramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions, Chem. Rev. 116 (2016) 13752–13990, https://doi.org/10.1021/acs.chemrev.6b00354.

[215] J. Kunzler, V. Percec, Living polymerization of aryl substituted acetylenes by $MoCl_5$ and WCl_6 based initiators: the ortho phenyl substituent effect, J. Polym. Sci., Part A: Polym. Chem. 28 (1990) 1221–1236, https://doi.org/10.1002/pola.1990.080280522.

[216] J.F. Kunzler, V. Percec, Living non-conjugated polyacetylenes, Polym. Bull. 18 (1987) 303–309, https://doi.org/10.1007/BF00256229.

[217] C.I. Simionescu, V. Percec, S. Dumitrescu, Polymerization of acetylenic derivatives. XXX. Isomers of polyphenylacetylene, J. Polym. Sci., Polym. Chem. Ed. 15 (1977) 2497–2509, https://doi.org/10.1002/pol.1977.170151018.

[218] C.I. Simionescu, V. Percec, Thermal cis–trans isomerization of cis–transoidal polyphenylacetylene, J. Polym. Sci., Polym. Chem. Ed. 18 (1980) 147–155, https://doi.org/10.1002/pol.1980.170180114.

[219] C.I. Simionescu, V. Percec, Polyarylacetylenes: structure and properties, J. Polym. Sci., Polym. Symp. 67 (1980) 43–71, https://doi.org/10.1002/polc.5070670105.

[220] C.I. Simionescu, V. Percec, Progress in polyacetylene chemistry, Prog. Polym. Sci. 8 (1982) 133–214, https://doi.org/10.1016/0079-6700(82)90009-0.

[221] V. Percec, M. Obata, J.G. Rudick, B.B. De, M. Glodde, T.K. Bera, S.N. Magonov, V.S.K. Balagurusamy, P.A. Heiney, Synthesis, structural analysis, and visualization of poly(2-ethynyl-9-substituted carbazole)s and poly(3-ethynyl-9-substituted carbazole)s containing chiral and achiral minidendritic substituents, J. Polym. Sci., Part A: Polym. Chem. 40 (2002) 3509–3533, https://doi.org/10.1002/pola.10458.

[222] V. Percec, J.G. Rudick, M. Peterca, M. Wagner, M. Obata, C.M. Mitchell, W.-D. Cho, V.S.K. Balagurusamy, P.A. Heiney, Thermoreversible Cis−cisoidal to cis−transoidal isomerization of helical dendronized polyphenylacetylenes, J. Am. Chem. Soc. 127 (2005) 15257–15264, https://doi.org/10.1021/ja055406w.

[223] J.G. Rudick, V. Percec, Induced helical backbone conformations of self-organizable dendronized polymers, Acc. Chem. Res. 41 (2008) 1641–1652, https://doi.org/10.1021/ar800086w.

[224] V. Percec, J.G. Rudick, M. Peterca, P.A. Heiney, Nanomechanical function from self-organizable dendronized helical polyphenylacetylenes, J. Am. Chem. Soc. 130 (2008) 7503–7508, https://doi.org/10.1021/ja801863e.

[225] B.L. Feringa, W.R. Browne, Macromolecules flex their muscles, Nat. Nanotechnol. 3 (2008) 383–384, https://doi.org/10.1038/nnano.2008.194.

[226] V. Percec, W.-D. Cho, M. Möller, S.A. Prokhorova, G. Ungar, D.J.P. Yeardley, Design and structural analysis of the first spherical monodendron self-organizable in a cubic lattice, J. Am. Chem. Soc. 122 (2000) 4249–4250, https://doi.org/10.1021/ja9943400.

[227] D. Jishkariani, C.M. MacDermaid, Y.N. Timsina, S. Grama, S.S. Gillani, M. Divar, S.S. Yadavalli, R.-O. Moussodia, P. Leowanawat, A.M.B. Camacho, R. Walter, M. Goulian, M.L. Klein, V. Percec, Self-interrupted synthesis of sterically hindered aliphatic polyamide dendrimers, Proc. Natl. Acad. Sci. U.S.A. 114 (2017) E2275–E2284, https://doi.org/10.1073/pnas.1700922114.

[228] P.G. de Gennes, H. Hervet, Statistics of « starburst » polymers, J. Phyique Lett. 44 (1983) 351–360, https://doi.org/10.1051/jphyslet:01983004409035100.

[229] D.A. Tomalia, A.M. Naylor, W.A. Goddard, Starburst dendrimers: molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter, Angew Chem. Int. Ed. Engl. 29 (1990) 138–175, https://doi.org/10.1002/anie.199001381.

[230] M.N. Holerca, M. Peterca, B.E. Partridge, Q. Xiao, G. Lligadas, M.J. Monteiro, V. Percec, Monodisperse macromolecules by self-interrupted living polymerization, J. Am. Chem. Soc. 142 (2020) 15265–15270, https://doi.org/10.1021/jacs.0c07912.

[231] C. Herman, Making monodisperse macromolecules through self-interruption, Spotlights on recent JACS publications, J. Am. Chem. Soc. 142 (2020) 15625–15626, https://doi.org/10.1021/jacs.0c09620.

[232] V. Percec, D.A. Wilson, P. Leowanawat, C.J. Wilson, A.D. Hughes, M.S. Kaucher, D.A. Hammer, D.H. Levine, A.J. Kim, F.S. Bates, K.P. Davis, T.P. Lodge, M.L. Klein, R.H. DeVane, E. Aqad, B.M. Rosen, A.O. Argintaru, M.J. Sienkowska, K. Rissanen, S. Nummelin, J. Ropponen, Self-assembly of Janus dendrimers into uniform dendrimersomes and other complex architectures, Science 328 (2010) 1009–1014, https://doi.org/10.1126/science.1185547.

[233] V. Percec, P. Leowanawat, H.-J. Sun, O. Kulikov, C.D. Nusbaum, T.M. Tran, A. Bertin, D.A. Wilson, M. Peterca, S. Zhang, N.P. Kamat, K. Vargo, D. Moock, E.D. Johnston, D.A. Hammer, D.J. Pochan, Y. Chen, Y.M. Chabre, T.C. Shiao, M. Bergeron-Brlek, S. André, R. Roy, H.-J. Gabius, P.A. Heiney, Modular synthesis of amphiphilic Janus glycodendrimers and their self-assembly into glycodendrimersomes and other complex architectures with bioactivity to biomedically relevant lectins, J. Am. Chem. Soc. 135 (2013) 9055–9077, https://doi.org/10.1021/ja403323y.

[234] M. Peterca, V. Percec, P. Leowanawat, A. Bertin, Predicting the size and properties of dendrimersomes from the lamellar structure of their amphiphilic Janus dendrimers, J. Am. Chem. Soc. 133 (2011) 20507–20520, https://doi.org/10.1021/ja208762u.

[235] S. Zhang, H.-J. Sun, A.D. Hughes, R.-O. Moussodia, A. Bertin, Y. Chen, D.J. Pochan, P.A. Heiney, M.L. Klein, V. Percec, Self-assembly of amphiphilic Janus dendrimers into uniform onion-like dendrimersomes with predictable size and number of bilayers, Proc. Natl. Acad. Sci. U.S.A. 111 (2014) 9058–9063, https://doi.org/10.1073/pnas.1402858111.

[236] A.D. Bangham, M.M. Standish, J.C. Watkins, Diffusion of univalent ions across the lamellae of swollen phospholipids, J. Mol. Biol. 13 (1965) 238–252, https://doi.org/10.1016/S0022-2836(65)80093-6.

[237] B.M. Discher, Y.-Y. Won, D.S. Ege, J.C.-M. Lee, F.S. Bates, D.E. Discher, D. A. Hammer, Polymersomes: tough vesicles made from diblock copolymers, Science 284 (1999) 1143–1146, https://doi.org/10.1126/science.284.5417.1143.

[238] S. Zhang, Q. Xiao, S.E. Sherman, A. Muncan, A.D.M. Ramos Vicente, Z. Wang, D. A. Hammer, D. Williams, Y. Chen, D.J. Pochan, S. Vértesy, S. André, M.L. Klein, H.-J. Gabius, V. Percec, Glycodendrimersomes from sequence-defined Janus glycodendrimers reveal high activity and sensor capacity for the agglutination by natural variants of human lectins, J. Am. Chem. Soc. 137 (2015) 13334–13344, https://doi.org/10.1021/jacs.5b08844.

[239] Q. Xiao, S. Zhang, Z. Wang, S.E. Sherman, R.-O. Moussodia, M. Peterca, A. Muncan, D.R. Williams, D.A. Hammer, S. Vértesy, S. André, H.-J. Gabius, M. L. Klein, V. Percec, Onion-like glycodendrimersomes from sequence-defined Janus glycodendrimers and influence of architecture on reactivity to a lectin, Proc. Natl. Acad. Sci. U.S.A. 113 (2016) 1162–1167, https://doi.org/10.1073/pnas.1524976113.

[240] C. Rodriguez-Emmenegger, Q. Xiao, N.Y. Kostina, S.E. Sherman, K. Rahimi, B. E. Partridge, S. Li, D. Sahoo, A.M.R. Perez, I. Buzzacchera, H. Han, M. Kerzner, I. Malhotra, M. Möller, C.J. Wilson, M.C. Good, M. Goulian, T. Baumgart, M. L. Klein, V. Percec, Encoding biological recognition in a bicomponent cell-membrane mimic, Proc. Natl. Acad. Sci. U.S.A. 116 (2019) 5376–5382, https://doi.org/10.1073/pnas.1821924116.

[241] Q. Xiao, M. Delbianco, S.E. Sherman, A.M.R. Perez, P. Bharate, A. Pardo-Vargas, C. Rodriguez-Emmenegger, N.Y. Kostina, K. Rahimi, D. Söder, M. Möller, M. L. Klein, P.H. Seeberger, V. Percec, Nanovesicles displaying functional linear and branched oligomannose self-assembled from sequence-defined Janus glycodendrimers, Proc. Natl. Acad. Sci. U.S.A. 117 (2020) 11931–11939, https://doi.org/10.1073/pnas.2003938117.

[242] N.Y. Kostina, K. Rahimi, Q. Xiao, T. Haraszti, S. Dedisch, J.P. Spatz, U. Schwaneberg, M.L. Klein, V. Percec, M. Möller, C. Rodriguez-Emmenegger, Membrane-mimetic dendrimersomes engulf living bacteria via endocytosis, Nano Lett. 19 (2019) 5732–5738, https://doi.org/10.1021/acs.nanolett.9b02349.

[243] C. Roche, H.-J. Sun, M.E. Prendergast, P. Leowanawat, B.E. Partridge, P. A. Heiney, F. Araoka, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, V. Percec, Homochiral columns constructed by chiral self-sorting during supramolecular helical organization of hat-shaped molecules, J. Am. Chem. Soc. 136 (2014) 7169–7185, https://doi.org/10.1021/ja5035107.

[244] C. Roche, H.-J. Sun, P. Leowanawat, F. Araoka, B.E. Partridge, M. Peterca, D. A. Wilson, M.E. Prendergast, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, V. Percec, A supramolecular helix that disregards chirality, Nat. Chem. 8 (2016) 80–89, https://doi.org/10.1038/nchem.2397.

[245] V. Percec, A.D. Asandei, Monodisperse linear liquid crystalline polyethers *via* a repetitive 2n geometric growth algorithm, Macromolecules 30 (1997) 7701–7720, https://doi.org/10.1021/ma970783h.

[246] F.A. Leibfarth, J.A. Johnson, T.F. Jamison, Scalable synthesis of sequence-defined, unimolecular macromolecules by Flow-IEG, Proc. Natl. Acad. Sci. U.S.A. 112 (2015) 10617–10622, https://doi.org/10.1073/pnas.1508599112.

[247] V. Percec, A.D. Asandei, M. Zhao, Stepwise synthesis of "main-chain" liquid-crystalline macrocyclics based on conformationally flexible mesogens, Chem. Mater. 8 (1996) 301–308, https://doi.org/10.1021/cm9503994.

[248] V. Percec, A.D. Asandei, G. Ungar, From regioirregular linear main-chain liquid-crystal polyethers exhibiting two uniaxial nematic phases to macrocyclic main-chain oligoethers displaying nematic and smectic phases, Chem. Mater. 8 (1996) 1550–1557, https://doi.org/10.1021/cm9602048.

[249] V. Percec, A.D. Asandei, M. Zhao, TPB': a constitutional isomeric mesogen based on conformational isomerism which generates pairs of completely isomorphic polyethers, Polymer 37 (1996) 3889–3897, https://doi.org/10.1016/0032-3861(96)00206-6.

[250] J.-F. Li, V. Percec, C. Rosenblatt, O.D. Lavrentovich, Biaxiality in a cyclic thermotropic nematic liquid crystal, Europhys. Lett. 25 (1994) 199–204, https://doi.org/10.1209/0295-5075/25/3/008.

[251] V. Percec, R. Yourd, Liquid crystalline polyethers and copolyethers based on conformational isomerism. 3. The influence of thermal history on the phase transitions of the thermotropic polyethers and copolyethers based on 1-(4-hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and flexible spacers containing an odd number of methylene units, Macromolecules 22 (1989) 3229–3242, https://doi.org/10.1021/ma00198a007.

[252] V. Percec, M. Kawasumi, Liquid-crystalline polyethers based on conformational isomerism. 18. Polyethers based on a combined mesogenic unit containing rigid and flexible groups: 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl)butane, Macromolecules 24 (1991) 6318–6324, https://doi.org/10.1021/ma00023a039.

[253] B.E. Partridge, L. Wang, D. Sahoo, J.T. Olsen, P. Leowanawat, C. Roche, H. Ferreira, K.J. Reilly, X. Zeng, G. Ungar, P.A. Heiney, R. Graf, H.W. Spiess, V. Percec, Sequence-defined dendrons dictate supramolecular cogwheel assembly of dendronized perylene bisimides, J. Am. Chem. Soc. 141 (2019) 15761–15766, https://doi.org/10.1021/jacs.9b08714.

[254] L. Wang, B.E. Partridge, N. Huang, J.T. Olsen, D. Sahoo, X. Zeng, G. Ungar, R. Graf, H.W. Spiess, V. Percec, Extraordinary acceleration of cogwheel helical self-organization of dendronized perylene bisimides by the dendron sequence encoding their tertiary structure, J. Am. Chem. Soc. 142 (2020) 9525–9536, https://doi.org/10.1021/jacs.0c03353.

[255] D.J.P. Yeardley, G. Ungar, V. Percec, M.N. Holerca, G. Johansson, Spherical supramolecular minidendrimers self-organized in an "inverse micellar"-like thermotropic body-centered cubic liquid crystalline phase, J. Am. Chem. Soc. 122 (2000) 1684–1689, https://doi.org/10.1021/ja993915q.

[256] H. Duan, S.D. Hudson, G. Ungar, M.N. Holerca, V. Percec, Definitive support by transmission electron microscopy, electron diffraction, and electron density maps for the formation of a BCC lattice from poly[N-[3,4,5-tris(n-dodecan-1-yloxy)benzoyl]ethyleneimine], Chem. Eur J. 7 (2001) 4134–4141, https://doi.org/10.1002/1521-3765(20011001)7:19<4134::aid-chem4134>3.0.co;2-w.

[257] V. Percec, M.N. Holerca, S.N. Magonov, D.J.P. Yeardley, G. Ungar, H. Duan, S. D. Hudson, Poly(oxazolines)s with tapered minidendritic side groups. The simplest cylindrical models to investigate the formation of two-dimensional and three-dimensional order by direct visualization, Biomacromolecules 2 (2001) 706–728, https://doi.org/10.1021/bm015550j.

[258] V. Percec, M.N. Holerca, S. Uchida, D.J.P. Yeardley, G. Ungar, Poly(oxazoline)s with tapered minidendritic side groups as models for the design of synthetic macromolecules with tertiary structure. A demonstration of the limitations of living polymerization in the design of 3-D structures based on single polymer chains, Biomacromolecules 2 (2001) 729–740, https://doi.org/10.1021/bm015559l.

[259] M.N. Holerca, D. Sahoo, M. Peterca, B.E. Partridge, P.A. Heiney, V. Percec, A tetragonal phase self-organized from unimolecular spheres assembled from a substituted poly(2-oxazoline), Macromolecules 50 (2017) 375–385, https://doi.org/10.1021/acs.macromol.6b02298.

[260] M.N. Holerca, D. Sahoo, B.E. Partridge, M. Peterca, X. Zeng, G. Ungar, V. Percec, Dendronized poly(2-oxazoline) displays within only five monomer repeat units liquid quasicrystal, A15 and σ Frank–Kasper phases, J. Am. Chem. Soc. 140 (2018) 16941–16947, https://doi.org/10.1021/jacs.8b11103.

[261] H. Jonsson, P.-E. Sundell, V. Percec, U.W. Gedde, A. Hult, Cationic bulk polymerization of mesogenic vinyl ethers induced by thermal decomposition of sulfonium salts, Polym. Bull. 25 (1991) 649–656, https://doi.org/10.1007/BF01032660.

[262] H. Jonsson, V. Percec, U.W. Gedde, A. Hult, Cationic bulk polymerization of vinyl ethers in the liquid crystalline phase, Makromol. Chem. Macromol. Symp. (1992) 54–55, https://doi.org/10.1002/masy.19920540110, 83–94.

[263] X. Feng, C.J. Burke, M. Zhuo, H. Guo, K. Yang, A. Reddy, I. Prasad, R.-M. Ho, A. Avgeropoulos, G.M. Grason, E.L. Thomas, Seeing mesoatomic distortions in soft-matter crystals of a double-gyroid block copolymer, Nature 575 (2019) 175–179, https://doi.org/10.1038/s41586-019-1706-1.

[264] M. Peterca, M.R. Imam, S.D. Hudson, B.E. Partridge, D. Sahoo, P.A. Heiney, M. L. Klein, V. Percec, Complex arrangement of orthogonal nanoscale columns *via* a supramolecular orientational memory effect, ACS Nano 10 (2016) 10480–10488, https://doi.org/10.1021/acsnano.6b06419.

[265] D. Sahoo, M. Peterca, E. Aqad, B.E. Partridge, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, V. Percec, Tetrahedral arrangements of perylene bisimide columns *via* supramolecular orientational memory, ACS Nano 11 (2017) 983–991, https://doi.org/10.1021/acsnano.6b07599.

[266] N. Huang, M.R. Imam, M.J. Sienkowska, M. Peterca, M.N. Holerca, D.A. Wilson, B.M. Rosen, B.E. Partridge, Q. Xiao, V. Percec, Supramolecular spheres assembled from covalent and supramolecular dendritic crowns dictate the supramolecular orientational memory effect mediated by Frank–Kasper phases, Giant 1 (2020) 100001, https://doi.org/10.1016/j.giant.2020.100001.

[267] W.B. Shockley, Transistor technology evokes new physics, Nobel Lecture (1956). December 11.

[268] J. Bardeen, Semiconductor research leading to the point contact transistor, Nobel Lecture, December 11, 1956.

[269] W.H. Brattain, Surface properties of semiconductors, Nobel Lecture (1956). December 11.