Architecture, Assembly, and Emerging Applications of Branched Functional Polyelectrolytes and Poly(ionic liquid)s

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ABSTRACT: Branched polyelectrolytes with cylindrical brush, dendritic, hyperbranched, grafted, and star architectures bearing ionizable functional groups possess complex and unique assembly behavior in solution at surfaces and interfaces as compared to their linear counterparts. This review summarizes the recent developments in the introduction of various architectures and understanding of the assembly behavior of branched polyelectrolytes with a focus on functional polyelectrolytes and poly(ionic liquid)s with responsive properties. The branched polyelectrolytes and poly(ionic liquid)s interact electrostatically with small molecules, linear polyelectrolytes, or other branched polyelectrolytes to form assemblies of hybrid nanoparticles, multilayer thin films, responsive microcapsules, and ion-conductive membranes. The branched structures lead to unconventional assemblies and complex hierarchical structures with responsive properties as summarized in this review. Finally, we discuss prospectives for emerging applications of branched polyelectrolytes and poly(ionic liquid)s for energy harvesting and storage, controlled delivery, chemical microreactors, adaptive surfaces, and ion-exchange membranes.

KEYWORDS: polyelectrolyte brushes, polyelectrolyte dendrimers, hyperbranched polyelectrolytes, star polyelectrolytes, poly(ionic liquid)s, oligo(ionic liquid)s, ionic self-assembly
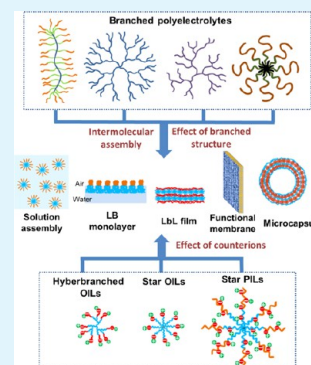
1. INTRODUCTION

Polyelectrolyte (PE) macromolecules with ionizable groups in their backbones or side chains are usually effectively charged in solution due to ionic dissociation controlled by ionic and pH conditions. Because of dramatic asymmetry in charge, mass, and size between the polyelectrolyte backbones and the counterions, co-ions, and solvent molecules, polyelectrolytes have a rich and significantly different phase behavior compared to conventional neutral macromolecules.[1] Extended chain conformations, a significantly lower critical concentration, and a higher osmotic pressure in solution are examples of these signature differences.[2] The structure and properties of linear polyelectrolytes have been extensively studied during the past several decades,[3] but our understanding of the properties of branched polyelectrolytes with complex chain architectures is still inadequate, especially for complex conditions such as the presence of heterogeneous surfaces and interfaces.

Recent advances in polymer chemistry allow for the synthesis of a variety of branched polyelectrolytes with well-defined architectures, such as cylindrical brushes,[4] dendritic molecules,[5] hyperbranched polymers,[6] pearl-necklace structures,[7] and star block copolymers,[8] with different novel classes of materials being introduced continuously (Figure 1, Table 1). The syntheses, structures, morphologies, and prospective applications of well-known cationic polyelectrolytes have recently been covered by Laschewsky et al.[9] Water-soluble macromolecular coassemblies of star-shaped polyelectrolytes with classical ionic groups were reviewed by Müller et al.[10] Various hyperbranched

materials and their assemblies at interfaces have been reviewed by Peleshanko et al.[11]

The chemical structures of common types of cationic and anionic polyelectrolytes are shown in Figure 2a, b. Highly branched polyelectrolytes with low levels of entanglements possess novel physical properties compared to those of their linear counterparts.[12,13] Star polyelectrolytes frequently show peculiar phase behavior due to a complex balance of intra- and intermolecular interactions.[14−17] For instance, they have a strong counterion confinement ability, resulting in high osmotic pressure (caused by the presence of the counterions) within the branched polyelectrolytes, which leads to strong extension of the arms under certain conditions. The branched polyelectrolytes can also be divided into strong and weak polyelectrolytes depending on their ionization ability, both of which can be stimuli-responsive to ionic strength and pH.

The crossover from a dilute to a semidilute solution regime for polyelectrolytes occurs at much lower polymer concentrations than for solutions of neutral chains.[1,18] It has been demonstrated that solutions of weak polyelectrolytes exhibit microphase separation upon a decrease in the solvent quality below the θ point.[19] At appropriate thermodynamic conditions, the system has a tendency to form limited clusters, although true macrophase separation may be inhibited. The most influential factors include counterion concentration and
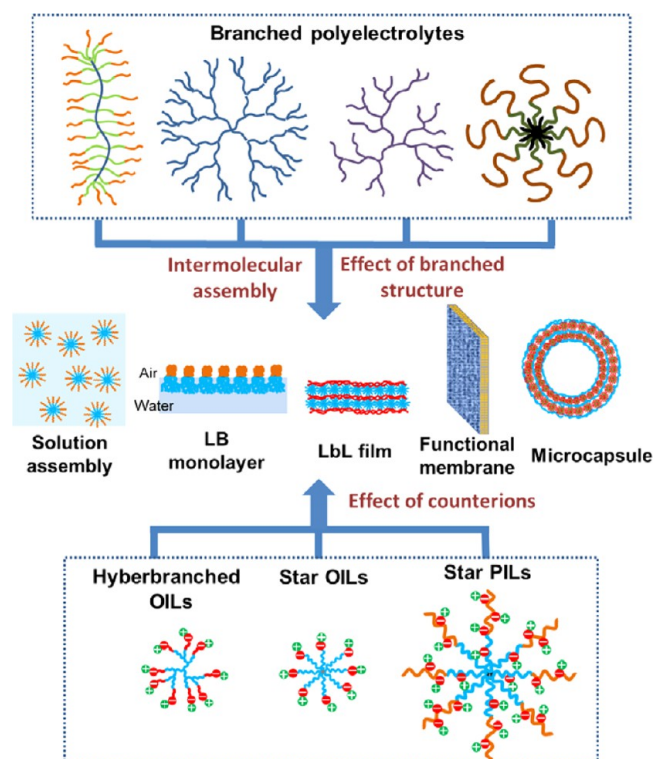
Figure 1. (Top) Structure of major types of branched polyelectrolytes: (from left to right) cylindrical brushes, dendrimers, and hyperbranched and star polyelectrolytes. (Bottom) Structure of major types of branched PILs and OILs. (Middle) Representative examples of assembled structures discussed in this review.

valency, pH, and temperature. Khokhlov et al.[20] showed that for partially charged weak polyelectrolytes, the counterions can be easily transferred between repeating units and from one chain to another, which facilitates phase separation in solution.

Theoretical studies have shown that, for star polyelectrolytes in addition to the steric repulsion, there is a relatively short-range attraction and a secondary repulsive barrier at longer distances.[21] The conformation of spherical polyelectrolyte brushes[22] and star polyelectrolytes[23] is very sensitive to the ionic conditions; for instance, the addition of multivalent ions leads to a collapse in which the surface layer or the arms drastically shrinks. The ion exchange and a strong binding of multivalent ions by polyelectrolyte chains is followed by a drop in osmotic pressure inside the brush, which is the driving force for the collapse.[24] Molecular dynamics simulations have shown that the collapse of star polyelectrolytes also depends on the arm number. At a low number of arms, pearl-necklace structures are formed on individual arms. Conversely, at a higher number of arms, interarm bundling is the dominant structural motif.[25]

For polyelectrolyte dendrimers, a theoretical study by Likos et al.[26] showed that Coulombic interactions lead to an increase in the size of dendrimer polyelectrolytes due to a combined effect of electrostatic repulsion and the presence of counterions. The bond length between monomers near the center increases to facilitate more effective usage of the space in the outer regions of dendrimers. There are also tunable and ultrasoft intermolecular interactions between the centers of the dendrimers. Another study on poly(propyleneimine) dendrimer solutions[27] showed that there is a certain degree of spatial arrangement or liquid-like ordering in acidic conditions

due to electrostatic repulsions with larger-scale intermolecular assemblies in the solution. An increase in the salt concentration in the solution induces a decrease in intermolecular correlations.

Likos et al.[28] studied the complexation behavior of oppositely charged colloidal particles and polyelectrolyte stars with a molecular dynamics approach. The results indicated that, besides electrostatic interactions, entropy controls the adsorption of the stars on a colloidal surface. The functionality of the stars has a significant influence on the adsorption process: higher functionality stars will not adsorb with all their arms anchored on the surface because of Coulomb interactions between the arms. The maximum load of the PE stars clearly depends on all quantities (i.e., functionality, arm length, and overall charge of the PE-stars as well as the size and charge of the colloidal particles). Larson et al.[29] used molecular dynamics simulations to show that there are strong interactions of cationic dendrimers with lipid bilayers, resulting in pore formation on the bilayers. On the contrary, linear cationic polyelectrolytes cannot perforate the lipid bilayer because of their deformation into a pancake morphology. Other developments in theory and simulations of the assembly of linear and branched polyelectrolytes have been summarized in several reviews.[30,31]

Biomacromolecules, such as proteins, nucleic acids and polysaccharides, have high concentrations of ionizable groups and are generally included in the class of polyelectrolytes. Self-assembled structures of these biopolymers play a critical role in biology. For example, the bacterial cell surface is decorated with branched polysaccharides, which can mediate cell adhesion.[32] Moreover, self-assemblies of biomacromolecules can respond to external stimuli in a sophisticated way, which directly affects biological functions. Synthetic branched polyelectrolytes are close in structure to biomacromolecules, and therefore, the self-assembly of branched polyelectrolytes provides an excellent model case for cell biology studies.[33]

Besides the traditional types of polyelectrolytes discussed above, in recent years, an emerging novel subclass of polyelectrolytes, so-called poly(ionic liquid)s (PILs), have attracted much attention. These macromolecules are usually synthesized by the polymerization of common ionic liquids (Figure 2c, d).[34−36] These polymeric electrolytes significantly broadened the possible practical uses of ionic compounds. PILs combine unique properties of monomeric ionic liquids with properties of macromolecules. Despite the similarities between PILs and conventional polyelectrolytes, PILs are usually glassy solids with relatively low glass transition temperatures, unlike regular polyelectrolytes, which can be highly crystalline and often show no well-defined glass transition. At the same time, the polymeric form of ionic liquids, with few exceptions,[37] usually lose the ability to exist in a liquid state over a broad range of temperatures. Although at this point there is no universally accepted definition of "poly(ionic liquid)s", they are usually regarded as macromolecules containing ionic groups that are characteristic of classical ionic liquids (so-called "ionic liquid groups", "ionic-liquid functionalities", or "imidazolium-type ionic" compounds).[38−40]

Oligomers occupy the intermediate molecular weight range between monomers and polymers and are regarded as a unique class of compounds composed of linked repeat units.[41] To this end, oligo(ionic liquid)s (OILs) with molecular weights below 10 kg/mol have traits of both ionic liquids and poly(ionic liquid)s. Unlike poly(ionic liquid)s, many oligo(ionic liquid)s

Table 1. Summary of the Properties of Linear and Branched Polyelectrolytes and Poly(ionic liquid)s (PILs) with Various Architectures

name	architecture	synthesis	properties	relevant examples (refs)
Polyelectrolytes				
linear PEs	flexible/semiflexible linear backbone	step or chain polymerization, post functionalization	wide variety of amorphous, crystalline, and LC polymers and electrolytes	1, 9, 217
cylindrical PE brushes	flexible backbone and many grafted shorter side chains	grafting through, grafting to, and grafting from	large size, low entanglement, lower CMC, rheological modifiers	66, 67, 69, 71, 75
star PEs	central core and multiple polyelectrolyte arms	core first or arm first method, click chemistry	lower viscosity, lower crystallinity degree, higher CMC, lower aggregation number	66, 82, 88, 89, 97, 103, 218
hyperbranched PEs	random branched polyelectrolyte chains	step-growth polycondensation, self-condensing, ring-opening polymerization	lower viscosity, flexible composition and degree of branching, enhanced solubility	104, 105, 109, 112, 114, 219
dendrimer PEs	central core with several generations of branches	divergent and convergent growth approach, click chemistry	uniform composition and structure, controlled crystallinity and chirality, dendritic encapsulation	119, 125, 128, 220–222
Poly(ionic liquid)s (PILs) and Oligo(ionic liquid)s (OILs)				
linear PILs	random and block copolymers (M_W > 10000)	direct polymerization of IL monomers, post polymerization introduction of IL groups, ion exchange	solubility and T_g are determined by the nature of the counterions	35, 36, 34, 141, 178–183, 192–194, 223–226
	saturated as well as unsaturated (conjugated) backbones	free radical and controlled free radical polymerization (ATRP, RAFT, NMP), ROMP	self-assembly of block copolymers	
	cationic, anionic, and zwitterionic IL groups	main-chain PIL: step-growth polymerization	layer-by-layer assembly / suitable as polymer electrolytes with doping, templated nanoparticle synthesis	
star PILs/OILs	star block copolymers (M_W > 10000)	star block copolymers (RAFT polymerization)	thermally induced phase separation, self-assembly in aqueous solutions	147–152, 155–162, 164, 165, 208
	cationic and anionic POSS-based OILs (M_W < 3000)	octaammonium POSS quaternization	improved thermal stability, low T_g (POSS)	
		alkylation of imidazole by POSS derivatives	variable charge density based on the degree of substitution / some representatives are liquid at room temperature (POSS)	
hyperbranched PILs/OILs	hyperbranched polyether, polyester polyamidoamine, polyalkyleneimine cores	modification of commercial Boltorn and glycidol HBPs	compact structure with high density of ionic groups	40, 110, 145, 146, 168, 170–177, 195, 227
	main-chain network structures	quaternization of commercial polyamide/polyamine materials	liquid crystalline properties, protic HBP OILs have a higher ionic conductivity than aprotic	
	spherical PIL brushes	A_2+B_3 and A_3+B_3 condensation of bis-imidazoles with alkyl halides (Menshutkin reaction)	formation of stable dispersions of the metal nanoparticles	
		photoemulsion polymerization	high free volume-high ionic conductivity / main chain HBP OILs are often insoluble	
dendrimer OILs	polyether, polyester, PAMAM dendrimers, PEI dendrimers	quaternization of commercial dendrimers	self-assembly of dendrons into supramolecular columnar phases	38, 144, 159, 166, 167, 185, 186
	amphiphilic dendrimers	alkylation of tertiary amines with dendritic electrophiles	aqueous self-assembly	
	M_W < 10000		photoluminescence, high proton conductivity	
			low T_g	
			photoresponsive properties	

Building Blocks of Conventional Branched Polyelectrolytes

(a) **Polycations:**
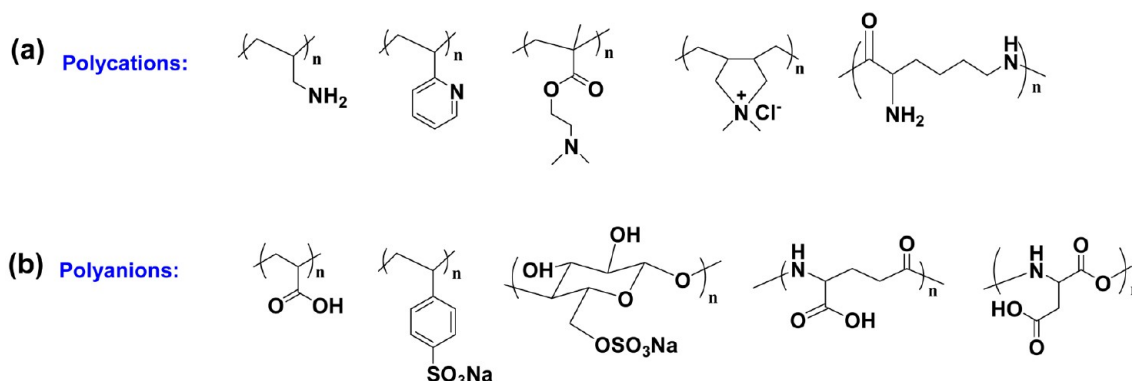
(b) **Polyanions:**

Building Blocks of Poly- and Oligo(ionic liquid)s

(c) **Polycations:**

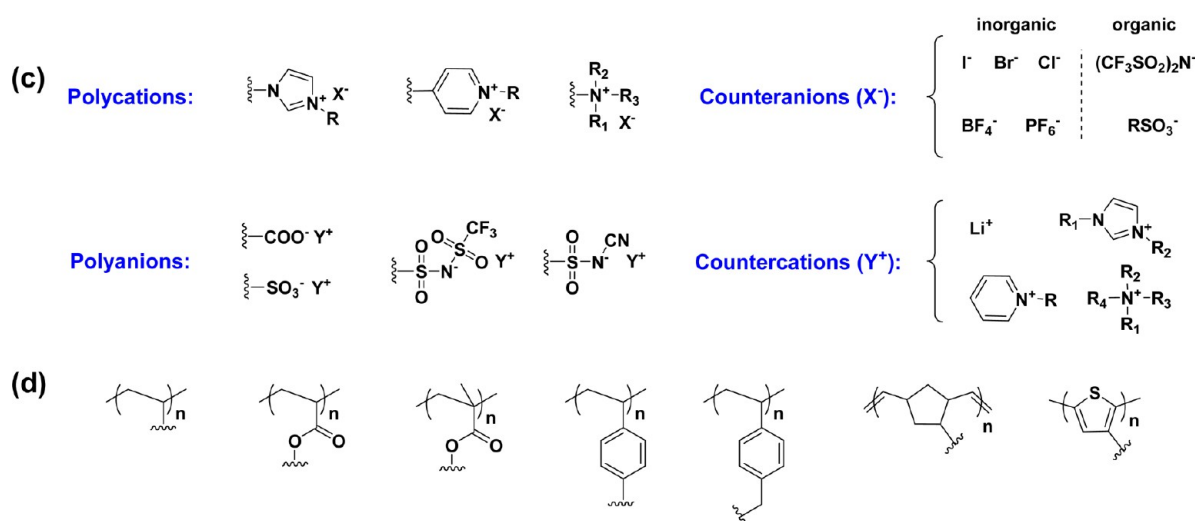**Polyanions:**

(d)

Figure 2. Chemical structures of common types of (a) cationic and (b) anionic arms of branched polyelectrolytes. (c) Chemical structures of common ionic groups of branched poly- and oligo(ionic liquid)s and their counterions. (d) Commonly used polymeric backbones of linear poly(ionic liquid)s.

are still able to preserve a liquid aggregate state over a broad range of temperatures, are often water-soluble, and have a strong dependence of their properties on the number and type of ionic end groups and constitutional units. Furthermore, oligo(ionic liquid)s can be polymerized into poly(ionic liquid)s.[42] Unlike low-molecular-weight ionic liquids, oligo-(ionic liquid)s can bear a variety of different ionic groups (anionic, cationic, protic, aprotic, zwitterionic), have various molecular architectures (linear, branched, block), and are capable of interfacial and bulk self-assembly.

A unique oligomeric state may spontaneously arise in the ensemble of such molecules that have a certain length, rigidity, conformation, and polarity. The oligomeric state may have a different lifetime and special anisotropy, but this depends mainly on the structure of the oligomeric molecules and cannot be rationalized by aggregation or phase transitions. In polymers, such behavior is not observed, and therefore, the formation of supramolecular structures may have a different origin for oligomeric and polymeric molecules. It should be pointed out that the term "oligo(ionic liquid)s" itself is not yet universally accepted but their intermediate and unique properties warrant their consideration as a separate class. Poly(ionic liquid)s are attractive for a variety of applications, including as ion-conductive media for solar cells[161] and photoluminescent

devices,[43] as building blocks for biomaterials, chemical nanocatalysts,[44] nanoreactors,[45] and antifouling agents,[158] and many other uses.[34,46,47,141,142,157] In this review, we will discuss the synthesis, structural characteristics, and properties of both branched oligo(ionic liquid)s and poly(ionic liquid)s with dendritic and starlike molecular architectures important for prospective and emerging applications.

Because of the presence of abundant functional terminal groups and tree-like architectures, the assembly of branched polyelectrolytes can occur in various complex ways.[48−50] The driving forces for the assembly include covalent-bonding, hydrophobic interactions, hydrogen bonding, electrostatic interactions, charge-transfer interactions, host−guest interactions, and coordination chemistry.[51] The assembled structures also have various morphologies in different states including core−shell particles, capsules, micelles, thin films, and microgels (Figure 1).[52−54] Nanoarchitectonics is a rising concept in nanomaterial science,[55,56] which refers to the manipulation of nanoscale structural units in an intended configuration.[57] To this end, branched polyelectrolytes can be used for designing advanced materials for device applications.[58]

The focus of this review is on summarizing recent results on the peculiar behavior of branched polyelectrolytes and poly(ionic liquid)s, both in solution and at interfaces, and
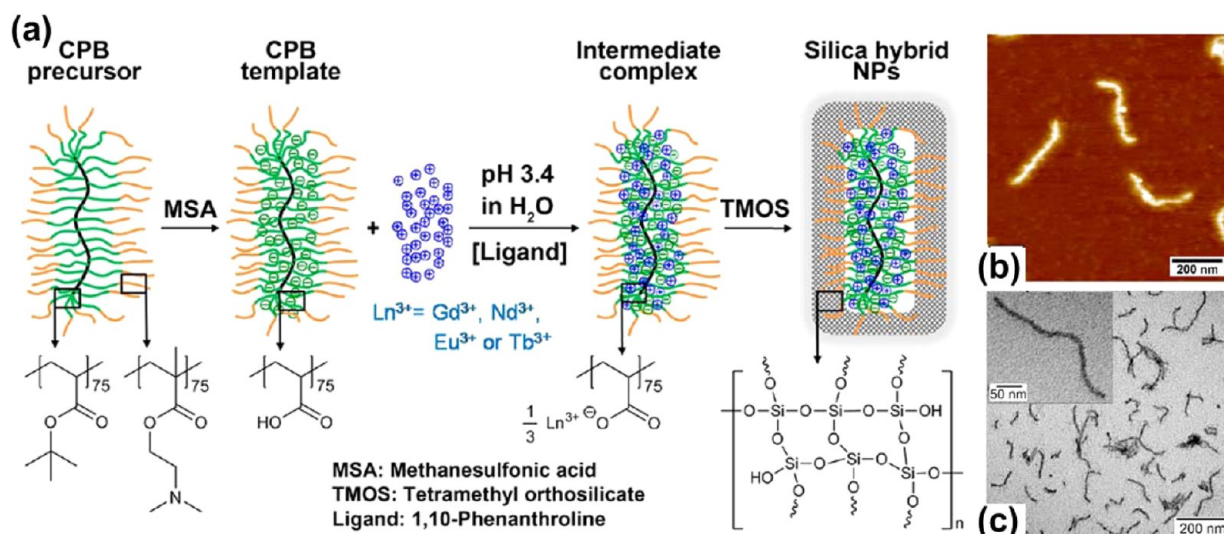
Figure 3. (a) Preparation of ion incorporated silica hybrid nanoparticles via template-directed assembly. (b) AFM images of the precursor CPB macromolecules. (c) TEM image of the Ln^{3+}-incorporated silica hybrid nanoparticles. Reproduced with permission from ref 71, copyright (2013) American Chemical Society.

methods for their assembly into functional nanostructured soft materials. More specifically, we will discuss the effect of chemical composition and architecture on their molecular aggregation, phase transition, and responsive behaviors, the morphology and organization of branched polyelectrolytes at the air−water interface, and the layer-by-layer (LbL) assembly of branched polyelectrolytes into higher-order microstructures. Understanding the principles of organization of this class of multifunctional nanomaterials from branched polyelectrolytes and polymeric ionic liquids will be invaluable for designing prospective materials for emerging applications, such as energy harvesting and storage, controlled delivery materials, chemical microreactors, adaptive surfaces, and ion-exchange membranes.

2. ASSEMBLY OF BRANCHED POLYELECTROLYTES

The major types of highly branched polyelectrolytes include cylindrical brushes, stars, hyperbranched molecules, and dendrimers, as shown in Figure 1. The common feature of the four categories is the presence of a central functionalizable core and multiple polyelectrolyte branches or arms. It is important to note that the architectural differences among these materials are essential, and therefore, the assembly behaviors of the four types of branched polyelectrolytes mentioned above will be discussed in separate sections below. For each section, we consider several recent and representative examples from recent literature.

The limited interdiffusion, low entanglement, multiple functionalities, and relatively weak intermolecular interactions of branched macromolecules pose great challenges in their self- and directed-assembly. Because of the abundance of ionizable groups in polyelectrolytes, the interaction between them is usually dominated by electrostatic forces, which can be used as the driving force for their assembly on properly functionalized surfaces.[1] On the other hand, other types of interactions, such as hydrogen bonding,[59] hydrophobic interactions,[60] host−guest interactions,[61] and π−π interactions,[62] can also be considered to facilitate the assembly of branched polyelectrolytes. The most popular techniques exploited for the assembly of branched polyelectrolytes include solution self-assembly,[66]

interfacial assembly,[8] Langmuir−Blodgett (LB) deposition,[63,64] and LbL assembly.[53,65]

2.1. Assembly of Cylindrical Polyelectrolyte Brushes. Cylindrical polyelectrolyte brushes (CPBs) are composed of a flexible backbone and a large number of shorter grafted side chains that are ionizable (Figure 1).[66] The unusual architecture of CPBs gives them some unique properties, such as large dimensions of macromolecules, a low extent of entanglement, and a lower critical micelle concentration (CMC).[67] Amphiphilic CPBs are able to self-assemble into complex micellar structures in solution, the main difference compared with micelles from the linear block copolymer being that the CPB-based micelles are usually larger in size and bear various surface functionalities.

For example, Wooley et al.[68] synthesized heterografted diblock CPBs via a "grafting through" strategy with one-half of the size chains as PAA and the other half as PS. When dialyzed against water from a DMF solution, which is a good solvent for both types of side chains, the CPBs self-assemble into spherical micelles with an average hydrodynamic diameter of 48 nm and an aggregation number of 60. Another report from the same group[69] showed that CPBs with PS-b-PMA-b-PAA triblock copolymer side chains are able to self-assemble into cylindrical nanostructures when transferred from DMF to water. Such assembly is also reversible by heating or changing the solvent. In another example, CPBs with a polystyrene tail and a cylindrical brush block with poly(acrylic acid) (PAA) side chains were observed to form starlike micelles comprised of four to five macromolecules.[70]

Additionally, the polyelectrolyte chains of CPBs can be used to selectively bind with metal ions to fabricate functional hybrid nanostructures. To this end, Müller et al.[71] synthesized core− shell CPBs with poly(acrylic acid)-*block*-poly[2- (dimethylamino)ethyl methacrylate] (PAA-b-PDMAEMA) side chains and used the CPBs as a template for the preparation of rare-earth metal cations incorporated into hybrid nano- particles, as shown in Figure 3. Several different kinds of rare- earth cations (Tb^{3+}, Eu^{3+}, Gd^{3+}) can be incorporated into the PAA block due to the tight chelation; the deposition and cross-
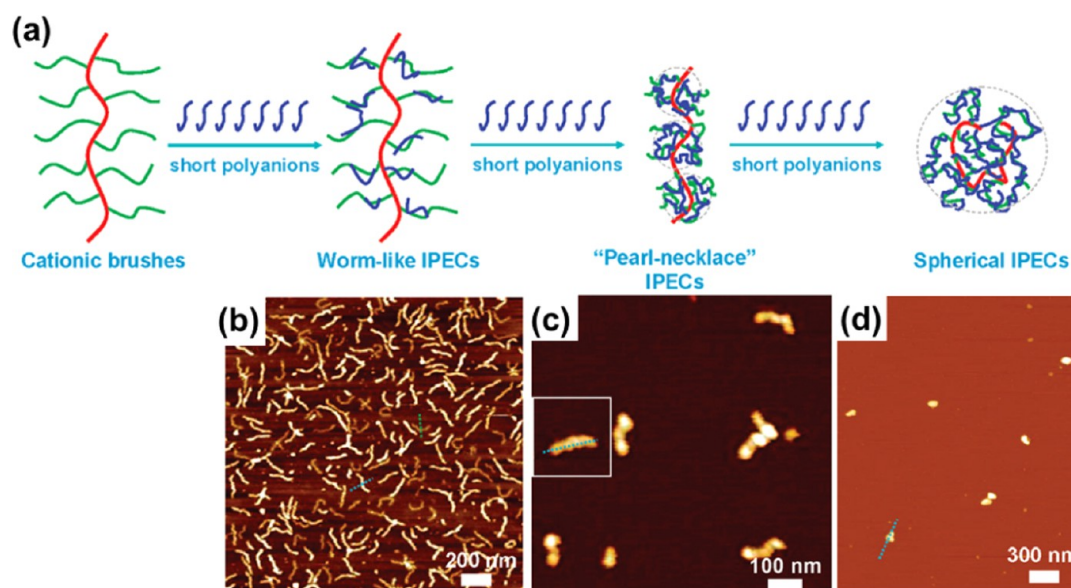
Figure 4. (a) Schematic of morphology changes of cationic CPBs (b, c, d) and corresponding AFM images of the worm-like, pearl-necklace and spherical morphologies. Reproduced with permission from ref 76, copyright (2010) American Chemical Society.

linking of tetramethyl orthosilicate on the PDMAEMA blocks result in a stable silica nanoshell.

It has been found that, in a dilute solution, CPBs interact with oppositely charged polyelectrolytes through ion pair formation to form well-defined and stable colloidal nano-assemblies or interpolyelectrolyte complexes (IPECs).[72,73] Molecular dynamics simulations showed that the nano-assemblies adopt pearl necklace morphologies comprised of CPB monomers and the guest polyelectrolyte monomers in an approximately stoichiometric ratio.[74] AFM imaging confirmed such novel complex morphologies on surfaces as well (Figure 4).[75] Furthermore, for IPEC complexes formed by poly{[2-(methacryloyloxy)ethyl] trimethylammonium iodide} (PME-TAI) CPBs and linear poly(styrenesulfonate) (PSS), the morphology can be tuned from worm-like micelles to intermediate pearl-necklace structures and eventually into fully collapsed spheres by increasing the percentage of PSS chains. Furthermore, the length of the linear PSS chains also has a significant effect on the complexation phenomenon.[76]

CPBs were also used to form complexes with DNA molecules in solution, and the results showed that their complexes coexist with the excess uncomplexed component.[77] Intercomplex bridging with eventual phase separation was observed if the number of complexes became comparable to the number of free molecules. Not only can CPBs interact with large oppositely charged polyelectrolytes to form different kinds of assemblies, they can also interact with smaller counterions in an interesting way. For example, the tetravalent cationic porphyrin binds to the PSS CPBs due to electrostatic and secondary $\pi-\pi$ interactions.[78] CPB macromolecules can be further interconnected into nanoscale networks. The variable interactions of CPBs with different counterions might lead to various tunable structures. For instance, when interacting with tetravalent double-DABCO (1,4-diazabicyclo[2.2.2]octane)-based counterions, the PSS CPBs experience a conformational change from worm-like to highly curled structures with an increasing counterion concentration.[79] Above the charge stoichiometry, the CPBs become interconnected and form

stable finite assemblies, which consist of the molecular brushes in curled (bent) conformations.

It has been shown that CPBs with poly(L-lysine) side chains and sodium dodecyl sulfate (SDS) can form complexes with intriguing structures.[80] An increasing amount of SDS initiates the complex transformation to a helical conformation with a local β-sheet structure on the side chains, followed by a spherically collapsed structure formation. A further study showed that the surfactant size, ionic conditions, and environmental pH all have significant influence on the shape and size of the supramolecular structures.[81] For example, only surfactants with certain alkyl chain lengths can promote the formation of stable helical complexes with poly(L-lysine)-based CPBs.[81] High ionic strength and acidic or basic pH conditions lead to the disappearance of the helical supramolecular structure.

2.2. Assembly of Star Polyelectrolytes. Among different categories of branched polyelectrolytes, star polyelectrolytes constitute a particularly intriguing class of macromolecules that are highly relevant in soft matter physics, chemistry, and materials science.[82] Star-shaped polyelectrolytes can be considered branched systems with well-defined composition and dimensionality of arms, which are relevant to novel colloidal soft nanoparticles with core−shell morphologies.[83,84] Because of their star architecture, these macromolecules show distinct micellar aggregation in bulk, solution, and at interfaces. For instance, star polymers show a critical micellar concentration that is a few orders of magnitude higher than that of their linear counterparts, and the association number is significantly lower than that observed for their linear counterparts.[85−87]

Star polyelectrolytes with asymmetrical arms can self-assemble in solution to form various novel nanostructures; they are also stimuli-responsive, and their morphology changes dramatically with variable external conditions, such as ionic conditions, pH, or temperature. It has been shown that weak star polyelectrolytes (PDMAEMA) with thermoresponsive properties can form stable intermolecular aggregates within a narrow temperature range at a pH close to pK_a in contrast to
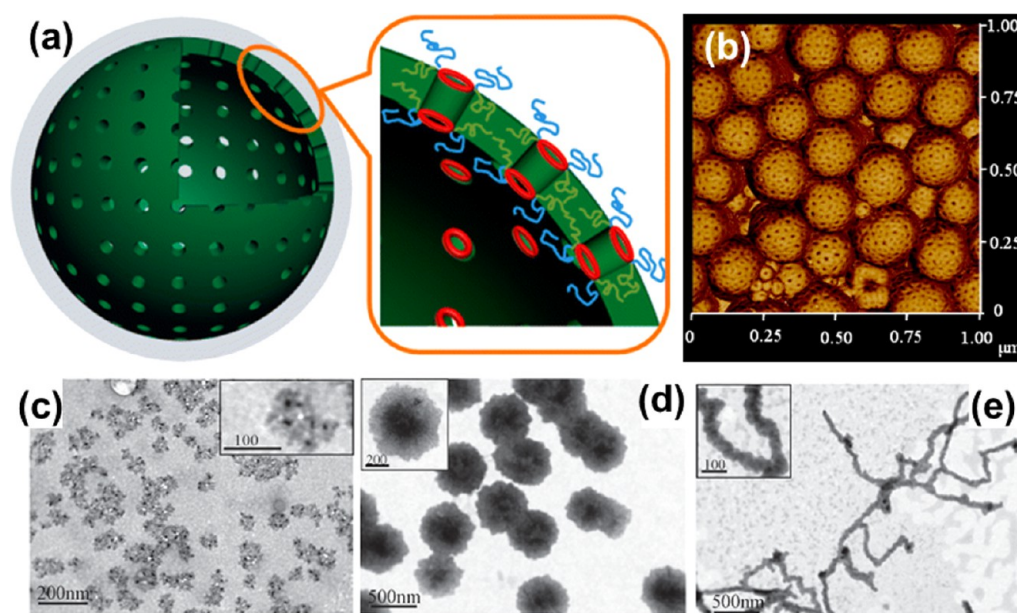
Figure 5. (a) Schematics of the vesicles prepared from miktoarm stars with pH-responsive nanochannels. (b) AFM images of cross-linked vesicles. TEM images of the (c) unimolecular micelle, (d) multicore micelle, and (e) worm-like micelle from PS-(P2VP-*b*-PAA) stars. Reproduced with permission from refs 89 and 91, copyright (2014) American Chemical Society and (2011) Royal Society of Chemistry, respectively.

their linear counterparts which undergo macrophase separation with increasing temperature under the same conditions.[88]

A recent report by Liu et al.[89] showed that a miktoarm copolymer consisting of 1 PtBA, 1 poly(2-cinnamoyloxyethyl methacrylate) (PCEMA), and an average of 1.14 poly(ethylene oxide) (PEO) chains can form vesicles with PtBA cylinders permeating the wall made of PCEMA, yielding unprecedented nanocapsules bearing regularly packed nanochannels (Figure 5a, b). A study on various star polyelectrolyte networks composed of hydrophilic DMAEMA and hydrophobic MMA monomers, with identical topology but different molecular buildups, showed significant differences in structure when swollen with water.[90] Small angle neutron scattering (SANS) measurements showed that, for the homopolymer and random copolymer star networks, only relatively small structural units were observed. However, for the heteroarm co-networks, the presence of well-defined hydrophobic domains were observed, indicating pronounced microphase separation in these systems.

In another study, Tsitsilianis et al.[91] reported the self-assembly of a star terpolymer bearing PS hydrophobic arms and P2VP-*b*-PAA diblock copolymer amphoteric arms in aqueous media. A variety of amphoteric assemblies were observed at different pH conditions of the medium. For instance, below the isoelectric point, the stars can assemble into core–shell unimolecular micelles, worm-like micelles, or multicore large compound micelles (Figure 5c–e). Above the isoelectric point, multistar aggregates, network-like large assemblies, and finally patchy compartmentalized micelles were formed. The authors further demonstrated that the heteroarm stars (PS$_{22}$(P2VP-*b*-PAA)$_{22}$) can be used as an effective dispersing agent for multiwalled carbon nanotubes (MWCNT) in aqueous media, leading to stable MWCNT–star nanohybrids in water with pH-responsive properties.[92]

Amphiphilic star polyelectrolytes can further be used at the air–water interface to form monolayers, which can be transferred to a solid substrate using LB technique. For instance, the interfacial assembly of PS$_n$P2VP$_n$ and PS$_n$(P2VP-*b*-PtBA)$_n$ star polymers has been recently studied.[93] This study showed that the surface morphology of PS$_n$P2VP$_n$ stars strongly depends on subphase conditions. At a low pH, the stars form large circular micelles, which readily transform to labyrinth morphology upon further compression. Conversely, PS$_n$(P2VP-*b*-PtBA)$_n$ stars with hydrophobic end blocks maintain a circular, unimolecular micelle morphology at different surface pressures.[94]

In another report,[95] the pH-responsive properties of Langmuir monolayers from PS$_n$(P2VP-*b*-PAA)$_n$ stars were studied at the air–water interface.[96] Star polymers with a small number of arms possess a more pronounced pH-dependent morphology, changing from circular micelles to labyrinth morphology upon monolayer compression. However, star polymers with a larger number of arms possess a stable circular micelle morphology under various pH conditions due to limited interpenetration and suppressed entanglement. A study by Sheiko et al.[97] showed that the phase behavior of a branched polymer mixture at the air–water interface is significantly different from that of linear polymers. By taking advantage of steric repulsion between branched polymers, long-range arrays of perfectly mixed macromolecules with a variety of polymer morphologies have been realized.

Because of the multiple functionalities of star polyelectrolytes, they have been regarded as promising building blocks for functionalized microstructures.[98] For example, Hammond et al.[99] fabricated nanoporous films from cationic PDMAEMA stars and anionic PAA stars via LbL assembly. The monolayers underwent extensive structural reorganization upon postfabrication treatment under different pH conditions in contrast to the unchanged morphology observed for their linear counterparts. Finally, Qiao et al.[100] demonstrated that highly ordered, porous honeycomb films can be prepared by the breath-figure technique using dendron-functionalized star polymers as precursors.

Star polymers have also been used as components to fabricate thin-shell microcapsules.[101] The fabricated micro-
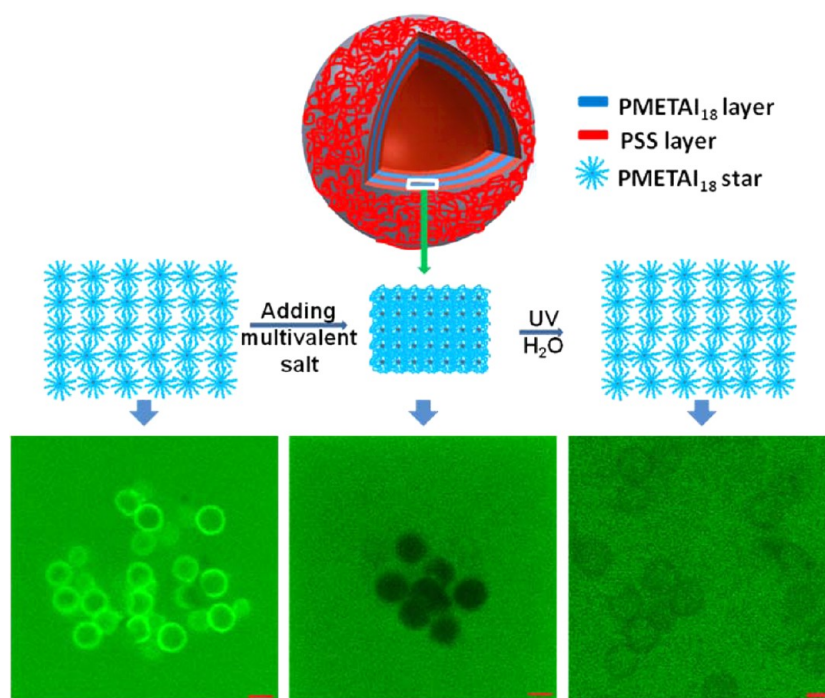
Figure 6. Responsive behavior of (PSS/PMETAI18)$_n$ LbL microcapsules as controlled by the variable multivalent salt state under UV irradiation. Confocal microscopy images show the corresponding permeability test of FITC-dextran molecules. Reproduced with permission from ref 103, copyright (2012) American Chemical Society.

structures possess complex internal structures and unique stimuli-responsive behavior.[102] The study of microcapsules from PMETAI star polyelectrolytes showed that shell permeability can be reversibly controlled by variable counterion valency as mediated by external UV irradiation (Figure 6).[103] The mechanism of responsive behavior was attributed to the fact that the addition of multivalent ions induces the collapse of the PMETAI stars. Thus, the shell of the microcapsules after this transformation becomes denser and less porous and the permeability decreases. UV irradiation can decompose the multivalent ions, which leads to the recovery of the porous structure and subsequent increased permeability.

2.3. Assembly of Hyperbranched Polyelectrolytes. Hyperbranched polyelectrolytes belong to a class of branched macromolecules with randomly branched polyelectrolyte chains.[104] The interesting physical properties of hyperbranched polyelectrolytes include enhanced solubility and lower viscosity compared with those of their linear counterparts.[105] The large number of functional groups and chain ends makes it easy for hyperbranched polyelectrolytes to interact with each other. It has been shown that amphiphilic hyperbranched polyelectrolytes with amine groups in the core region and alkyl tails in the shell can self-assemble into nanofibrillar micellar structures at the air−water surface and form nanofibers in the course of crystallization from solution.[106] The monolayer of the hyperbranched copolymer was also demonstrated as a potential scaffold for the synthesis of silver nanoparticles.[107] The coupled constraints of the air−liquid interface and the unique morphology of the multifunctional hyperbranched polymer controlled the growth of silver nanoparticles with dimensions of 2−4 nm.

Because of their abundant functional groups, hyperbranched polyelectrolytes have been used to change the surface properties of various nanostructures. The unique globular structures of the hyperbranched macromolecules offer new possibilities for controlling phase transitions by variation of the molecular weight instead of changing the chemical nature of the surface polymer layer. For instance, thermosensitive hyperbranched polyglycerols modified with NIPAM groups were used to coat water-soluble gold nanoparticles through noncovalent bonding, giving rise to soft nanoparticles with readily controllable LCSTs over a very broad temperature range.[108]

In another study, hyperbranched polyethylenimine was immobilized on the surface of multiwalled nanotubes (MWNTs) via electrostatic interactions between the positively charged protonated amines within the polymer and the carboxyl groups on the chemically oxidized MWNT surface.[109] The branched polyelectrolyte not only provides many sites for the location of protein but also effectively reduces the lateral repulsion of protein species within the adsorbed layer. The new material designed in this study as a biosorbent for the adsorption of proteins provides better selectivity for the adsorption of BSA over the oxidized MWNTs and the MWNTs functionalized by the linear polyelectrolyte.

Hyperbranched polyelectrolytes can also be used to form complexes with oppositely charged polyelectrolytes, nanoparticles, and small molecules. For example, hyperbranched polylysine was used to interact with various anionic sodium alkyl sulfate surfactants electrostatically.[110] The hyperbranched polylysine−surfactant complexes were found to form liquid crystalline (LC) mesophases, and their thermal stability and structure depended both on the molecular weight of the polylysine as well as on the nature of the anionic surfactant. The LC hyperbranches showed thermotropic behavior and underwent crystal−nematic and nematic−isotropic transitions upon an increase in temperature.

Another important category of hyperbranched polyelectrolytes is hyperbranched conjugated polyelectrolytes (HCPEs), introduced as novel optical, electronic, and magnetic materials.[111] These materials exhibit good solubility and
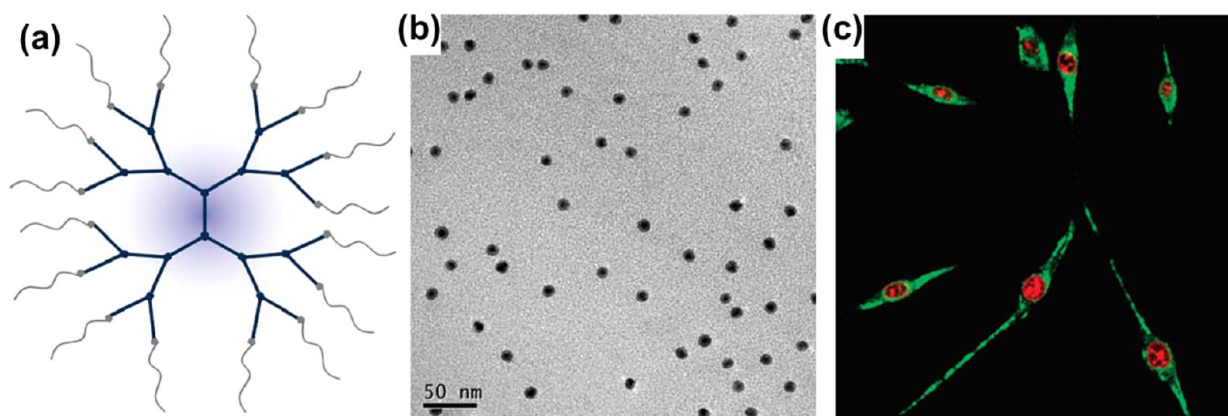
Figure 7. (a) Chemical structure of HCPE. (b) TEM image of HCPE nanoparticles. (c) CLSM image of labeled cancer cells. Reproduced with permission from ref 113, copyright (2009) American Chemical Society.
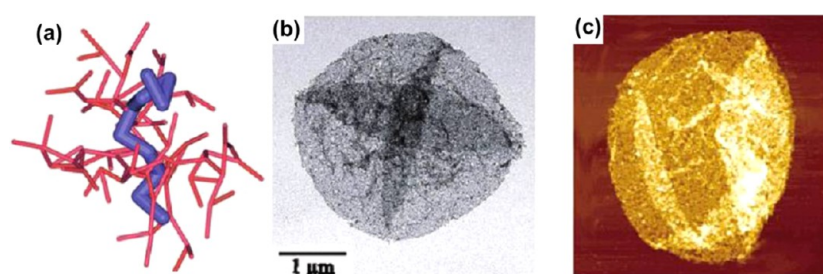

Figure 8. (a) Simulated dendrimer-linear chain complex. (b) TEM and (c) AFM of PSS/4G PAMAM microcapsules. Reproduced with permission from refs 119 and 128, copyright (2002, 2008) American Chemical Society.

excellent processability. The hyperbranched structure is advantageous because of its low viscosity, reduced aggregation, high solubility, and high photostability compared to those of the linear conjugated polymers. These materials exhibit a tunable emission color and may be advantageous for disrupted inter- and intramolecular charge-transfer.[112]

For instance, Liu et al.[113] designed and synthesized fluorescent HCPE with a unique core−shell structure for cell imaging. Hyperbranched cationic polyfluorene located in the core region served as a stable light-emitting center, and linear poly(ethylene glycol) (PEG) covering the periphery of the HCPE passivated the macromolecular surface while also providing good cytocompatibility (Figure 7). Because of the shape persistence of the rigid core, the HCPE macromolecules form single-molecular nanospheres that facilitate the uptake process for cell imaging.

HCPE can also interact with oppositely charged metal ions in a selective way for highly sensitive sensing applications. For instance, a series of hyperbranched cationic conjugated polyelectrolytes containing different amounts of phosphorescent Ir(III) complex have been designed and synthesized.[114] These complexes can self-assemble into nanoparticles in aqueous solution with sizes of ∼100 nm. Energy transfer processes from the host polyfluorene to the guest Ir(III) complex have been observed, and the authors suggested that the hyperbranched polyelectrolytes can be used as light-up heparin probes with good selectivity and high sensitivity. In another example, water-soluble hyperbranched polyfluorenes bearing carboxylate side chains have been synthesized for selective ion interactions.[115] Indeed, the hyperbranched polyelectrolytes with a lower branch unit content (2%) showed excellent solubility and higher fluorescence quantum yield than

their linear counterparts. Fluorescence quenching of the hyperbranched polyelectrolytes by different metal ions was also investigated, and they showed high selectivity and sensitivity to Hg^{2+} and Cu^{2+} ions.

Moreover, HCPEs with oppositely charged segments can interact to form multilayer hybrid structures. For example, Reynolds et al.[116] reported the synthesis of hyperbranched conjugated polyelectrolytes and their self-assembly and application in ionic materials for sensitizing TiO_2 solar cells. The ionic interactions of oppositely charged hyperbranched conjugated polyelectrolytes resulted in an increased chromophore concentration and a resulting enhanced optical density. These changes facilitated efficient light harvesting, which can be of interest for enhanced energy transport and efficient charge migration in hybrid solar cells.

2.4. Assembly of Polyelectrolyte Dendrimers. Polyelectrolyte dendrimers can be used as functionalized building blocks for the fabrication of functional microstructures from different components.[117,118] The interactions of dendrimers with a linear polymer have been studied both theoretically and experimentally. Gurtovenko et al.[119] used dynamics simulations to investigate the role of electrostatic interactions in molecular complexes comprised of cationic dendrimer polyamidoamine (PAMAM) with oppositely charged linear polyelectrolytes (Figure 8a). Their simulation showed that the complexation leads to a remarkable condensation of the tightly interacted components.

Furthermore, the formation of the molecular complexes results in a considerable dehydration of the chain, which becomes more pronounced when the electrostatic interactions are strengthened. Thus, polyelectrolyte dendrimers clearly demonstrate the ability for efficient compaction of guest linear

chains and protective screening of the chains from the surrounding medium. A theoretical study by Muthukumar et al.[120] showed that, depending on the solution ionic strength and the sizes of the dendrimer and linear chains, their complex can have three different confined conformations: a dendrimer may encapsulate a chain, a chain and a dendrimer may mutually interpenetrate, or a unique "chain-walking" phenomenon (a dendrimer walking along a longer linear chain) may occur. Thus, it is important to compare the relative size of the target molecules when using dendrimers in controlled delivery.

The PAMAM dendrimer is the most intensively studied type because of its easy synthesis, low polydispersity and commercial availability.[121,122] The PAMAM dendrimers are usually positively charged at low pH due to protonation of amine groups.[123] They can also be transformed to neutral or anionic dendrimers by partial or complete modification of the dendrimer periphery with neutral or negatively charged groups,[124] which helps lessen the cytotoxicity of PAMAM dendrimers in drug delivery applications.[125]

The assembly of PAMAM dendrimers on oppositely charged latex particles has recently been studied.[126] The results showed that varying the dendrimer content results in the charge changing from negative to positive values through the isoelectric point (IEP). The most intense aggregation was observed near the IEP. The effect of surface charge heterogeneities becomes important for higher dendrimer generations. The adsorption of PAMAM dendrimers onto mica surfaces was investigated as a function of ionic strength, pH, and dendrimer generation.[127] The adsorption was found to follow a diffusion-limited aggregation with formation of nanopatterned surfaces.

PAMAM dendrimers have been used to build multilayer structures via electrostatic interactions. For instance, Caruso et al.[128] fabricated multilayered polyelectrolyte/dendrimer films and microcapsules by using fourth-generation PAMAM dendrimers and linear PSS via LbL deposition (Figure 8b, c). The dendrimer-based ultrathin films and microcapsules can serve as nanoreservoirs for the uptake and release of various compounds. Furthermore, the same group[129] showed that the stability of such microcapsules can be improved by increasing inter- and intramolecular attractive forces between the PSS chains in the capsules through electrostatic interactions, hydrophobic interactions, and a combination of them.[130] In another report,[131] the surface-modified PSS/4G PAMAM LbL films were assembled through cross-linking and covalent grafting with fatty-alkyl chains. Subsequently, PEG chains were adsorbed on the dendrimer film surface. Colloid particles coated with the modified LbL films showed reduced adhesion to biological cells.

In another example, N,N-disubstituted hydrazine phosphorus-containing dendrimers were used as components to build multilayer microcapsules with oppositely charged polyelectrolytes (PSS or PAH) via electrostatic interactions.[132] The results showed that the dendrimer-based microcapsules were much softer than microcapsules created from conventional linear polyelectrolytes. The softening of these shells is attributed to an enhanced permeability of the polyelectrolyte/dendrimer multilayer shells because the phosphorus-containing dendrimers exhibit a hydrophobic core interior and a hydrophilic charged surface such that the electrostatic interactions and complexation with PSS can only take place in peripheral regions. Using a similar method, the same group also prepared biocompatible

DNA/phosphorus dendrimer multilayer microcapsules with potential applications in controlled drug delivery.[133]

PAMAM dendrimers have also been used to fabricate multilayer films and as tailored nanoreactors for the synthesis of metal nanoparticles. For instance, Li et al.[134] prepared LbL thin films with a third-generation PAMAM dendrimer and the linear components PSS or PAA. Furthermore, they grew silver nanoparticles within the films from a corresponding salt solution. The composite multilayer thin films with embedded nanoparticles have a strong negative redox potential with potential applications in catalysis. Similarly, gold nanoparticles were prepared in situ inside LbL films comprised of PAMAM dendrimers and PSS,[135] and there is a 20 nm bathochromic shift in the absorption of the film compared with Au-dendrimer nanocomposites in aqueous solution. Palladium nanoparticles were also prepared within the interior of PAMAM dendrimers. The dendrimer-encapsulated catalysts were used to hydrogenate allyl alcohol and α-substituted derivatives.[136] LbL films based on PAMAM dendrimers can also be used as a gas-permeable membrane, which show much higher gas flux than similar LbL films from linear polyelectrolytes.[137]

Besides ionic pairing, dendrimers can also be assembled with other molecules via hydrogen bonding. For instance, Zhang et al.[138] reported that carboxyl-terminated polyether dendrimers can be used to fabricate LbL films with linear PVP through hydrogen bonding. By postformation treatment, the smooth LbL films experience a dramatic structural change from a uniform morphology to a film with a microporous morphology. It was proposed that the partial dissolution of polyether dendrimers and readsorption from the multilayer interior and surface into the basic solution as well as the gradual reconfiguration of linear PVP polymer chains are responsible for the reconfiguration of the initial uniform films.

Multilayered films can also be built from two kinds of oppositely charged dendrimers of different generations.[139] Electrostatic LbL ultrathin films were fabricated from adjacent generation PAMAM dendrimers with surface amine groups and carboxylic groups. As reported, the average thickness of an individual molecular layer in these multilayer films is much smaller than the expected diameter of the ideal spherical dendritic macromolecules shaped as spherical soft nanoparticles. Therefore, it has been suggested that the self-assembled dendrimers assume a compressed, oblate shape with the axial ratio in the range of 1:3−1:6. The high interfacial interaction strength between "sticky" surface groups along with short-range van der Waals forces and long-range capillary forces are considered to be responsible for the formation of compacted multilayer structures.

3. STRUCTURE AND ASSEMBLY OF POLY- AND OLIGO(IONIC LIQUID)S

3.1. Synthesis and Architecture of Branched Poly- and Oligo(ionic liquid)s. Poly(ionic liquid)s usually have weakly bound counterions with much larger sizes and mobilities when compared to conventional linear polyelectrolytes. The relatively low glass transition temperatures, high ion mobility, and processability of poly(ionic liquid)s are distinct features of these materials that make them ideal prospective candidates for solid ion-conducting materials.[35] These materials provide an opportunity to design anionic and cationic fragments in phase-separated structures with tunable thermal characteristics while maintaining the required mechanical strength and structural integrity.
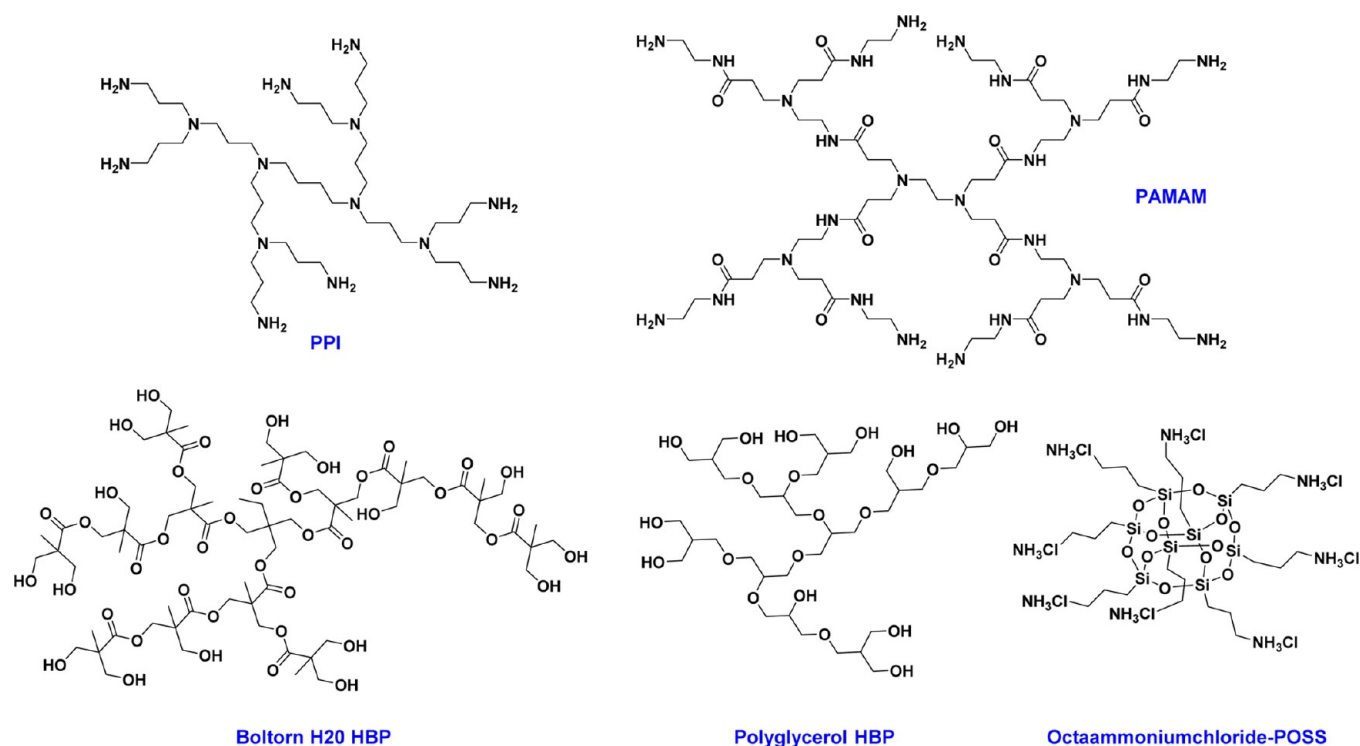
Figure 9. Examples of branched compounds as core-starting materials for poly- and oligo(ionic liquid)s.

The synthesis of poly(ionic liquid)s having linear architectures has been extensively reviewed by Antonietti et al., Mecerreyes et al., and Shaplov et al.[140−142] In general, poly(ionic liquid)s can be prepared either by polymerizing the appropriately functionalized ionic liquids or by post-polymerization modification of conventional polymers via polymer analogous reactions. Controlled free radical polymerization methods, such as atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) polymerization, have been employed to prepare the homopolymers as well as block copolymers that incorporate the poly(ionic liquid) segments. The ionic groups are mostly represented by quaternized derivatives of N-methylimidazole, tert-aliphatic amines, and pyridine (Figure 2). Despite the large number of studies on poly(ionic liquid)s and oligo(ionic liquid)s reported to date, their architectures are mostly limited to linear homo and block copolymers. Therefore, the role of polymer architecture on self-assembly, interfacial behavior, and ionic conductivity is summarized below along with the introduction of specific chemical routines for the synthesis of these materials. Polymeric brushes based on ionic liquid monomers are also reported but outside the scope of this review.[36,140,143]

To date, only a few examples of well-defined starlike or bottle brush poly(ionic liquid)s can be found in the literature. The branched poly(ionic liquid)s are mostly represented by dendrimers and hyperbranched polymers.[144−146] On many occasions, poly(ionic liquid)s having a relatively low molecular weight can be considered as a standalone class of oligomeric compounds or oligo(ionic liquid)s (OILs). The combination of a dendritic structure with a modest molecular mass makes it possible to introduce a large number of terminal ionic liquid groups and maintain a high mobility. Among the known representatives of this type of hyperbranched ionic structure,

the vast majority incorporate cationic groups located at the periphery of branched chains.

These oligo(ionic liquid)s are mostly synthesized by the neutralization of known amino-containing dendrimers and hyperbranched polymers with the generation of proton-containing (protic), or quaternization with the generation of nonproton-containing (aprotic), ionic liquid groups. Alternatively, the same scaffolds, which are end-functionalized with amino-containing heterocycles, carboxylic acids, and sulfonic acids and their derivatives, can be employed for neutralization (Figure 9). As counterions, anions and long-chain alkylated sulfate anions are traditionally used for ionic liquids. Of special interest are the oligo(ionic liquid)s incorporating functionalized anions. Both protic and aprotic dendritic oligo(ionic liquid)s and poly(ionic liquid)s have been synthesized. Effective methods for modifying the structure and properties of synthesized compounds, including their ability to self-assemble, are the chemical structure modification of substituents at the quaternized aliphatic nitrogen atom or heterocycle, counterion exchange, changing the charge density, and modifying the length of the spacer between the ionic groups and the core.

3.2. Star Poly- and Oligo(ionic liquid) Materials. In a number of reports, starlike branched structures containing ionic liquid groups were synthesized using polyhedral oligomeric silsesquioxane (POSS) as a branched core.[147−160] On the basis of the range of molecular masses involved, these compounds can be regarded as OIL compounds. Their molecular weight depends on the length of the spacer and the type of ionic group and starts at 1338 g/mol for derivatives with one arm[147] to 3448 g/mol in a star POSS with eight arms[150] and usually does not exceed 10000 (9940) g/mol for second-generation POSS dendrimers.[159] Controlled branching of side groups leads to POSS-IL with dendritic structures.[159] Among them, the most explored are aprotic cationic POSS-IL, whereas literature on the protic POSS-IL of this structure does not exist to the best of
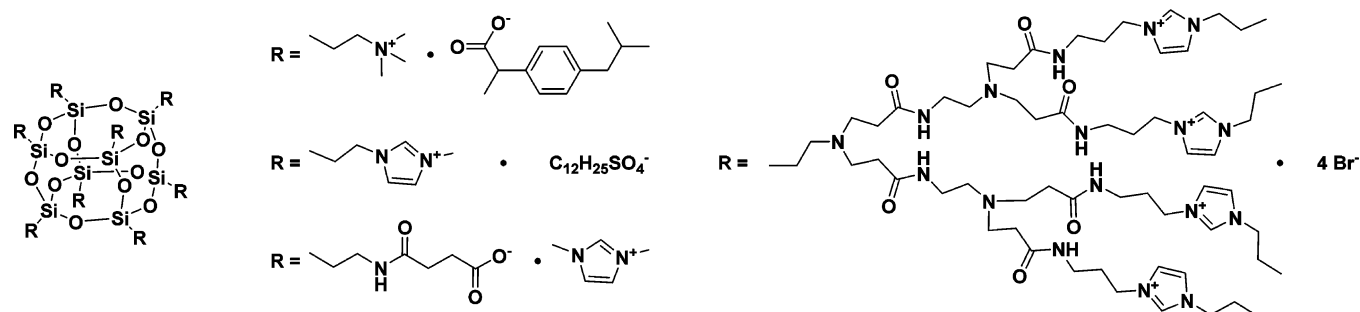
Figure 10. Examples of POSS-based aprotic star-shaped oligo(ionic liquid)s with cationic and anionic end groups.[148,150,151,159]
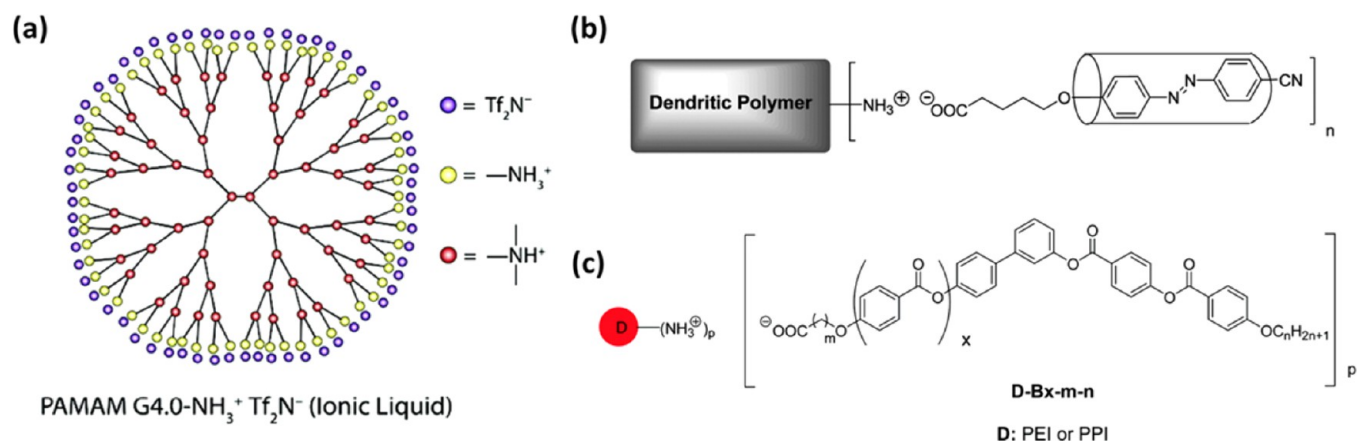

Figure 11. Examples of dendrimer-based oligo(ionic liquid)s with cationic end groups. (a) PAMAM-based photoluminescent OIL. (b) Photosensitive nematic OIL based on PPI and PAMAM dendrimers. (c) OILs based on bent-core structures and PPI dendrimers. Reproduced with permission from refs 144, 166, and 167, copyright (2005, 2008, 2011) American Chemical Society.

our knowledge. The IL groups are represented by terminal aliphatic tertiary amines with various lengths of the aliphatic substituent at the nitrogen atom[147−149,151,156,158] along with 1-substituted imidazole groups.[150,153−155,159,161,162] The classical anionic groups are usually used as counterions (Figure 2).

The charge density is regulated either by synthesis of monosubstituted POSS with varied spacer lengths or by the degree of quaternization of these amino-containing substituents in the case of octasubstituted POSS.[147,149,153−155] The variation of nitrogen substitution in the ionic group, the counterion structure, and the charge density have a dramatic effect on the properties of POSS-IL compounds. In recent years, there has been significant progress in the development of efficient synthetic approaches to the synthesis of mono and octasubstituted POSS precursors.[163] These various types of oligo(ionic liquid)s are described below.

Quaternization of POSS containing eight propylene chloride groups by 1-methylimidazole with a subsequent exchange of chloride ions onto dodecylsulfate ions led to the first example of octaimidazolium-based, room-temperature, branched POSS-ILs (melting temperature of 18 °C relative to 185 °C for the case with chloride anions) (Figure 10).[150] These aprotic cationic POSS-ILs are water-soluble with a decomposition temperature of 172 °C. As suggested, such types of imidazolium-based POSS can function as a carrier for heterogeneous catalysis and high performance electrolytes.

Octakis(N,N,N-trialkyl-propylammonium)-POSS (alkyl C_1−C_8) with anions of iodine, bis(trifluoromethyl sulfonyl)imide (TFSI), and ibuprofen have also been prepared (Figure 10).[148] The nature of the cations plays a key role in determining the thermal behavior of these POSS-ILs. It was shown that the presence of water induces self-organization of the polar ammonium groups on the film surface. These compounds can be exploited as microbiological substances, electrolytes for electrochemical devices (solar and fuel cells), and platforms for directed ionic self-assembly.

Most reports utilized only aliphatic tertiary amines with various lengths of aliphatic chains on the nitrogen atom along with 1-methylimidazole and some of its derivatives in which the ionic groups are located at chain ends. Stable, room-temperature anionic aprotic POSS-ILs with POSS-octapropyl-carboxy anions and 1-methyl-3-N-butylimidazolium cations have been reported.[157] The properties of this compound were compared with an initial POSS-octapropylcarboxylic acid and its arm analogue. The comparison demonstrated that the POSS core plays a significant role in the thermal properties of these compounds. A very low glass transition temperature of −52 °C (−40 °C for the arm analogue) and a melting temperature of 23 °C (48 °C for the arm analogue) have been reported.[152] The organic outer shell also has a strong effect on the optical properties of branched compounds. It was noted that the change in ionization of the terminal groups of the reported compounds lowers the glass transition and melting temperatures (Figure 10).[151] Furthermore, the excluded volumes originating from the star-shaped structures could generate hydrophobic spaces inside molecules. These POSS-ILs might be applicable as a superior medium for solubilizing polysaccharides or other insoluble materials. It was discovered that when the initial POSS-octapropylcarboxylic acid acts as a
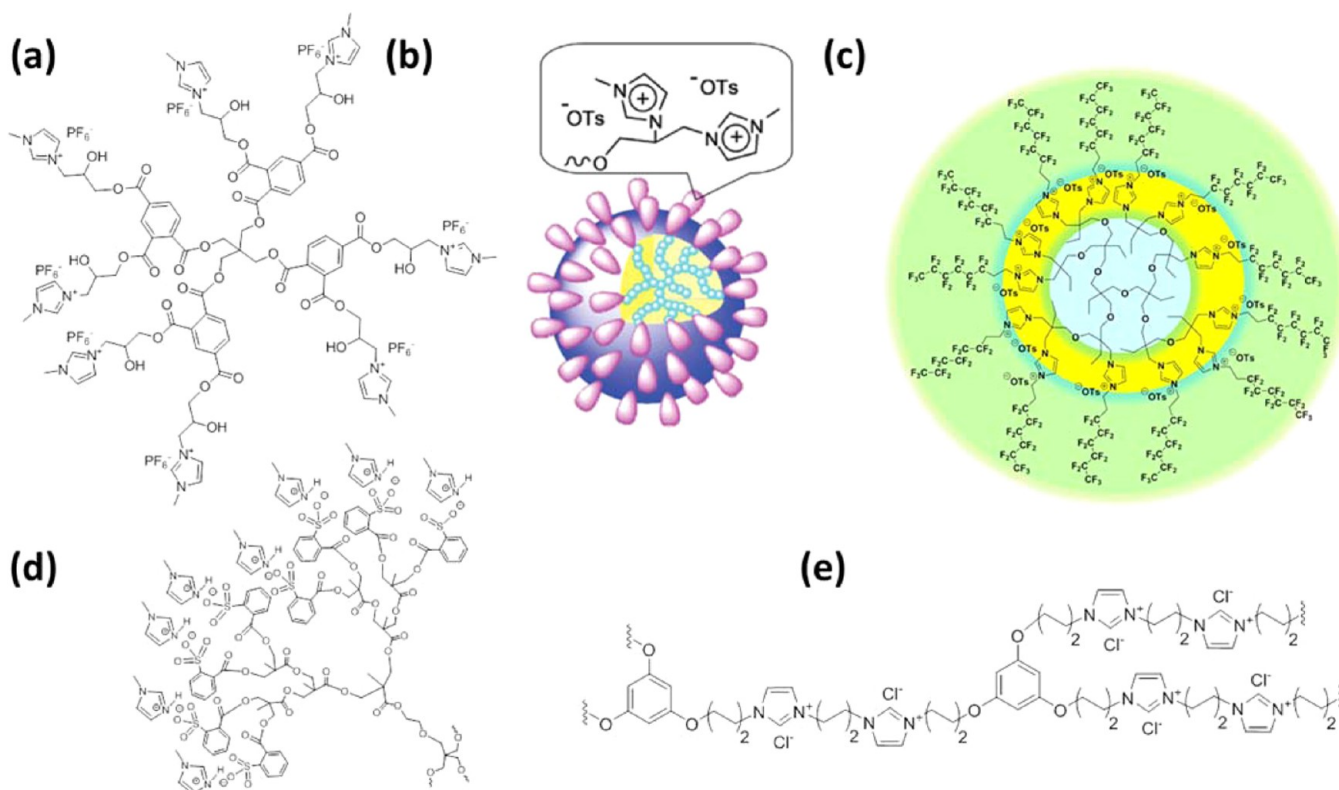
Figure 12. Examples of hyperbranched polymer-based poly(ionic liquid)s with cationic and anionic end groups. (a) Pentaerythritol-based HBP PIL.[171] (b) Polyglycerol-based HBPIL.[169] (c) Structured semifluorinated PIL.[172] (d) Polyester-based protic anionic PIL.[174] (e) Branched PIL with imidazolium chloride main chain segments.[175] (b) and (c) are reproduced with permission from refs 169, Copyright (2009) John Wiley and Sons, and 172, copyright (2013) American Chemical Society.

molecular filler for classical ionic liquids, the ionic liquid melting temperature decreases.[164]

The aforementioned starlike oligo(ionic liquid)s are inorganic—organic compounds in terms of their global chemical composition. The reports on fully organic starlike poly(ionic liquid)s in the literature are scarce. Among them, four-arm star block copolymers containing poly(ionic liquid) segment poly(N-vinyl-3-ethylimidazolium bromide) and poly(N-isopropylacrylamide) as a thermoresponsive segment that separated inner and outer segments and opposite sequences were synthesized by RAFT polymerization.[165] These branched polymers have much higher molecular weights than the compounds described above. Peculiarities of thermally induced phase separation behavior and assembled structures of these poly(ionic liquid)s in aqueous solutions are discussed in section 3.6.

3.4. Poly- and Oligo(ionic liquid) Dendrimers. The first study of protic oligo(ionic liquid)s with a dendritic structure reported their synthesis using bis(trifluoromethane sulfone)-imide for the neutralization of amino groups of classical amino-containing PAMAM dendrimers.[144] This branched compound had strong photoluminescence and high proton conductivity (Figure 11a). This type of oligo(ionic liquid) is promising for the development of anhydrous proton-conductive electrolytes.

In the case of POSS-based dendrimers of different generations with TFSI anions, the glass transition temperatures were similar: −22 °C for the first generation and −23 °C for the second generation. By adding varying amounts of LiTFSI to these POSS dendrimers, corresponding Li-containing electrolytes could be obtained. It was noted that the addition of

LITFSI led to a lowering of T_g for the branched oligo(ionic liquid)s in contrast to the traditional IL. Depending on the amount of LiTFSI, the T_g was −29 to −37 °C for the first generation and −35 to −36 °C for the second generation of POSS-ILs. The second T_g appearance is explained by nanophase separation between the two components of the dendrimer assemblies. For the POSS-IL dendrimers of the first generation and with less LiTFSI addition, a maximum ionic conductivity of 4.03×10^{-5} S cm^{-1} (51 °C) was observed (Figure 10).[159]

Furthermore, noncovalent supramolecular systems obtained by the neutralization of PAMAM and amino-terminated poly(propyleneimine) dendrimers with cyanoazobenzene carboxylic acid have been described (Figure 11b).[166] The study reported that the self-assembly of the rodlike anionic mesogenic groups and cationic dendrimers results in LC behavior with the formation of a nematic mesophase. Similar results can be obtained by substitution of dendrimers by hyperbranched polyethylenimines with primary and tertiary amino groups at the periphery. Notably, the photoresponsive nature of a counterion makes the synthesized compounds attractive for photo-optical applications.[166]

A similar approach to functional counteranions was used for the synthesis of salts of amino-containing dendrimers and hyperbranched polymers (Figure 11c).[167] Carboxyl-containing bent-core poly(biphenylen ester) structures with short or long terminal aliphatic chains and spacers were used for neutralization of regular poly(propyleneimine) dendrimers and random hyperbranched poly(ethyleneimine) of different generations. These ionic compounds show mesophase behavior with

lamellar and columnar phases formed over a broad temperature range, even for nonmesogenic carboxylic acid precursors.

Amphiphilic aliphatic oligoesters of dendrimeric architecture with quaternary methylimidazole, pyridine, or aliphatic tert-amine ionic groups (where counterions are chloride, tetrafluoroborate, and hexafluorophosphate) in a dendron focal position deserve a special mention. These ionic liquid groups promote self-assembling into supramolecular columns or spheres organized into two-dimensional hexagonal or rectangular and three-dimensional cubic or tetragonal LC or crystalline lattices as discussed in section 3.6.[38]

3.5. Hyperbranched Poly- and Oligo(ionic liquid)s.

Hyperbranched cationic poly- and oligo(ionic liquid)s (HBPILs) are based on oligoesters, oligoethers,[168,169] polyamidoamine,[110] and polyalkyleneimine cores. The oligo(ionic liquid)s with terminal quaternized amino groups with various lengths of the alkyl substituent (C_8-C_{18}) were prepared by modifying the commercially available second generation hyperbranched polyester-polyol (Boltorn H30) by epoxypropyl alkyl dimethylammonium chloride.[170] These oligo(ionic liquid)s were shown to accelerate the saponification of polyethylene terephthalate. By using a series of sequential reactions of pentaerythriol with trimellitic anhydride and epichlorhydrin, three generations of hyperbranched polyesters with terminal chloride groups were synthesized. Subsequent quaternization of chloride groups with N-methyl imidazole resulted in three different generations of poly(ionic liquid)s with 24, 32, and 56 terminal imidazolium groups with chloride or hexafluorophosphate as counteranions (Figure 12a).[171] The ionic conductivity of compounds with terminal imidazolium hexafluorophosphate ions increases with an increasing number of ionic groups to reach 4.9×10^{-3} S cm^{-1} at 80 °C due to the higher free volume of randomized structures.

Hyperbranched polyethers with terminal hydroxyl groups were employed in polymer-analogous reactions to obtain HBPILs with terminal imidazolium groups.[169] The employed reaction included the substitution of a hydroxyl group by a tosyloxy group with subsequent quaternization with 1-alkylimidazole (Figure 12b). Initial hyperbranched polyethers with terminal hydroxyl groups were synthesized based on glycidol and 3-ethyl-3-hydroxymethyl oxetane. The hyperbranched polyglycerols with terminal 1-methyl imidazolium tosylate groups possess LCST transitions in organic media. Such HBPILs can be useful as thermosensitive separation agents and thermosensitive reaction promoters or inhibitors.

In another study, hyperbranched polyglycerols with terminal 1-methyl imidazolium tetrafluoroborate and hexafluorophosphate groups were used to obtain polymer electrolytes with LiTFSI.[145] The anion size in such HBPILs influences ionic conductivity and, for electrolytes with tetrafluoroborate, anion conductivity reaches 3.5×10^{-4} S cm^{-1} at 30 °C. The ionic liquid groups pyridinium and 1,2-dimethylimidazolium p-(diphenylphosphino)benzenesulfonate were made for polyglycerol modified with ω-bromo-alkanoyl chlorides.[168] Variation of the spacer length between the IL functionalities and polyglycerol (C_2-C_{10}) allowed for adjustment of the charge density and flexibility of the polycations as reflected by their glass transition temperature changes (9−49 °C for pyridinium and 26−80 °C for 1,2-dimethylimidazolium derivatives).

A new family of HBPILs with an onion-like topology ("hyperILs") was recently developed.[146,172] These compounds contain a core of hyperbranched poly(1,3-diether), a polar inner imidazolium cation shell, and a nonpolar outer n-alkyl(C_1-C_{18}) or semifluorinated alkyl (($(CH_2)_2(CF_2)_5CF_3$) shell. These compounds combine high thermal stability (up to 300 °C), extraordinary robustness, and phase transfer activity. The replacement of alkyl groups in the outer shell by partially fluorinated octyl groups leads to new properties of these onionlike HBPILs, such as the potential for compartmentalization (Figure 12c).[172] Such ionic liquid nanoreactors can be used to perform chemical reactions in confined, isolated, and restricted ionic liquid geometries.

Polymerization of 3-ethyl-3-hydroxymethyl oxetane in the presence of hydroxylated graphene with subsequent introduction of 1-methyl imidazolium tosylate groups resulted in branched poly(ionic liquid)s grafted to the graphene sheet.[40] Because of the compactness, flexibility, and multifunctionality of such branched poly(ionic liquid)s, the resulting material possesses a very high density of ionic groups near the graphene surface, which accounts for their excellent dispersibility and stability in water. Moreover, these PIL-functionalized graphene sheets can form planar graphene layers on various surfaces. Along with dendritic IL-polyamidoamines, HBP-OILs based on polylysine and its hyperbranched analogues were prepared.[110] These hyperbranched polylysine compounds with various molecular weights and with terminal ammonium N-alkyl (C_8-C_{18}) sulfate groups are capable of forming an LC phase. Depending on the alkyl chain length, columnar hexagonal packing or lamellar ordering are observed.

Protic complexes of hyperbranched PAMAM dendrimers of different generations were synthesized with dodecylsulfate as a counterion; these complexes exhibit liquid crystalline properties.[173] Thermotropic LC phases showed columnar, rectangular, and lamellar morphologies. The templating effect of this phase on the in situ formation of Au nanoparticles has been shown as well. The size of the nanoparticles is dictated by the local organization of the mesophases and by the molecular weight of the HBP-OILs.

Unlike the cationic dendritic oligo(ionic liquid) and poly(ionic liquid) compounds described above, anionic oligo(ionic liquid)s and poly(ionic liquid)s of the same structure have not been sufficiently explored to date. Recently, the synthesis of the first representative of hyperbranched oligo(ionic liquid)s has been conducted by reacting a second generation Boltorn HBP with benzoic and 2-sulfobenzoic acid cyclic anhydride (Figure 12d).[174] By neutralizing the obtained hyperbranched polyacids with 1-methylimidazole, the authors obtained protic anionic oligo(ionic liquid)s as well as aprotic anionic oligo(ionic liquid)s for carboxyl-containing OILs. The nature of the anion has a large influence on the glass transition temperature of these compounds and ionic conductivity in anhydrous conditions. For the protic form, T_g is −16 °C and increases to 32 °C for the aprotic form in the case of a carboxylate anion and decreases to −9 °C in the case of a sulfo anion. The protic sulfonated oligo(ionic liquid) has a high ionic conductivity of 3.22×10^{-3} S cm^{-1} at 100 °C. The protic oligo(ionic liquid)s with carboxylic terminal groups possess an order-of-magnitude lower conductivity, and the conductivity of its aprotic form falls to 1.22×10^{-6} S cm^{-1} at 120 °C. Sulfonated oligo(ionic liquid) is thermally stable up to 270 °C, whereas the thermal stability of carboxylate-containing oligo(ionic liquid)s is limited to 190 °C.

The oligo(ionic liquid)s described above possess the common feature of the chain end location of their ionic groups. Alternatively, oligo- and poly(ionic liquid)s can incorporate the quaternized amino or imidazolium groups in
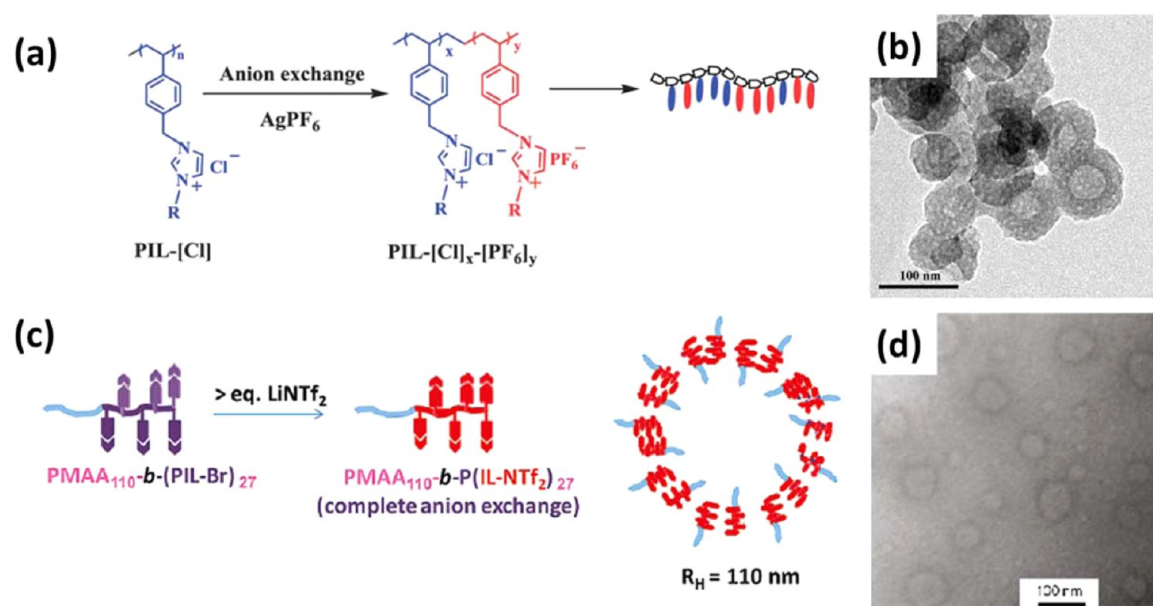
Figure 13. (a, b) Self-assembly of amphiphilic random copolymers, PIL-[Cl]$_x$[PF$_6$]$_y$, with the hydrophilic/hydrophobic segments resulting from a partial anion-exchange of poly(ionic liquid) homopolymers. (c, d) Poly(acrylamide) and poly(methacrylic acid) block copolymers with PIL and their micellar structures. Reproduced with permission from refs 178, copyright (2013) Royal Society of Chemistry, and 180, copyright (2009) American Chemical Society.

the main chain or branching points such as those prepared by the Menshutkin reaction.[175] The first type can be prepared by polymerization of AB$_2$ monomers.[176] Their amphiphilic nature is a result of the presence of the hydrophobic moieties at the chain ends. They behave like polysoaps and show many similarities to their linear analogues concerning their surface activity and solubilization capacity, but their viscosity is extremely low. The synthesis of a second class of HBPILs is based on the reaction of A$_3$ + B$_3$ monomers (Figure 12e).[175,177] Despite the presence of ionic imidazolium fragments in the main chain, these compounds are insoluble in water and common organic solvents.

3.6. Assembly of Poly- and Oligo(ionic liquid)s: Selected Examples. Poly(ionic liquid)s are extremely sensitive to the nature of the counterion and, as a result, the solubility and solution self-assembly of polymers containing poly(ionic liquid) segments can be controlled by the exchange of counterions. Guo et al. reported on a linear poly(1-(4-vinylbenzyl)-3-methyl imidazolium chloride) homopolymer that underwent a partial ion exchange of the Cl$^-$ anion to an organic-soluble PF$_6^-$ anion, resulting in an amphiphilic random copolymer.[178] The formation of well-defined spherical micelles was observed in aqueous solution with their size dependent mostly on the molecular weight distribution and not the molecular weight or the anion type (Figure 13a, b). Such behavior can be explained by the random copolymer nature of the investigated material. In this respect, a more well-defined block copolymer architecture may provide better control for poly(ionic liquid) self-assembly. Indeed, Stancik et al. reported that a block copolymer of polystyrene with 1-methyl-3-(4-vinylbenzyl)-imidazolium chloride formed elongated micellar systems in toluene with the geometry and dimensions dependent on the PIL block length.[179] Vijayakrishna et al. demonstrated that linear IL-based block copolymers based on poly(acrylamide) and poly(methacrylic acid) compounds are capable of aqueous self-assembly.[180] The type of resulting polymeric micellar and polymersome structures can be changed

by the counterion exchange (inorganic bromide to TFSI anion) and chemical modification of the non-IL block (Figure 13c, d).

Mori et al. prepared temperature-responsive block copolymers containing poly(N-vinylimidazolium salt) as an ionic segment and PNIPAM as a thermoresponsive segment through controlled RAFT polymerization.[181] The nature of the counterion and the substituent attached to the imidazole group had a pronounced effect on the LCST behavior of the resulting polymer. A more detailed study on micellization of poly(N-isopropylacrylamide)-b-poly(1-butyl-3-vinylimidazolium bromide) was later conducted by Wang et al.[182] The ability of imidazole-based poly(ionic liquid) segments to form transition metal complexes was employed by Li et al. for the templated formation of block copolymer micelle encapsulated gold nanoparticles.[183] In this case, poly(ethylene glycol)-block-poly[1-methyl-3-(2-methacryloyloxy propylimidazolium bromide)] (PEG$_{113}$-b-PMMPImB$_{24}$) formed vesicles upon the addition of AuCl$_4^-$ that could be reduced with sodium borohydride, resulting in hybrid core−shell structures.

Examples of solution-based self-assembly of branched poly- and oligo(ionic liquid)s are quite rare. Negatively and positively charged polyaryl ether dendrimers with a porphyrine core and terminal carboxylate or trimethylammonium groups were synthesized and used for electrostatic assembly.[184,185] These dendrimer electrolytes form organized structures in protic media. Second-generation PAMAM dendrimers neutralized with a different number of equivalents of myristic acid have also been shown to assemble in aqueous environments.[186] The formation of micelles, lamellae, or nanospheres with a lamellar structure depends on the number of fatty acids introduced onto the PAMAM core. The resulting nanoparticles could be loaded with hydrophobic 9,10-diphenylanthracene, indicating the potential of such structures for use in drug delivery applications.

A responsive star polymer having four PNIPAM-b-PIL arms was synthesized by RAFT polymerization by Mori et al.[165] The poly[1-ethyl-3-vinylimidazolium bromide] served as an IL block that could be placed either at the core or on the
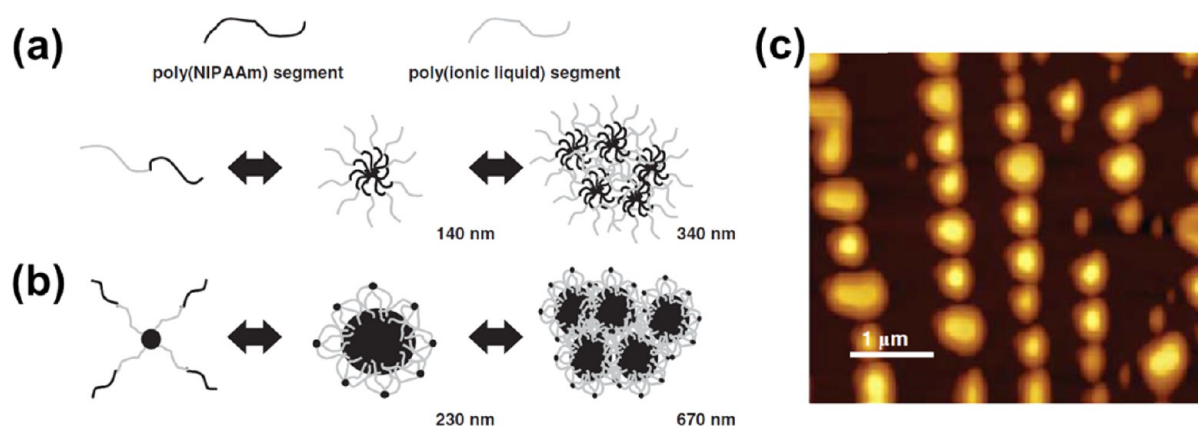
Figure 14. (a) Self-assembly of linear PNIPAM-PIL block copolymer in aqueous solution. (b) Self-assembly of stimuli-responsive star PNIPAM-PIL block copolymer in aqueous solution. (c) AFM topographical images of star polymer assemblies on mica. Reproduced with permission from ref 165, copyright (2012) Nature Publishing Group.
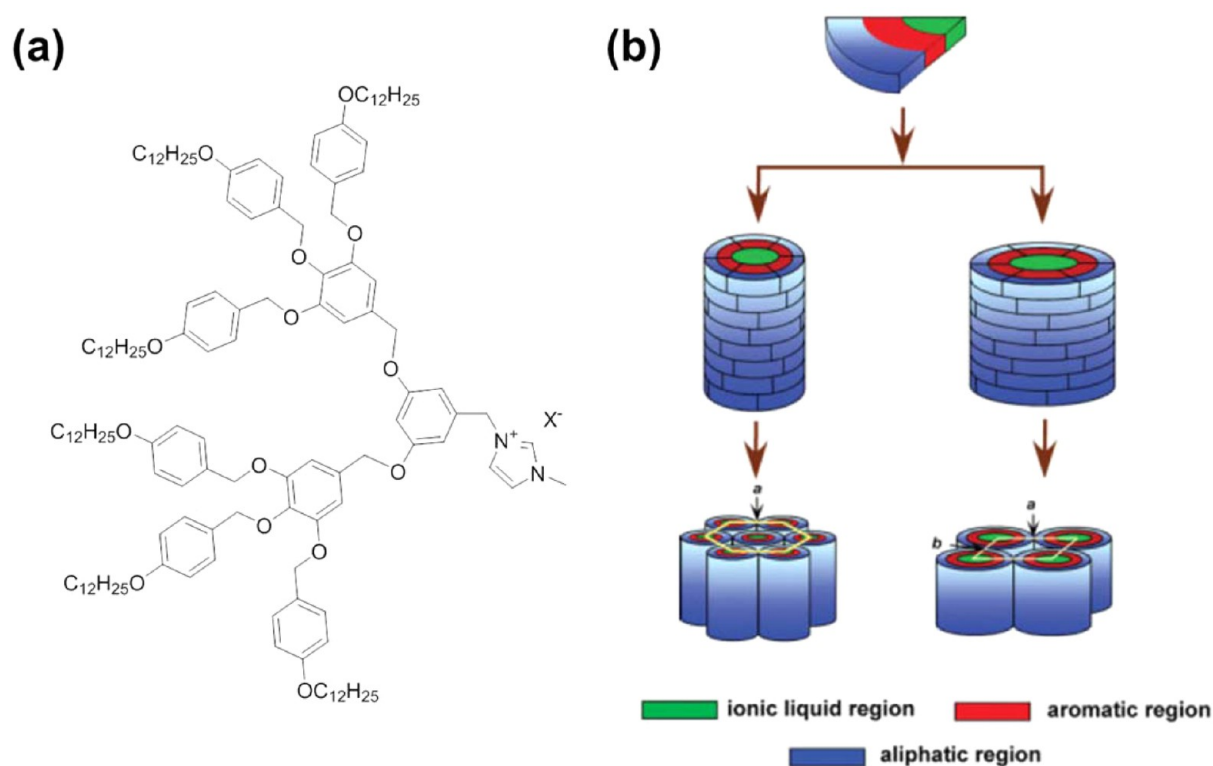

Figure 15. (a) Chemical structure of a dendritic ionic liquid with an ionic group in a focal point. (b) Columnar organization of the dendritic ionic liquids. Reproduced with permission from ref 38, copyright (2009) John Wiley and Sons.

periphery of the star. In this case, the stimuli-responsive self-assembly behavior was demonstrated by controlling the temperature variation and ionic strength of the solutions (Figure 14). This behavior was also found to be dependent on the location of the thermoresponsive segment within the arms. The star block copolymer with inner PNIPAM segments exhibited rapid aggregation, forming large micellar clusters at temperatures above the LCST. The star macromolecules with an outer thermoresponsive block showed a two-step transition into small micelles at 33 °C followed by the formation of dehydrated clusters.

The morphology, particular ordering, orientation, and connectivity of conductive ionic domains play an important role in defining the ion conductivity of materials prepared from PILs. Polymer-based electrolytes or ion-exchange membranes can be prepared from block copolymers with incompatible ionophobic and ionophilic blocks. Such polymer architectures result in polymeric membranes with phase-separated morphologies and nanometer-sized pores.[187−189] Self-assembly of the ionophobic block provides the structural support, whereas the channels formed from ionophilic blocks provide a transport path for ionic species. This approach was demonstrated with dendritic compounds that formed columnar liquid crystalline phases (Figure 15).[38] The orientation of these nanoscale domains in a direction of desired ion travel can be achieved by altering the electric field or shear force directions.[190] It has been demonstrated that it is possible to tune the phase separation by using hydrophilic or hydrophobic counterions for the same

type of block copolymer incorporated into a poly(ionic liquid) block (Figure 16).[226] Furthermore, it is possible to impregnate such membranes with ionic liquids to improve their conductivity.[191]
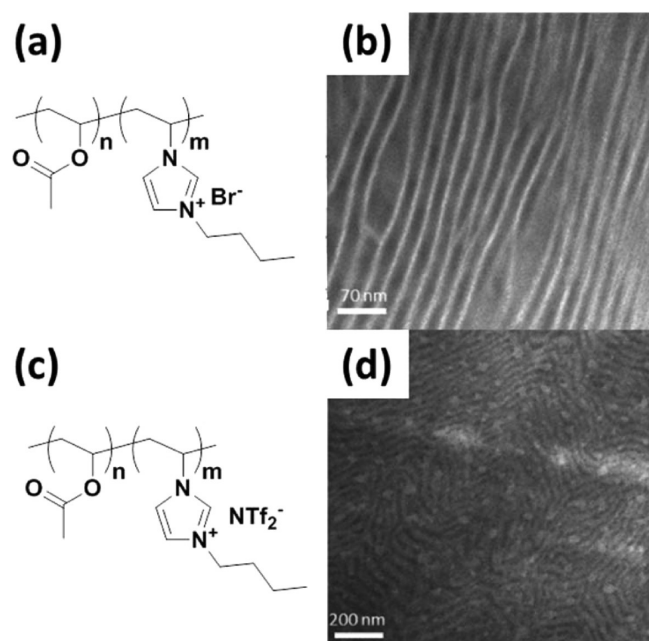

Figure 16. (a) Chemical structure of a poly(ionic liquid) with a hydrophilic anion. (b) TEM image of a thin film (c) Poly(ionic liquid) after ion exchange with a hydrophobic anion. (d) TEM image of a thin film. Reproduced with permission from ref 226, copyright (2014) American Chemical Society.

Because of their ionic nature, poly(ionic liquid) materials can be used for electrostatic LbL assembly of multilayer films. However, examples of these structures are scarce. One of the applications of such films can be in the preparation of carbon membranes doped with heteroatoms. These poly(ionic liquid)s were shown to give a high carbonization yield due to low vapor pressure (Figure 17a).[192] Furthermore, LbL films prepared from poly(ionic liquid)s may exhibit some unusual surface behavior, such as the electrowetting phenomenon. In this case, the water contact angle changes significantly when an electric potential is applied to the polymer film.[193] A poly(ionic liquid) layer can also be immobilized on different surfaces via "click" chemistry to effectively change surface properties such as hydrophobicity and wetting.[194] Effective replacement of the counterions on grafted poly(ionic liquid) films provides further possibilities for functionalizing surfaces.

Finally, Yuan et al. reported the formation of layered poly(ionic liquid) nanoparticles in aqueous solutions by precipitation polymerization (Figure 17b).[195] The latexes had dimensions between 20 and 40 nm and showed different multilammelar morphologies depending on the poly(ionic liquid) side chain length. At higher concentrations, a hierarchical assembly into worm-like mesostructures was observed.

4. EMERGING APPLICATIONS

Highly branched architectures provide many fundamental differences in the physical and chemical properties and assembly behavior of macromolecules with a high density of inner and terminal ionizable groups compared to conventional linear macromolecules. Recent efforts have focused on the synthesis and characterization of branched polyelectrolytes for understanding of their fundamental behavior from the viewpoint of traditional structure–property relationships. In recent years, because of advances in polymer chemistry, branched polyelectrolytes, including cylindrical polyelectrolyte brushes, star polyelectrolytes, hyperbranched polyelectrolytes, and polyelectrolyte dendrimers, all with a variety of complex architectures and in reasonable quantities, have become widely available. As a result, more studies now focus on exploring the highly branched polyelectrolyte macromolecules for the purposes of assembly and fabrication of functionalized soft nanomaterials with tailored properties and specific applications in mind. Some interesting recent examples will be discussed in this section.

In many cases, the complex structure of branched polyelectrolytes with well-defined inner and outer chemical compositions and typical dimensions from several to tens of nanometers make them ideal templates for the fabrication of hybrid organic–inorganic nanoparticles with interesting optical, electric, and magnetic properties. The main advantage of using branched polyelectrolytes for such applications are a high monodispersity and versatile compositions, which can be tuned for the fabrication of various complex, core–shell, hollow, Janus, or multicompartmental metal and semiconductor nanoparticles.[196] CPBs, star polyelectrolytes, and polyelectrolyte dendrimers have all demonstrated novel behavior as prospective efficient nanoreactors for the synthesis of metal nanoparticles via spatially localized chemical reduction.

In the case of drug delivery applications, branched polyelectrolytes, especially dendrimers, are able to act as nanocarriers with controlled loading and unloading abilities if their potential toxicity can be mediated. Moreover, star polyelectrolytes and polyelectrolyte dendrimers can be utilized as major components for the assembly of ultrathin microcapsules or multilayered films, which have higher loading capacities, more functionalities, and multicompartmental structures.[101,103] Furthermore, branched polyelectrolytes have also been used to modify the cell surface by forming thin shells. For example, silk fibroin with grafted poly(L-lysine) or poly(L-glutamic acid) side chains were used for cell encapsulation (Figure 18).[197] The results showed that shells assembled with polycationic amino acids adversely affected the properties of microbial cells with the formation of large cell aggregates. Excessive cytotoxicity has been noticed in many cases and should be carefully considered. Meanwhile, hydrogen-bonded shells with a high PEG grafting density were the most cytocompatible, and formed stable colloidal suspensions of individual cell encapsulates.

Because of the abundance of surface functional groups, branched polyelectrolytes are also good candidates for surface modification and can act as giant surfactant molecules. Star polyelectrolytes and hyperbranched polyelectrolytes have been shown to help the dispersion of individual carbon nanotubes and graphene oxide sheets in solution. For instance, the PS_nP2VP_n heteroarm star copolymer has been used as an effective dispersing agent for the exfoliation of graphene and the subsequent graphene shuttle between immiscible media, such as organic solvent/water and water/ionic liquid.[198] The overall exfoliation yield, including concentration, solubilization yield, monolayer percentage, and large graphene size, is among the highest observed to date using polymeric stabilizers.
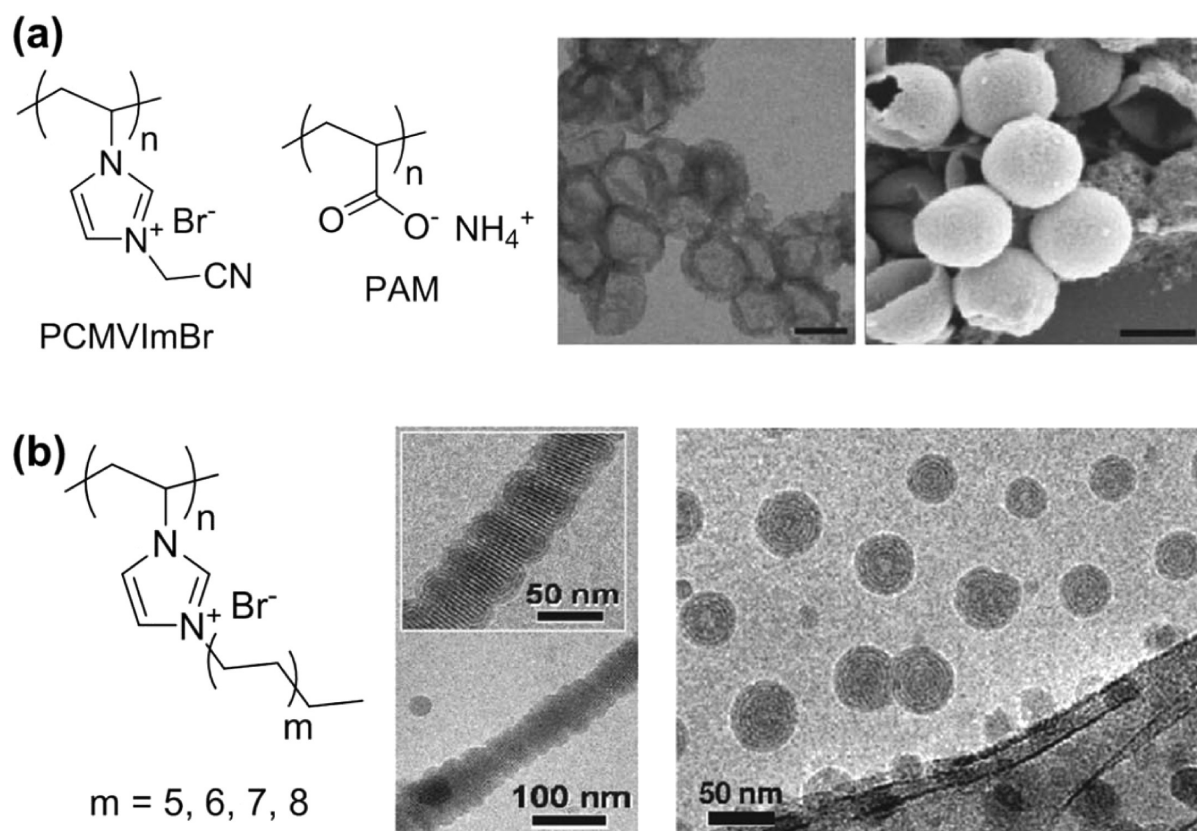
Figure 17. (a) Nitrogen-doped carbon capsules prepared by LbL assembly of poly(ionic liquid)s on silica templates. (b) Poly(ionic liquid) nanoparticles formed by precipitation polymerization from water. Worm-like morphology on the TEM image at high concentrations. Reproduced with permission from refs 192 and 195, copyright (2012, 2011) American Chemical Society.
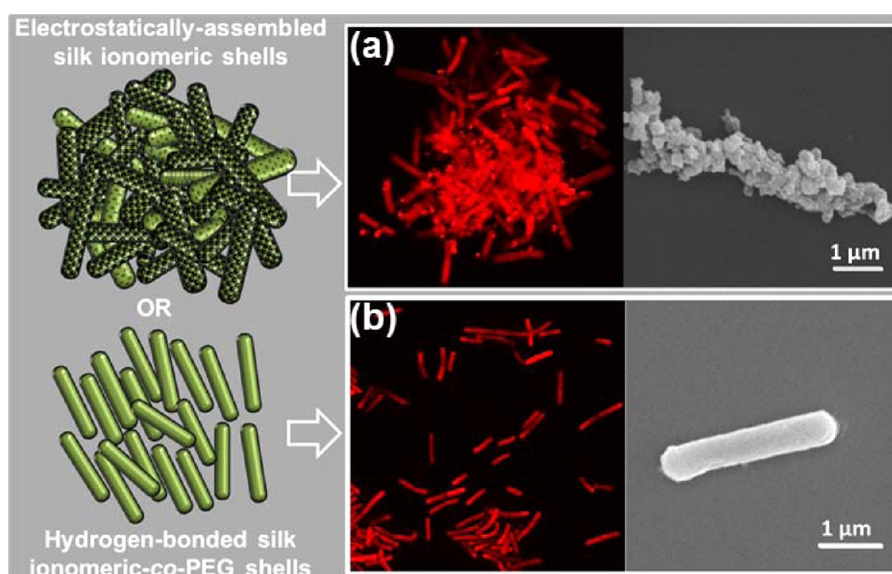

Figure 18. *B. subtilis* cells encapsulated in 4 bilayer thin shells composed of branched silk polyelectrolytes via (a) electrostatic interaction or (b) hydrogen bonding. Images on the right are confocal microscopy and SEM, respectively. Reproduced with permission from ref 197, copyright (2015) American Chemical Society.

Conjugated branched polyelectrolytes also have the potential for energy harvesting and storage, sensing, and detection applications. They can also be used for applications in cell imaging and the detection of biological species and metal ions. However, these developments are currently limited. In a few examples, hyperbranched conjugated polyelectrolytes have been used as an energy and charge transport material for hybrid solar cells. For instance, Liu et al.[199] reported the synthesis of a gadolinium ion-chelated hyperbranched conjugated polyelectrolyte (HCPE-Gd) that has an average hydrodynamic diameter of 42 nm and a quantum yield of 10% in aqueous solution. The HCPE-Gd can be internalized in
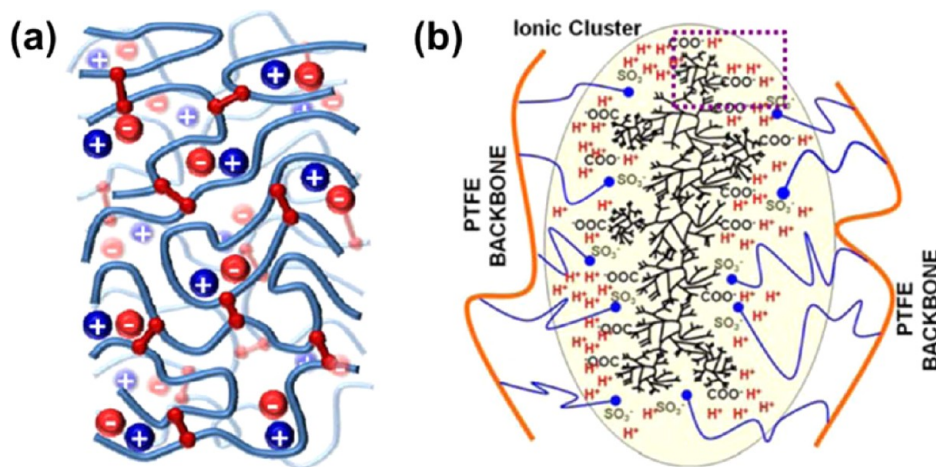
Figure 19. (a) Cross-linked polymeric membrane impregnated with an IL component. (b) Nafion PEM impregnated with a carboxylated hyperbranched polymer. Reproduced with permission from ref 191, copyright (2013) John Wiley and Sons, and ref 227.

cancer cell cytoplasm with good photostability and low cytotoxicity. It can also serve as an efficient dual-modal imaging nanoprobe for in vivo cancer diagnosis.

The controlled self-organization of highly branched polyelectrolytes and poly(ionic liquid)s through ionic-driven self-assembly can facilitate the construction of ordered, nanosized network architectures for solid ionic conductive materials. Specifically, branched poly- and oligo(ionic liquid)s with high charge densities and large counterions are promising materials for the fabrication of ion-conductive membranes and solid-state electrolytes with tailored ionic transport properties. These ionic materials combine good mechanical stability with intrinsic advantages of ionic liquids, such as high chemical stability, low vapor pressure, nonflammability, and potentially high mobility and ionic transport.[200] For these materials, the ionic mobility and conductivity increases as the free volume and porosity increase and the glass transition temperature decreases. The branched polymers possess a high concentration of free chain ends and, therefore, generally have more free volume than their linear counterparts combined with a lowered glass transition temperature.[201]

The positive effect of a branched macromolecular architecture on ionic conductivity was confirmed for PEG-based molecules by observing higher ionic conductivity of star and hyperbranched polymers than those of their linear analogues.[202,203] These unique properties of branched poly- and oligo(ionic liquid)s make this family of macromolecules a promising candidate, in combination with other nanoparticles, for use in optoelectronic devices such as anhydrous ion-conducting electrolytes for various electrochemical devices, in separation processes for component encapsulation and dispersion, for interface-controlled catalysis, and for nanoreactors for nanoparticle preparation.

Because frequently exploited functionalized POSS cores with IL groups are capable of controlled self-organization, they are promising candidates for ion conductive materials. Such POSS-based dendrimers were synthesized with PF_6^- and TFSI-anions as well and are the first examples of imidazolium salt-terminated POSS-based dendrimers.[159] The reaction of octasilane POSS with N,N-dimethylallylamine yields a branched spherosilicate-type POSS with tertiary nitrogen atoms in the outer shell with various densities of terminal IL groups.[156]

The antimicrobial activity of these compounds individually and as part of siloxane coatings was shown to be controlled by the degree of quaternization and the length of the alkyl radical. Such biocide coatings are promising as antibiofouling and fouling release applications in demanding marine environments.[158] Coatings and biocide films can also be prepared by sol−gel condensation of 3-(N,N-dimethylalkyl)-propyltreemetoxysilane with ologosiloxane diol and triacetoxy-(methyl)silane.[204]

The interesting properties of POSS-containing oligo(ionic liquid)s, such as their low melting temperature and high ion conductivity, enable the use of these ionic materials as electrolytes in various electrochemical devices, such as solar and fuel cells[155] and as ionic self-assembly platforms, IL fillers, antimicrobial additives,[204,205] solvents for polysaccharides, and other poorly soluble materials, surface modifiers, and carriers for heterogeneous catalysis. In addition, it was reported that the dendritic PAMAM derivatives with a POSS core and imidazolium end-functionalities are candidates for the construction of ordered networks for solid ion-conductive materials.[159]

Recently introduced poly- and oligo(ionic liquid)s are promising for the fabrication of ion-conductive membranes with good mechanical stability. Solvent-free electrolyte materials are necessary for the development of new technologies related to energy production, storage, and conversion. The high operational temperature of traditional proton-exchange membranes (PEM) used in fuel cells is desirable due to faster reaction kinetics and a higher stability of platinum catalysts at these conditions. For instance, Nafion membranes have to be hydrated and therefore have an operation temperature limited by the boiling point of water. One possible approach is to impregnate the proton-conducting membranes with high boiling point protic solvents. However, these materials are quite corrosive and flammable. Some examples of the utilization of ionic liquids with low vapor pressure show ion conductivity with the IL component acting as a plasticizer for the polymeric membrane and assisting the charge transport (Figure 19a).[191]

Generally, for fuel cell applications, it is necessary to achieve high proton transference numbers. It was shown that, when used in the absence of water, the ionic liquids based on quaternary amines without acidic protons provide unsatis-
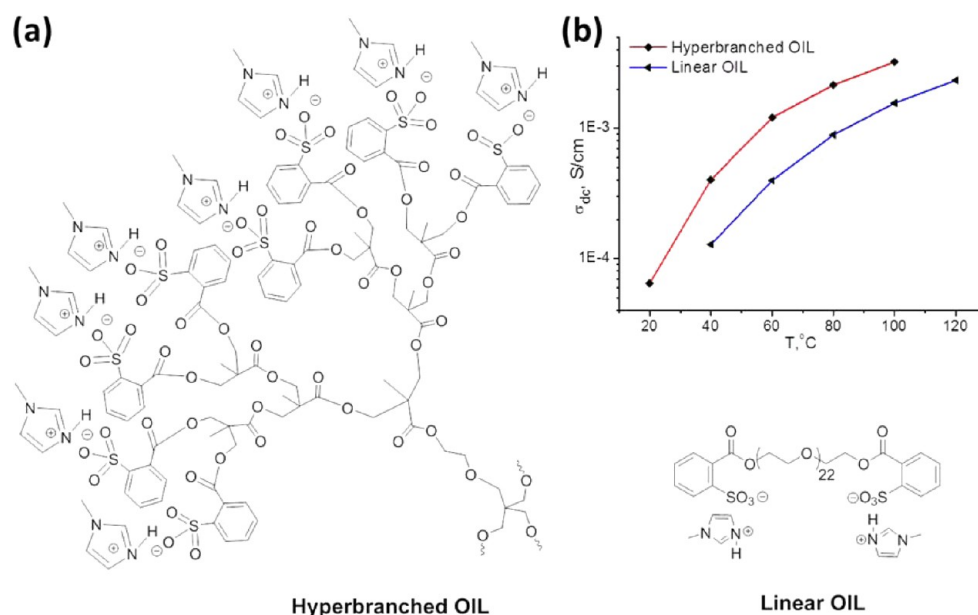
Figure 20. (a) Chemical structures of protic linear and hyperbranched sulfonate OILs. (b) Temperature dependence of the ion conductivity of OILs. Reproduced with permission from ref 174, copyright (2014) Elsevier.

factory results, whereas the imidazoles with an acidic proton are more prospective additives.[206] However, the low molecular weight ionic liquids have a tendency to leak out of the membrane, making practical applications difficult. In additional to potential deprotonation, material leaking leads to the possibility of evaporation of ionic liquids.[207] The impregnation of the polymeric matrices and existing ion-exchange membranes with oligomeric or polymeric ionic liquids provides a way to improve the performance of the devices while maintaining their durability. Recently, Nazir et al. achieved an improved performance of a commercially available Nafion membrane in anhydrous conditions by impregnating it with a hyperbranched polymeric network containing carboxylic groups.[227]

Large organic counterions can dramatically reduce the melting point of ionic liquids compared to inorganic salts. However, poly(ionic liquid)s are mostly solids, and despite lower glass transition, the restricted chain mobility leads to low conductivities of purely poly(ionic liquid) membranes. In this respect, oligo(ionic liquid)s with molecular weights around several thousand grams per mol may provide higher chain mobility than traditional high molecular weight PILs. Moreover, better retention properties facilitate higher membrane stability. With this approach in mind, Shevchenko's group recently suggested an alternative route in which the cross-linked membrane was doped with a branched POSS-OIL compound bearing sulfo groups.[208] The synthesized membranes were thermally stable up to 219 °C, and maximum values of the ionic conductivity of 1.03×10^{-4} S cm^{-1} were attained at 120 °C under anhydrous conditions with a dopant concentration of 50%.

Another example of ion conductive materials was reported with hyperbranched protic and aprotic anionic oligo(ionic liquid)s (Figure 20a).[174] The structure, thermal stability, and ionic conductivity of the synthesized, predominantly amorphous, compounds in the range of 20−120 °C in anhydrous conditions were governed by the molecular architecture of the oligomeric chains and the type of cation/anion moieties. The ionic conductivity of the synthesized oligo(ionic liquid)s varied over a broad range, reaching 10^{-3} S cm^{-1} at temperatures over 100 °C (Figure 20b).

A synthesis method for linear cationic oligo(ionic liquid)s with thermal stability up to 200−270 °C (oligo(ester urethane)s) with segmented structuring) has also been proposed.[209] The flexible segment of these compounds is oligo(ethylene oxide) with a molecular weight of 1000, and the hard urethane-urea segments are formed from diisocyanate and amine derivatives of nitrogen heterocycles: 1-(3-aminopropyl)-imidazole, 2-aminopyridine, and 2-amino-3-methylpyridine neutralized with ethanesulfonic acid and p-toluenesulfonic acid. The type of cation has a significant effect on proton conductivity in the temperature range of 80−120 °C under anhydrous conditions. Imidazolium and pyridinium oligo(ionic liquid)s show conductivities of $\sim 10^{-4}$ S cm^{-1}; for 3-methylpyridinium OILs, their conductivities are significantly lower. The synthesized oligo(ionic liquid)s are being investigated as prospective ion-conducting media in various electrochemical devices, such as for proton-exchange membranes for fuel cells and anhydrous lithium power sources.

5. CONCLUSIONS

Branched polyelectrolytes and poly(ionic liquid)s possess significant advantages for molecular assembly. First, branched polyelectrolytes do not aggregate as easily as their linear counterparts. They can form more ordered and labile phases in solution and at interfaces due to their compact shape. Second, branched polyelectrolytes with multiple functionalities and enhanced noncovalent interactions enable rich and responsive assembling behavior. Third, polyelectrolytes with branched structures frequently behave as well-defined soft three-dimensional objects. Their higher-order assembled structures usually have hierarchical, compartmentalized structures, which are very desirable in applications such as drug delivery, controlled transport, and self-healing.

Despite the significant prospects for practical applications of branched polyelectrolytes, there are still several major

challenges to be overcome in order to make major successful progress. First, the supramolecular assemblies demonstrated for branched polyelectrolytes are still not as diverse as assemblies formed from linear polymers. For instance, complex helical or cubosome structures have yet to be discovered for branched macromolecules. Second, the assembly process of branched polyelectrolytes is still not easily controllable, although this is a common problem for noncovalent bond driven assembly of flexible macromolecules, and the stability of the assembled structures is questionable in some cases. Third, sophisticated theoretical understanding of the assembly process is still lacking due to the complexity of interactions and conformations for theoretical considerations.[210] Lastly, it is critical to scale up the synthesis and assembly and to reduce the polydispersity of the molecules and assemblies.

The field of poly(ionic liquid)s has been growing at a fast pace over the past decade. The research focus, however, has mostly remained on low molar mass ionic compounds and linear polymers with side chain ionic liquid groups. Thus, the majority of branched macromolecular ionic liquid analogues reported to date are represented by branched polymers with modest molecular weights or cross-linked networks and latexes with poorly defined molecular characteristics. The same is true for branched PILs with ionic groups in the backbones, which usually result in insoluble materials.

These issues make it difficult to gain a fundamental understanding of the architectural peculiarities of macromolecules bearing ionic liquid functionalities. It can be expected that systematic structure−property studies that would involve extended libraries of macromolecules with fixed ionic groups and monomer types but different polymeric architectures will ultimately result in the discovery of new practical materials with finely tuned nanostructures, mechanical properties, interfacial behavior, and tunable ionic conductivity.

Overall, attention is primarily focused on branched poly- and oligo(ionic liquid)s bearing imidazole- and aliphatic amine-based ionic groups as far as cationic macromolecules are concerned. Yet a number of novel poly(ionic liquid)s bearing other heterocycles, such as pyrazoles, triazoles, oxazoles, and thiazoles that can be quaternized are steadily increasing.[211] In this respect, a recent report from Mori et al. on the synthesis of branched triazole-bearing polymers is encouraging.[212] Because of their ionic nature, the solubility of poly(ionic liquds) in common organic solvents is often limited and restricts their wide applicability. This issue complicates precise characterization of synthesized poly- and oligo(ionic liquid)s and, in particular, an accurate molecular weight determination. This challenge was recently addressed in a report by He et al. who disclose a novel GPC procedure that employs an eluent with organic anionic additives, such as Tf_2N^-, BF_4^-, and PF_6^-, to characterize poly(ionic liquid)s with high reliability.[213] As was highlighted in section 3.6, the number of reports on solution and interfacial assembly is rather low, considering the wealth of literature on conventional branched polyelectrolytes. Such assemblies are discussed mostly for dendritic molecules bearing different types of ionic groups and lipophilic groups in a focal point and at the periphery. Achieving robust and high-yielding synthetic methodologies is critically important and might explore not just conventional synthetic routines but also click chemistry protocols.[214,215]

To conclude, we envisage that, in the near future, noncytotoxic dendrimers will find applications in drug and gene intracellular delivery.[216] Low-cost and well-defined hyperbranched polymers can be utilized for reinforcing or plasticizing composite polymeric materials. Cylindrical brushes and asymmetric stars can form organized complex mesophases with three-dimensional conjugation. Truncated poly- and oligo(ionic liquid)s with proper counterion selection can be further explored as solid ionic materials with controlled ionic transport.

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Notes
The authors declare no competing financial interest.

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