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SUPRAMOLECULAR NANOSTRUCTURES OF LUMINESCENT ORGANOBORON POLYMERS

by

FEI CHENG

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ABSTRACT OF THE DISSERTATION

SUPRAMOLECULAR NANOSTRUCTURES OF LUMINESCENT ORGANOBORON POLYMERS

by Fei Cheng

Dissertation Advisor: Professor Frieder Jäkle

Over the past several decades, organoboron compounds have been widely studied with respect to applications as reagents in organic synthesis, Lewis acid catalysts, luminescent materials, chemical sensors, ceramic precursors and nuclear detectors. Besides the basic physical and chemical properties, materials for most practical applications require favorable processing characteristics. Polymeric materials are advantageous in this respect and especially, self-assembled functional polymeric nanostructures are promising for the development of new optical, electronic, biological and energy-related materials. Therefore, research on the synthesis and properties of well-defined boron-containing polymers is an emerging area that has drawn great interest of chemists and material scientists.

This dissertation describes a "molecule-polymer-material" bottom-up methodology for the fabrication of nanostructured materials based on luminescent organoboron polymers. A series of novel organoboron monomers with tunable photophysical properties and excellent stability were developed via efficient organic and organometallic reactions. Using reversible addition-fragmentation chain transfer (RAFT) polymerization, well-defined luminescent organoboron homopolymers and block copolymers with controlled molecular weight and narrow molecular weight distribution were successfully synthesized. Corecrosslinked star polymers with a luminescent boron quinolate core were also achieved by "arm-first" RAFT polymerization of a difunctional boron quinolate crosslinker.

These block copolymers and star polymers serve as versatile building blocks for nanostructure fabrication. In selective solvents, the block copolymers and star polymers form self-assembled nanostructures, such as micelles, vesicles, large spherical and spindleshaped aggregates. By introducing pyridine-functionality onto the block copolymer structure, luminescent polymeric Lewis bases were synthesized and utilized for the preparation of polymer/inorganic co-assembled nanostructures. The borinic acid functionalized block copolymers act as effective H-bonding donors that form supramolecular co-assemblies with poly(4-vinylpyridine) (H-bonding acceptor). Triarylborane compounds and polymers have been utilized as chemical sensors for toxic anions, such as fluoride and cyanide. Through rational polymer architecture design, we synthesized a series of dimesitylphenylborane-functionalized polymers, including homopolymer, block copolymer and block-random copolymers, for F⁻ binding studies. For the first time, (1) we elucidate the chain-architecture effect on F⁻ binding and observed amplified fluorescence quenching for the homopolymer structure; (2) a dual responsive chemical sensor for F^{-} was developed based on the block copolymer micelles in DMF, that F^{-} binding leads to the fluorescence quenching and the dissociation of block micelles; (3) the positively charged block-random copolymer was found to be an effective F⁻ sensor in polar solvents, such as DMF and DMF/water mixture, due to the electrostatic interaction.

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Chapter 1 General Introduction: Boron-Containing Polymers as Versatile Building Blocks for Functional Nanostructured Materials^[a]

Bottom-up self-assembly of polymers, especially block copolymers, has been established as a powerful method for fabrication of nanostructured materials. With precise design and synthesis of polymeric building blocks and optimization of the self-assembly process, the size and morphology of self-assemblies can be controlled on the nanoscale.¹ As a result, specific functional groups in the polymer building blocks can be placed at well-defined positions in the self-assembled nanospace. These are very important requirements for practical applications of functional polymers in solution, thin film and solid state.²

An attractive new class of polymers receiving more and more interest recently contains boron functional groups as an integral part.³⁻⁵ Boron is positioned just to the left of carbon in the periodic table and therefore contributes one less electron to its compounds. This leads to a number of interesting characteristics, including a tendency of tricoordinate boron species to act as Lewis acids toward a broad range of electron-rich substrates as well as to form conjugated π -systems that are often strongly colored and highly luminescent.^{6, 7} Moreover, boron-containing compounds undergo a nuclear reaction upon exposure to neutrons, for which the ¹⁰B isotope has an exceptionally large cross-section. Thus, boron-containing polymers are promising for applications as supported catalysts, luminescent materials, biological imaging agents, chemical sensors and neutron detectors, stimuli-responsive materials, and as ceramic precursors.³⁻⁵

[a] This chapter is adapted from a journal publication (ref. 72)

Taking advantage of the impressive achievements of controlled/living polymerization techniques,⁸ over the past several years the first boron-containing polymers with more complex architectures have emerged. In this chapter, we will highlight these new developments with a focus on the synthesis of boron-containing polymers of controlled architecture, their self-assembly in solution and bulk state, and their applications as new functional nanostructured materials. The discussion will cover different classes of polymers with functional groups ranging from boronic acids to ionic borates, borane and carborane clusters, and π -conjugated organoborane chromophores.

1.1 Boronic Acid-Containing Polymers

It is well known that boronic acids can reversibly bind to sugars and other 1,2- or 1,3diol compounds.⁹ As illustrated in Figure 1-1 for phenyl boronic acid $(pK_a \sim 9)^{10}$ as a simple example, in basic solution, the boronic acid group reacts with a diol, forming a boronic ester with a 5 or 6-membered ring. Neutral or acidic conditions typically result in hydrolysis of the boronic ester. On the other hand, in anhydrous organic solvents or in the presence of a Lewis base, trimerization leads to reversible formation of a boroxine ring with release of three water molecules.¹¹



Figure 1-1. Boronic ester and boroxine formation.

Polymers that contain boronic acid groups have a similar ability to bind to sugars and glycoproteins, and hence they have been extensively applied as supports in separation science and in the biomedical field.³ Successful introduction of boronic acid groups into block copolymer architectures on the other hand could open up new opportunities as a result of their self-assembly behavior. For instance, micellar or vesicular assemblies of boronic acid block copolymers are promising candidates for use in drug delivery vehicles and therapeutic agents. Boronic acid polymers are also expected to serve as versatile building blocks for stimuli-responsive self-assembled materials, given that boronic acids are weak electrolytes, whose solubility and charge state can be reversibly switched by pH changes. A challenge is, of course, to find suitable synthetic methods for the preparation of well-defined boronic acid-containing block copolymers. The reactive boronic acid groups tend to be incompatible with conventional living polymerization techniques, and in some cases, the direct polymerization of boronic acid monomers has been reported to result in cross-linked gels.¹² To address these issues, boronic ester-containing polymers have been synthesized as precursors, whose deprotection gives the targeted boronic acid-

containing polymers. More recently, the direct synthesis of boronic acid-containing polymers has also been realized by reversible addition-fragmentation chain transfer (RAFT) polymerization.



Figure 1-2. Synthesis of boronic ester block copolymer.¹³

The first well-defined boron-containing block copolymer was reported by our group in 2005 (Figure 1-2).¹³ Using atom transfer radical polymerization (ATRP), 4pinacolatoborylstyrene was polymerized to give a product with narrow molecular weight distribution (PDI < 1.1). Chain extension with styrene led to a narrow block copolymer without any detectable amount of macroinitiator precursor or thermo-initiated polystyrene. ATRP of 4-pinacolatoborylstyrene with a poly(ethylene glycol) macroinitiator was more recently reported by the van Hest group.¹⁴ After deprotection of the pinacol ester group, the amphiphilic block copolymer poly(ethylene glycol)-*b*-poly(styrene boronic acid) (PEG-*b*-PSBA) was obtained. Vesicles were generated via co-assembly of PEG-*b*-PSBA / PEG-*b*-PS in water (Figure 1-3). When the PSBA weight fraction is lower than 10%, the PSBA forms evenly distributed domains in the continuous PS matrix. The PEG-*b*-PSBA can be removed from the vesicles by sugar binding at high pH, forming a permeable membrane. The vesicles were loaded with *Candida Antarctica* Lipase B (CALB), and used as nanoreactors for the hydrolysis of *p*-nitrophenyl acetate. The permeability and catalytic activity of these nanoreactors can be tuned through changes in the weight fractions of PSBA in the precursor.



Figure 1-3. Proposed formation of vesicles with a permeable membrane. CALB (*Candida Antarctica* Lipase B) is incorporated into vesicles formed upon co-assembly of PEG-*b*-PSBA and PEG-*b*-PS in water. Addition of sugars leads to release of PEG-*b*-PSBA, which results in formation of permeable vesicles allowing substrates to enter and products to exit. Note that the PEG segments (blue) forming the outer layers of the vesicles are omitted in the schematic drawings.¹⁴

An alternative method for the preparation of boronic acid-functionalized block copolymers takes advantage of the selective exchange of the trimethylsilyl groups in species ArSiMe₃ with BBr₃.¹⁵ The amphiphilic block copolymer, poly(styreneboronic acid)-*b*-polystyrene (PSBA-*b*-PS) was obtained via silicon-boron exchange and subsequent hydrolysis as illustrated in Figure 1-4.¹³ The pH, and solvent-dependent self-assembly of the block copolymer were studied by transmission electron microscopy (TEM) and dynamic light scattering (DLS).¹⁶ At high pH (0.1 M NaOH), the block copolymer forms spherical micelles ($<D_h> = 18$ nm) of high interface curvature, due to strong electrostatic repulsion of the ionic R-B(OH)₃⁻ groups (Figure 1-5, left). In contrast, at lower pH (0.001 M NaOH), the coexistence of neutral boronic acid groups RB(OH)₂ reduces the curvature and leads to short worm-like structures ($<D_h> = 35$ nm). In

acetone/water and THF/water mixtures, other morphologies, including vesicles and larger compound micelles could also be realized (Figure 1-5, right).



Figure 1-4. Synthesis of boronic acid block copolymers by post-modification.¹³



Figure 1-5. Self-assembled structures of PSBA-*b*-PS block copolymer in different solvents.¹⁶

The Sumerlin group first introduced RAFT polymerization as a tool for the preparation of boron-containing polymers.¹⁷ A trithiocarbonate chain transfer agent (CTA) was used to control the polymerization of 4-pinacolatoborylstyrene. In the second step, the chain extension with *N*,*N*-dimethylacrylamide (DMA) afforded well-defined block copolymers. To generate the boronic acid block copolymer, the pinacolato ester group was

quantitatively removed in a transesterification process that involved passing the polymer through a boronic acid-immobilized column.

Although boronic acid-containing polymers can be obtained by deprotection of boronic ester precursors, the direct polymerization of boronic acid monomers offers advantages such as lower cost and simpler operation. In more recent work, Sumerlin and co-workers directly polymerized the boronic acid monomer, 3-acrylamidophenylboronic acid (APBA) by RAFT polymerization and also prepared block copolymers with poly(N,Ndimethylacrylamide) (PDMA) and poly(N-isopropylacrylamide) (PNIPAM) as the second block.^{18, 19} The PAPBA block establishes a pH-responsive equilibrium between neutral hydrophobic boronic acid and anionic hydrophilic boronate groups. The PAPBA polymer is also able to reversibly bind to diols, forming water-soluble ionic boronate ester species. Thus, in aqueous solution at high pH, the block copolymer is molecularly dissolved, whereas micelles with a PAPBA core and PDMA or PNIPAM shell form when the pH is below the pK_a . Upon addition of glucose to the micelle solution at relatively lower pH, the micelles dissociate into single chains with formation of soluble boronate ester groups. For the PAPBA-b-PNIPAM block copolymer, temperature changes can be used as an additional stimulus. When the LCST (lower critical solution temperature) of PNIPAM is reached, the block copolymer self-assembles into micelles with a PAPBA shell and PNIPAM core (Figure 1-6). This multi-responsive behavior (pH, sugar, and thermal response) was monitored by DLS. Of particular interest is that the self-assembly of the block copolymers can be exploited for detection of sugars, where the sugar binding is visualized by disappearance of the light scattering that is characteristic of selfassembled micelles.



Figure 1-6. Self-assembly of PAPBA-*b*-PNIPAM in response to pH, sugar and temperature.¹⁹

To enable applications of boronic acid polymers under physiological conditions, sugar binding has to occur at neutral pH. Toward this end, the van Hest group introduced a styryl monomer with a dialkylaminomethyl group adjacent to the boronic acid group (Wulff-type boronic acid).²⁰ Lewis acid-base interaction between B and N lowers the pK_a of the boronic acid, which favors sugar-binding at neutral pH. A block copolymer containing such a boronic acid-functionalized block in combination with a hydrophilic poly(ethylene glycol) (PEG) block was synthesized by RAFT polymerization using a PEG-based CTA (Figure 1-7). In a buffer solution at neutral pH, the block copolymer micelles dissociate upon binding to monosaccharides.



Figure1-7. Sugar-binding to a Wulff-type boronic acid-containing block copolymer at neutral pH.²⁰

Formation of borate and boronate ester links was also employed for surface coating, colloidal flocculation, and charging of the surface of colloidal particles.²¹⁻²³ The Pelton group used phenylboronic acid-modified polyvinylamine (PVAm) to laminate cellulose films.²¹ The greatest adhesion was achieved at high pH with 150 kDa PVAm, with 16% of the amine groups bearing phenylboronic acid groups. In other work, they deposited polyol-stabilized PS latex particles on a boronic acid-derivatized regenerated cellulose surface.²³ The deposition relies on the formation of boronate ester linkages. This process is reversible and the deposited particles can be released at pH 4. These reversible surface modification based on borate and boronate ester formation provide an economical and convenient method to create surfaces that are biocompatible, feature designed patterns and contain other functionality.

As already noted above, in anhydrous organic solvents, boronic acids can reversibly form boroxines with elimination of three molecules of water (Figure 1-1). Besides their more traditional applications, such as in flame retardants and as dopants for lithium ion batteries, recently, boroxine formation has been used to construct supramolecular tri-arm star polymers.¹¹

The successful synthesis of telechelic boronic acid polymers is a key step in the preparation of boroxine-centered star polymers. Several methods have been developed. We used a silylated ATRP initiator to synthesize telechelic PS; silicon-boron exchange and subsequent hydrolysis gave the respective boronic acid-terminated polymer.²⁴ Sumerlin and co-workers introduced RAFT polymerization with a boronic acid-functionalized CTA.²⁵ The tri-arm star polymer with a boroxine core was then generated either by azeotropic distillation in an organic solvent²⁴ or by addition of a base²⁵ such as

piperidine. When no base was added, the presence of water led to facile dissociation back into the boronic acid-terminated linear polymers. Similarly, in the case of the respective ditelechelic polymers, a cross-linked polymeric network can be generated reversibly.²⁴

Very recently, the Iovine group demonstrated that boronic acid-terminated polycaprolactone (PCL) polymers can be prepared by ring-opening polymerization with a pinacol-protected initiator.²⁶ The hydroxyl end group of PCL was then converted to an azide group, and further modified with various functional groups, such as phenyl, pyridyl, phenyl boronic ester and zinc porphyrin. Deprotection of the pinacol ester led to a boronic acid group at the other end of the polymers. Star polymer formation was again achieved by addition of either pyridine or 7-azaindole as a Lewis base (Figure 1-8). This approach allows for preparation of supramolecular star polymers with functional peripheral groups.



Figure 1-8. Functional supramolecular tri-arm star polymers via boroxine formation.²⁶

Conducting polymers that are functionalized with boronic acid groups are equally promising for applications in sensing and controlled release, and as building blocks for nanostructured materials.^{5, 27} They have the potential benefit that electrochemical methods provide another tool for signaling in sensory applications. For instance,

electrochemically polymerized poly(aniline boronic acid) (PABA) has been widely used as a potentiometric sensor for saccharides. Nanostructures based on PABA, have been prepared by in situ chemical polymerization of aniline boronic acid in aqueous HCl or in aliphatic alcohols.^{28, 29} Depending on the interaction between the boronic acid side groups and the solvents, Freund and co-workers obtained spherical nanoparticles, globular network, and nanofibers (Figure 1-9). Polymer films produced from these nanostructures maintained high conductivity and showed enhanced redox stability. In another twist, the He group used an in situ polymerization method to prepare composites based on singlewalled carbon nanotubes (SWNT), single-stranded DNA (ssDNA), and poly(aniline boronic acid).³⁰ The polymerization of 3-aminophenylboronic acid proceeded 4500 times faster in the presence of the ssDNA/SWNT composite, which was attributed to an interaction between the monomers and nanotubes. Moreover, the as-formed composites were shown to contain PABA of longer conjugation length. As a result, the composites are more stable and conductive.³¹ These boronic acid-containing conducting polymers and composites are of interest as sensors, coatings, and for flexible electronic devices.



Figure 1-9. TEM images of PABA nanostructures prepared in different solvents and after precipitation and purification, redispersed in the same solvent: Left: 0.1 M HCl, 2 h polymerization time; Right: 1-propanol 5 h.²⁸

1.2 Organoborate-Containing Polymers

While the reversible formation of anionic boronate species upon sugar binding or an increase in pH renders boronic acids hydrophilic and plays a key role in sensory applications, it is the inert nature of tetraarylborates that has led to widespread interest in these molecules as counterions to protect highly reactive organometallic catalysts, and as electrolytes in voltammetric applications and lithium ion batteries.^{32, 33} To further enhance the stability and processability and to take advantage of confinement effects, the immobilization of organoborates onto polymeric scaffolds has been pursued by direct polymerization as well as post-modification methods.

Cationic transition metal complexes play important roles in many catalytic processes and the nature of the counterion tends to critically affect the catalytic activity. For instance, metallocene complexes stabilized by weakly coordinating borate anions, e.g. tetrakis(pentafluorophenyl) borate ($[B(C_6F_5)_4]^-$), are widely used as highly active and selective catalysts for olefin polymerization.³⁴ However, the reactive surface of traditional inorganic supports, such as silica or alumina, often is not very compatible with these metallocene catalysts. To address this issue, Frechet and co-workers developed a microsphere support in which ammonium functionalities were covalently attached through modification of a Merrifield-type PS resin; $[B(C_6F_5)_4]^-$ served as the counterion.³⁵ Metallocene catalysts were then loaded onto the support by treating the borate-functionalized polystyrene beads with a toluene solution of the transition metal complex Cp₂HfMe₂. The highly swollen beads provide a catalytic environment close to that achieved in homogeneous catalysis, yet the low polarity of the interior of the beads ensures that the catalytic activity is retained. Copolymerization of ethylene and 1-hexene led to discrete spherical polyolefin beads with sizes of 0.3~1.4 mm. A conceptually different approach was taken by Uozomi, in which they covalently linked fluorinated borate moieties to PS beads for use in olefin polymerization.³⁶

While the catalyst support represents a minor component and is therefore generally retained after formation of the polyolefin products, in other catalytic processes, the ability to easily recycle a heterogeneous catalyst is the primary motivation for immobilization. Using emulsion polymerization, Mecking and Vogt and co-workers prepared submicron PS particles that contain covalently linked tetraphenyl borate groups. They loaded the particles with a cationic rhodium catalyst by ion-exchange and used them as supported catalysts for hydrogenation reactions. Very low metal leaching was observed over several recycling processes.³⁷

Our group introduced the first amphiphilic block copolymers with weakly coordinating borate groups covalently attached to the polymer, i.e. poly(styryltriphenylborate-*b*-polystyrene) (PSBPh₃-*b*-PS) and poly(styryltris(pentaflurophenyl)borate)-*b*-polystyrene (PSBPf₃-*b*-PS), via sequential ATRP and post-modification.³⁸ The counterions of the borate block can be varied by ion exchange with sodium or tetrabutylammonium halides. In selective solvents such as water or methanol, the block copolymers form spherical micelles with a PS core and poly(organoborate) corona. In contrast, in toluene, reverse micelles are obtained with an organoborate core and PS corona. The reverse micelles formed from PSBPf₃-*b*-PS in toluene were loaded with Rh by treatment with the transition metal complex [Rh(cod)(dppb)]⁺(OTf)⁻ (Figure 1-10). The uptake of the Rh complex was confirmed by TEM. These weakly coordinating organoborate block copolymers are promising as nanoreactors for catalysis.



Figure 1-10. Left: Schematic illustration of organoborate block copolymer self-assembly in toluene (X = F, H). Right: TEM image of block copolymer micelles loaded with $[Rh(cod)(dppb)]^{+.38}$

Borate functionalities have been also attached to dendrimers. For instance, Mager et al. reported a series of weakly coordinating carbosilane dendrimers with organoborate functionalities at the periphery.³⁹ The negatively charged dendrimers were used as cocatalysts for metallocene-catalyzed olefin polymerization. Ethene, propene, as well as ethene/propene and ethene/1-hexene mixtures were successfully polymerized. Importantly, the polymerizations could be performed in aliphatic solvents such as *n*-hexane, which is suitable for industrial production. Noteworthy is also that dendritic poly(pyrazolylborates) were used as scaffolds for other transition metals, such as rhodium or iridium.⁴⁰

A different application of borate-containing polymers is as electrolytes for lithium ion batteries.⁴¹ Again, the weakly coordinating nature of borates is beneficial to minimize ion pairing that tends to reduce the lithium ion mobility. Typically, ethylene glycol or ethylene oxide segments are used to further facilitate transport of lithium ions through reversible binding to the ether functionalities. As an example, the Ohno group synthesized alkylborane and boric ester-type polymer electrolytes via hydroboration and dehydrocoupling polymerization of vinyl or hydroxyl-functionalized PEO oligomers and

mesitylborane.⁴² The polymers show moderate ionic conductivities with relatively high selectivity for lithium ions. They also converted boric ester into borate-containing polymers by treatment with phenyl lithium to immobilize the ions onto the polymer chains. While the ionic conductivity of the borate type polymer was relatively low, a markedly higher lithium transference number was observed ($t_{Li^+} = 0.82-0.78$). When pentafluorophenyl lithium or naphthyl lithium was used, a one order of magnitude increase in conductivity was achieved due to the improved dissociation of the lithium borate.

To apply borate counterions in nanostructured materials that display a bicontinuous network-like morphology is a promising approach to further increase the ion conductivity. Kato and co-workers recently introduced new types of ion conductive materials based on ionic liquids showing liquid crystalline bicontinuous cubic (LC Cub_{bi}) phases (Figure 1-11).⁴³ The fan-shaped ionic liquid compounds feature an ammonium group at the focal point of the lipophilic alkylphenyl part, and a tetrafluoroborate counterion. These materials show excellent ion conductivity in the LC Cub_{bi} state, which was attributed to the presence of 3-dimensionally interconnected channel networks. The Pulsed-Field-Gradient Nuclear Magnetic Resonance (PFG-NMR) technique was used to study the self-diffusion of ions in the confined nanospace. In the Cub_{bi} state, a network of ion channels allows the anions to diffuse independently from the cations.⁴⁴ Differently, in the isotropic phase, the anions and cations form pairs and/or clusters, and thus the materials show decreased ionic conductivity.



Figure 1-11. Nano-ion channel network based on a LC bicontinuous cubic structure with *Ia3d* symmetry.⁴³

The application of borate-containing polymers as active layers for electronic devices has been explored by the Bazan group.⁴⁵ They fabricated a bilayer p-n junction by casting a cationic polyelectrolyte with fluoride counterions and a neutral conjugated polymer with dimesitylborane groups, which are known to be able to bind fluoride. An applied bias causes charge injection and fluoride ion migration from the polyelectrolyte layer to the neutral layer. Binding of fluoride to the boryl groups in the neutral layer leads to formation of the borate functionality. The original polyelectrolyte and neutral layer are therefore positively and negatively charged, respectively, leading to a p-n junction. The obtained device shows excellent light-emitting and current rectification performance (Figure 1-12).



Figure 1-12. Schematic illustration of a chemically fixed p-n junction. ⁴⁵

The above examples demonstrate the applications of borate-containing polymers in catalysis, as ion conducting materials and in electronics. All these applications take advantage of the negative charge on the borate. It is reasonable to foresee growing interest also in the charge-reverse counterpart to the borate, the cationic boronium-containing polymers and nanomaterials. We recently reported the synthesis of the first organoboronium amphiphilic block copolymers with 2,2'-bipyridine as a strong donor ligand, and examined the self-assembly in methanol and toluene.⁴⁶ The block copolymers form micellar structures in these selective solvents, and different counterions can be easily installed by ion exchange. The boronium-containing polymers are promising building blocks to construct composite materials with negatively charged dye molecules, polymers, nanoparticles, and biomolecules such as DNA.

1.3 Carborane-Containing Polymers

Borane and carborane clusters have over the years not only attracted broad interest because of their unusual 3-dimensional structure and non-classical bonding, but have also proven to be very useful building blocks for new materials. Several characteristic properties deserve special mention: first of all, the concentration of boron in these molecules is very high, making them superior candidates for applications in boron neutron capture therapy (BNCT) for cancer treatment;⁴⁷ in addition, the high stability of carborane clusters makes them suitable for high temperature and chemically inert materials.⁴⁸ Related is also the use of carborane anions as "chemical superweaklings", in which the unusual cluster bonding (3D aromaticity) leads to effective delocalization of

negative charge, thus enabling applications similar to those of weakly coordinating perfluoroarylborates discussed in the previous section.^{32, 49}

Borane and carborane cluster-containing polymers have been widely employed as precursors for boron carbide, boron nitride, and related ceramic materials.⁵⁰ Block copolymers that feature these clusters as building blocks are promising as precursors for porous ceramics, which in turn could serve as templates for nanomaterials synthesis, in gas storage and separation, and as supports for catalysts. Moreover, incorporation of carboranes into polymers and nanostructures is potentially beneficial for BNCT applications, where the size of the reagents greatly influences the ability to selectively deliver them to tumor cells. Applications as resists in microlithography⁵¹ and as materials with exceptional thermal stability are also envisioned.

In an effort at preparing nanostructured ceramic materials, Malenfant and co-workers synthesized an organic-inorganic block copolymer, polynorbornene-blockpolynorbornenedecaborane (PNB-b-PDB) via ring-opening metathesis polymerization (ROMP) of a decaborane-functionalized norbornene monomer initially introduced by Sneddon and co-workers^{52,53} Bulk self-assembly was achieved by dissolving the polymer in a good solvent followed by solvent evaporation.⁵³ Interestingly, the polymer morphology depends on the solvent: when THF is used, a hexagonally packed cylindrical morphology with PNB cylinders and PDB as continuous phase is observed, while chloroform affords a lamellar structure. Upon pyrolysis in ammonia atmosphere, thin films cast from THF form a mesoporous boron nitride structure with highly ordered cylindrical morphology. The surface area is 950 m² g⁻¹, which is the highest to date for such a material. The pyrolysis of thin films cast form chloroform in nitrogen atmosphere

leads to layered boron carbonitride/carbon ceramic composites (Figure 1-13). In a complementary approach, Sneddon and co-workers prepared nanostructured ceramic materials by using a small molecule carborane precursor, 6,6'-(CH₂)₆-(B₁₀H₁₃)₂, and alumina membranes or SiO₂ colloidal crystals as template.⁵⁴ Nanofibers, nanotubes and nanoporous materials were obtained after removal of the template.



Figure 1-13. Self-assembly of a decaborane-functionalized block copolymer into cylindrical and lamellar morphologies and subsequent pyrolysis to form porous ceramic materials.⁵³

The solution self-assembly of amphiphilic carborane-containing block copolymers was investigated by the Coughlin group.⁵⁵ An amphiphilic block copolymer precursor was synthesized by ROMP, followed by deprotection of the second block. In water, the resulting block copolymer forms micelles with a carborane core, which are promising as delivery vehicles for BNCT. Carborane-containing block and random copolymers were also synthesized via ATRP of an acrylate-type carborane monomer and a poly(ethylene glycol) monomethyl ether methacrylate (MPEGMA).⁵⁶ Both block and random copolymers.

Instead of the synthesis of carborane-containing polymers, Matejicek and co-workers fabricated complex micelles by using a boron cluster [3-cobalt bis(1,2-dicarbollide)]⁻ anion (CoD⁻) and a double hydrophilic block copolymer, poly(ethylene oxide)-*block*-

poly(methacrylic acid) (PEO-*b*-PMA).⁵⁷ Hydrogen bonding and ionic interactions between CoD⁻ and the PEO block lead to an insoluble NaCoD/PEO complex and ultimately to aggregation of the block copolymer. Nano-sized complex micelles with a PMA shell and NaCoD/PEO core were observed by light scattering and electron microscopy.

Carborane-functionalized dendrimers (star-shaped macromolecules) represent another type of material with potential applications in medicine, catalysis, liquid crystalline substances, and thermally stable materials. Adronov and co-workers incorporated carborane units into aliphatic polyester dendrimers; fourth- and fifth-generation dendrimers with multiple carborane cages were prepared.⁵⁸ Further modification of the periphery of the dendrimers with hydroxyl-terminated polyester afforded aqueous solubility. These carborane-containing dendrimers show boron neutron capture ability and thus serve as potential BNCT agents. Hosmane and co-workers developed a silicon tetrachloride mediated cyclotrimerization reaction of benzyl derivatives of carboranes to synthesize star-shaped molecules.⁵⁹ C_3 -symmetric π -conjugated compounds were obtained, in which the peripheral carborane groups reduce π - π stacking interactions and thus enhance the fluorescence quantum yields. Deboronation of the o-carboranes led to water-soluble luminescent compounds. Higher generation dendrimers with up to 81 carborane cages in the periphery were prepared by Astruc and Hosmane and co-workers, who utilized azide-alkyne "click" coupling reactions to install the carborane moieties (Figure 1-14). Formation of the carborane-functionalized dendrimers was confirmed by GPC and MALDI-TOF analysis and the hydrodynamic radius of the 81-cluster dendrimer was estimated by dynamic light scattering to be a remarkable $R_h = 12.9$ nm. The presence of the carborane moieties resulted in unusually high thermal stability.⁶⁰



Figure 1-14. Schematic drawing of a dendrimer containing 81 carborane cages. ⁶⁰

1.4 Luminescent Boron-Containing Polymers

Luminescent polymers play an important role in today's materials science, involving chemical sensors, optical and electronic devices, as well as imaging applications.⁶¹ Thousands of chromophores have been discovered and incorporated into polymeric structures over the past several decades. In very recent years, boron chromophores and luminescent boron-containing polymers have drawn particular interest, due to their facile synthesis, good stability, the broad selection of available ligands, tunable absorption and emission through the entire visible spectral window, as well as other novel photophysical

properties, such as two-photon absorption, room-temperature phosphorescence and dual emission.^{5, 7} From a structural point of view, luminescent polymers with boron chromophores in the main-chain, side-chain, or at the chain-end have been synthesized.

The Fraser group used hydroxyl-functionalized difluoroboron dibenzoylmethane (BF2dbm) as initiator to polymerize lactide.⁶² Poly(lactic acid) (PLA) polymers with a luminescent BF₂dbm end-group show interesting and unusual photophysical properties. namely, intense fluorescence, delayed fluorescence, two-photon absorption and oxygensensitive room-temperature phosphorescence (RTP). In dichloromethane solution, the polymer and initiator show similar absorption and emission. However, in the solid state, with an increase in molecular weight, the emission shifts from green to blue (507 to 443 nm). For the low molecular weight polymers, the concentration of BF₂dbm is higher in the polymer matrix, and the excited state of BF₂dbm is stabilized by chromophorechromophore interactions. On the contrary, higher molecular weight polymers having lower BF₂dbm content provide less stabilization of the excited state, and thus longer wavelength emission is observed.⁶³ Since the molecular weight can be well controlled by the polymerization time, this work presents a simple and effective color-tuning method, which can be used to generate molecular probes and sensors. In addition, because the thermal decay pathway from the triplet state is restricted by the polymer matrix, solidstate RTP was observed for BF2dbmPLA in the absence of oxygen. By using iodidesubstituted difluoroboron dibenzoylmethane (BF2dbm(I)) as initiator, (BF2dbm(I))PLA with a high phosphorescence-to-fluorescence ratio was achieved.⁶⁴

To investigate the biological applications of these polymers, Fraser and co-workers prepared boron polylactide nanoparticles (BNPs) by adding the polymer solution into water.⁶⁵ Biocompatible, water-soluble BNPs were obtained, which maintain the fluorescence, two-photon absorption and oxygen-sensitive room-temperature phosphorescence (RTP). The BNPs were successfully used to label chinese hamster ovary (CHO) cells (Figure 1-15). Taking advantage of the dual-emissive and the oxygensensitive RTP properties, they also used the (BF2dbm(I))PLA and BNPs as oxygen sensor and imaging agent for tumor tissue.⁶⁴ To enhance the stability of BNPs in biological conditions and facilitate the tumor uptake, they created complex nanoparticles with polyethylene glycol-block-poly(D-lactide) (mPEG-PDLA) and (BF2dbm(I))PLLA by coprecipitation, where the (BF₂dbm(I))PLA and PDLA block form the core of the particles and the PEG block forms a water-soluble shell that stabilizes the complex BNPs.⁶⁶ Besides, the synthesis and photophysical study of BF2dbm-terminated polycaprolactone (PCL) and PCL-PLA block copolymers were also reported.⁶⁷



Figure 1-15. Luminescence images of an aqueous suspension of BF₂dbmPLA nanoparticles (left), and fluorescence and bright field microscopy image overlay of CHO cells incubated for one hour with filtered BF₂dbmPLA nanoparticle suspension (right). ⁶⁵

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) chromophores possess high quantum yields, low rates of intersystem crossing, large molar absorption coefficients,
and good photostability. They are used as biolabeling agents and for electronic devices.⁶⁸ The Chujo group synthesized conjugated BODIPY-containing polymers via Sonagashira coupling reaction. A diiodo-substituted BODIPY and various aryl-diynes were used as building blocks (Figure 1-16).⁶⁹ Due to the π - π stacking interaction between BODIPY chromophores, the polymers form supramolecular aggregates in solution and the solid state. The π - π interactions can be modulated by using different aryl-diyne monomers, which was demonstrated by UV-vis characterization in chloroform. The π - π interactions also influence the aggregated structure of the polymer cast from THF. Weak interactions with 2,7-diethynyl-9,9-dihexyl-9H-fluorene give nano-sized particles, while stronger interactions with 1,4-diethynylbenzene as the building block result in nano-sized particles and higher-order fiber-like structures formed by aggregation of single particles.



Figure 1-16. BODIPY polymer synthesis and SEM image of polymer with building block (b) dried at room temperature for 3.0 h on a glass plate. ⁶⁹

While the BODIPY chromophore is incorporated into the polymer main-chain in the previous example, Chujo and co-workers used RAFT polymerization to synthesize poly(methyl methacrylate) (PMMA) with pendant BODIPY groups.⁷⁰ The BODIPY modified PMMA polymers were in turn used as macro-CTAs to control the polymerization of styrene. Well-defined homo- and block copolymers with BODIPY in

the side chain were obtained. The authors suggest that π - π interactions between BODIPY groups in the side chain drive the self-assembly of homo- and block copolymers. The homopolymers form micrometer-sized blubber particles or chain-like structures. For the block copolymers, the PS shell prevents the formation of large aggregates, and nanoparticles with a PS shell were observed.

Using a BODIPY modified CTA, Chujo and co-workers also prepared telechelic PNIPAM polymers with a BODIPY end group.⁷¹ In situ reduction of HAuCl₄ in the presence of PNIPAM results in gold nanoparticles (AuNPs) that are covered by PNIPAM, with the BODIPY groups located at the free end of the PNIPAM chains. The PNIPAM-coated AuNPs show thermo-responsive emission in water. Above the LCST, the PNIPAM polymers shrink towards the AuNP core. With the resulting decrease in the distance between BODIPY and AuNP core, a decreased emission from BODIPY was observed, which was attributed to fluorescence resonance energy transfer (FRET) and quenching due to BODIPY dye aggregation. The thermo-responsive emission of the BODIPY-PNIPAM modified AuNPs was reversible regardless of the number of heating/cooling cycles applied.

1.5 Summary and Outlook

In light of their potential applications in catalysis, luminescent materials, chemical sensors, electronic devices, cancer therapy and other biomedical applications, nanomaterials derived from boron-containing polymers have become a new interest of chemists and material scientists. Future research on this topic is expected to involve:

Development of new functional boron motifs: After more than a century, the chemistry of boron and its compounds is still a growing research area. Ever new boron-containing small molecules with interesting properties and functionalities are being discovered. As the selected examples in this brief review illustrate, incorporation of new boron moieties into polymers will lead to functional materials with a diverse range of desirable properties and new applications.

Polymer synthesis: Direct polymerization of boron-containing monomers and postmodification procedures have been employed to synthesize boron-functionalized polymers. While in some cases, through highly efficient modification reactions, a general polymer precursor can produce a wide range of functional boron polymers, the advantages of direct polymerization methods lie in the broad applicability to numerous types of boron monomers and the ability to more easily realize well-defined polymer structures. Especially controlled free radical and living ring-opening polymerization techniques appear to be very promising routes to new boron-functionalized polymers.

Self-assembly and materials fabrication: Polymer self-assembly in solution, thin film, and bulk state is widely used for fabrication of new materials. The examples discussed in this review demonstrate that through rational design of the polymer structure, self-assembled boron-containing materials with precisely controlled size, morphology, and functionality distribution can be realized. Besides, nanomaterial and surface chemistry are beginning to emerge as simple and efficient ways to prepare boron-functionalized nanoparticles and composite materials.

As major achievements in terms of architectural control have been realized over the past just about five years and opened up a myriad of new applications of boroncontaining polymers, this field is anticipated to attract more chemists, material scientists, physicists, and the industrial world.

1.6 Outline of the Dissertation

This Dissertation focuses on the synthesis of luminescent organoboron polymers via RAFT polymerization and their supramolecular nanostructures. In Chapter 2, I will introduce well-defined organoboron quinolate block copolymers with various functionalities, and their self-assembled nanostructures through use of selective solvents, chemical crosslinking and metal complexation. In Chapter 3, I will describe the synthesis of nanosized star polymers with a luminescent boron quinolate core via "arm-first" polymerization, and their application as building blocks for superstructures and as a scaffold for post-modification. In Chapter 4, I will discuss tricoordinate boron block copolymers with borinic acid and triaryl borane functionalities, and there applications in H-bonding induced nanostructures, composite material synthesis and fluoride ion sensing.

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Chapter 2 Luminescent Boron Quinolate Block Copolymers

Luminescent organoboron polymers have received much recent attention due to their potential use in light emitting devices, chemosensor materials, and for biomedical applications.^{1,2} A broad range of synthetic methods, including hydroboration and organometallic condensation polymerization, transition metal-catalyzed polymerization, conventional and controlled free radical polymerization, and post-polymerization modification processes have been developed, and a variety of different boron-containing chromophores have been utilized to functionalize polyolefins.³ Considering the well-known self-assembled nanostructured materials of block copolymers and the possibility for realizing stimuli-responsive luminescent behavior in solution, incorporating these organoborane chromophores into block copolymer structures is a desirable objective.

Much of the early work on boron-containing block copolymers has been directed at borane and carborane-functionalized systems for applications as precursors to nanostructured ceramic materials.⁴⁻⁶ The development of boronic acid-functionalized polymers that are responsive to changes in pH and temperature, as well as the presence of sugars and other polyols has also developed into a flourishing research field.⁷⁻¹⁰ However, only recently have the first examples of luminescent boron-containing block copolymers been reported. Chujo and co-workers applied reversible addition-fragmentation chain transfer (RAFT) polymerization to synthesize luminescent block copolymers with boron dipyrromethene (BODIPY) dyes in the side chain.¹¹ In THF, driven by π - π stacking interactions of the BODIPY groups, the block copolymers form luminescent nanoparticles with enhanced quantum efficiency. Temperature-responsive BODIPY

copolymers with dimethylaminoethyl methacrylate (DMAEMA) were introduced by Chujo and copolymers with 2-(2-methoxyethoxy)ethyl methacrylate by Liras and coworkers.^{12,13} Using a difluoroboron dibenzoylmethane chromophore-functionalized initiator for the ring-opening polymerization of lactide and caprolactone, Fraser and coworkers prepared a series of biocompatible luminescent polymers and block copolymers.^{14,15} With increasing molecular weight, the luminescence of the polymers shifts from green to blue in the solid state, which was attributed to reduced excited-state stabilization upon dilution of the chromophore. The polymers were used as bio-imaging agents to label living cells and tumor tissues¹⁶ and as a new class of mechano-responsive materials.¹⁷

In this chapter, we will discuss the synthesis and self-assembly of luminescent boron quinolate block copolymers. We chose boron quinolates as chromophores for block copolymer functionalization because of their easy synthesis, excellent stability and tunable photophysical properties. We used RAFT polymerization¹⁸ because it allows for well-defined polymer architectures with controlled molecular weights and molecular weight distribution. The synthesized boron quinolate block copolymers were employed as building blocks for nanostructures through simple self-assembly in selective solvents and other supramolecular interactions, such as coordination and chemical crosslinking.

2.1 RAFT Polymerization of Boron Quinolate Monomers: Polymerization Kinetics and Amphiphilic Block Copolymers^[a]

[a] This section is adapted from a journal publication (ref. 49)

In this section, we describe the RAFT polymerization of two new luminescent 8hydroxyquinolate-based organoboron monomers with a small molecule chain transfer agent (CTA) and PEO-macro CTAs.



Figure 2-1. Synthesis of organoboron quinolate monomers and polymers.

The organoboron monomers M1 and M2, were prepared in high yields using a series of organometallic substitution reactions (Figure 2-1). First, 4-trimethylstannylstyrene was treated with 4-*t*-butyl-1-dibromoborylbenzene. Selective tin-boron exchange led to the intermediate *t*-BuC₆H₄(St)BBr in high yield according to ¹H and ¹¹B NMR analysis of the crude product. The intermediate was directly converted into the targeted monomers by treatment with the respective 8-methoxyquinolate ligands in a facile ether cleavage reaction. Purification by column chromatography and subsequent recrystallization gave the spectroscopically pure monomers as bright yellow (M1) and orange (M2) crystalline solids. Both monomers were fully characterized by multinuclear NMR and elemental

analysis. As shown in Figure 2-2, the ¹H NMR spectra reveal the presence of the vinyl groups in the region from 5.0 to 6.7 ppm and signals characteristic of the quinolato moieties at ca. 8.5 ppm, in an integral ratio of 1:1.



Figure 2-2. ¹H and ¹¹B NMR spectra of M1 and M2 in CDCl₃.

To examine the polymerizability, we first studied the polymerization kinetics of M1 in the presence of $CTA1^{19}$ as a model system (Figure 2-1). The polymerization was conducted in anisole at 80 °C with AIBN as the initiator ([M1]:[CTA1]:[AIBN] = 33:1:0.33). Figure 2-3(A) shows the first-order kinetic plot, indicating a constant radical concentration up to 73% monomer conversion. The molecular weight of polymer PM1 increased linearly with monomer conversion (Figures 2-3(B) and (C)), and the polydispersity of PM1 remained relatively low, going up slightly from 1.12 to 1.21. Similar results were obtained from a kinetic analysis of the polymerization of M2 (Table 2-1). In both cases, the GPC molecular weights (MW) were significantly lower than the theoretical values; however, this is consistent with the marked difference between the chemical structures of PM1 and PM2 and the polystyrene (PS) standards used.²⁰ Indeed, the absolute molecular weights of purified PM1 and PM2 were determined by static light scattering (SLS) to be M_n =13500 g/mol and M_n =12900 g/mol, respectively, which is more in line with the expected MW based on the % conversion (Table 2-1). The NMR data of the products were in good agreement with those reported for polymers prepared by post-modification procedures²⁰ and were consistent with an atactic polymer microstructure.



Figure 2-3. (A) Kinetic plot for the polymerization of M1 (500 mg) in anisole (2 mL) at 80 °C; [M1]:[CTA1]:[AIBN]=33:1:0.33; (B) plot of M_n vs. monomer conversion as determined by ¹H NMR integration (vinyl signal of M1 vs anisole methyl group); (C) GPC curves for the polymerization of M1.

Table 2-1. Results for homo and block copolymerization of M1 and M2

Polymer	[M]:[CTA]:[I] ^a	$\operatorname{conv} {}^{b}$	$M_{ m n, RI}$ c	PDI _{RI} ^c	$x_{\mathrm{RI}}{}^{d}$	$M_{ m n,LS}$ e	$x_{\rm LS}^{\ e}$	$M_{ m n,th}{}^f$	$x_{ m th}/y^{-f}$
		(%)	(g/mol)			(g/mol)		(g/mol)	
PM1	[33]:[1]:[0.33]	73	5840	1.21	15	13500	34	9520	24/-
PM2	[33]:[1]:[0.33]	67	4500	1.18	9	12900	25	11400	22/-
PEO(45)-b-PM1(71)	[100]:[1]:[0.80]	71	14700	1.32	38			27800	71/45
PEO(440)-b-PM1	[100]:[1]:[0.33]	33	27900 ^g	1.10 ^g	22			32200	33/440
PEO(440)-b-PM2	[50]:[1]:[0.33]	35	31300 ^g	1.08 ^g	23			28500	18/440

^{*a*} Stoichiometric ratio of monomer:CTA:initiator (AIBN); ^{*b*} % conversion based on NMR integration (PM1, PM2, PEO(45)-*b*-PM2) or the weight of isolated product (PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2); ^{*c*} number-average molecular weight (M_n) and polydispersity index (PDI) by GPC-RI detection in THF vs. narrow PS standards; ^{*d*} x_{RI} = (M_{n,RI} – MW of PEO – MW of CTA)/MW of monomer); ^{*e*} based on GPC-MALLS detection using dn/dc of 0.194 for PM1 and 0.229 for PM2; similar results were obtained when assuming 100% sample recovery; ^{*f*} M_{n,th} = x_{th} × MW of monomer; x_{th} = ([monomer]₀/[CTA]₀) × % conversion; the degree of polymerization of PEO (*y*) is based on M_n = 2000 and M_n = 19300 of the PEO precursor given by the supplier. ^{*g*} THF / 2vol% NEt₃ was used as the eluent.

Having established reasonably good control for the polymerization of M1 and M2, we next examined the use of macroCTAs derived from mono-functional poly(ethylene oxide)²¹ (Figure 2-1). A kinetic study was performed for the polymerization of M1 using CTA2 with a low MW PEO chain (y=45; Figure 2-4). A linear increase in MW was evident, but the PDI slightly increased to ca. 1.32 and a slight low MW shoulder remained, possibly suggesting somewhat inefficient chain transfer. For the preparative synthesis of PEO-*b*-PM1 and PEO-*b*-PM2 we used CTA3 with a longer PEO chain (y=440) to ensure good solubility of the products in water. The block copolymers PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2 were successfully obtained and showed narrow polydispersities based on GPC analysis in THF with 2 vol% NEt₃ (Table 2-1). The expected boron block lengths (x_{th}) were estimated based on the isolated yield of the polymers. The data for PEO(440)-*b*-PM1 and PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2 were in reasonable agreement with those from NMR and elemental analysis.



Figure 2-4. (A) Kinetic plot for the chain extension of **CTA2** with **M1** (780 mg) in anisole (3 mL) at 80 °C; molar ratio of [**M1**]:[**CTA2**]:[AIBN]=100:1:0.8; (B) plot of M_n (from GPC vs. PS standards) vs. monomer conversion as determined by ¹H NMR integration (vinyl signal of **M1** vs anisole methyl group); (C) GPC curves for the chain extension of PEO with **M1**.

The molecular weights of the block copolymers by GPC are consistent with chain extension with the functional borane monomer, but should be viewed as qualitative, because (i) the results for the respective homopolymers suggest that the MWs by GPC relative to PS are significantly underestimated (factor 2-3); and (ii) a certain extent of polymer-column interaction cannot be fully precluded. To minimize these effects, 2 vol% NEt₃ were added to the GPC eluent for analysis of PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2.

The photophysical properties of the polymers were examined and compared with those of the monomers (Table 2-2). In THF, PM1 and PM2 show absorptions that are almost identical to those of the respective monomers. M1 and PM1 also show very similar bright green emission at $\lambda_{em} = 506$ nm ($\Phi_F = 15$ to 20%). In contrast, the emission of PM2 at $\lambda_{em} = 619$ nm ($\Phi_F = 0.2\%$) is blue-shifted by ca. 20 nm with a ca. 6-fold intensity enhancement compared to M2. This may, in part, arise from the steric effects of neighboring repeating units or from a polarity change due to embedding of the chromophore into the polymer chain.

Sample	M1	PM1	PEO(440) -b-PM1	M2	PM2	PEO(440) -b-P2
$\lambda_{abs} (nm)$	395	395	395 (391 in H ₂ O)	440	440	440 (440 in H ₂ O)
$\varepsilon (\mathrm{cm}^{-1}\mathrm{M}^{-1})$	3370			3650		
λ_{em} (nm)	506	506	506 (503 in H ₂ O)	640	619	619 (621 in H ₂ O)
$arPhi_{Fl}$ (%)	20	15	20	0.03	0.2	0.2

Table 2-2. Photophysical data of monomers and polymers in THF solution

We performed the self-assembly studies of the block copolymers in aqueous solution. The block copolymers were dissolved in THF as a common solvent, deionized water was added dropwise under stirring, and the resulting solutions were then dialyzed against deionized water for 3 days to remove THF. PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2 formed stable micelles with $R_{h,app}$ of 63 and 41 nm, respectively, according to dynamic

light scattering (DLS) analysis (Figure 2-5). The micellar solutions emit green and red light, respectively, with almost identical emission maxima as for the homopolymers (Figure 2-6). These aqueous micellar solutions were found to be stable for at least three months under ambient conditions.



Figure 2-5 (A) Size distribution histograms (intensity averaged) of PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2 in water; (B) Photographs illustrating the emission of PEO(440)-*b*-PM1 and PEO(440)-*b*-PM2 in water upon irradiation with UV light (365 nm); (C) Fluorescence microscopy image ($10\mu m \times 10\mu m$) of an aqueous solution of PEO(440)-*b*-PM1 drop-cast onto a plastic substrate ($\lambda_{exc} = 450$ nm, detected at $\lambda = 500-550$ nm). Spot size is diffraction-limited and shows correct particle location but not dimensions.



Figure 2-6 UV-visible (A) and fluorescence (B) spectra of PEO(440)-*b*-PM1 (SA1, λ_{exc} = 391 nm) and PEO(440)-*b*-PM1 (SA2, λ_{exc} = 440 nm) in water.

2.2 Boron Quinolate Block Copolymers via Sequential RAFT Polymerization ^[b]

In this section, we introduce a general and versatile approach to well-defined luminescent boron quinolate block copolymers, in which we used sequential RAFT [b] This section is adapted from a journal publication (ref. 50) polymerization to prepare a range of different block copolymers. Depending on the structure of the second monomers, the boron quinolate monomers can be polymerized in the first and/or second step.

As a model system, two different synthetic routes were used for the preparation of PSbased block copolymers as shown in Figure 2-7. In the first method, we synthesized two organoboron quinolate homopolymers (PM1 and PM2) by RAFT polymerization, which were then used as macro-CTAs to control the polymerization of styrene (Route A, Figure 2-7). The synthesis of the boron homopolymer precursors with a trithiocarbonate CTA was reported in last section. The polymerization kinetic study and GPC results of the purified polymers demonstrated good polymerization control, and low dispersity macro-CTAs were obtained. The absolute molecular weights of PM1 and PM2 were determined to be 13500 and 12900 g/mol by GPC-MALLS analysis.



Figure 2-7. Synthesis routes to PS-based block copolymers.

To synthesize the block copolymers, bulk polymerization of styrene was conducted at 70 °C with AIBN as the initiator, and PM1 or PM2 as macro-CTA. The conversion was

kept relatively low, as the styrene monomer served as the solvent for the resulting block copolymer. The GPC-RI results for the block copolymers and the corresponding precursors are shown in Figure 2-8(A) and (B). Reasonably narrow and symmetric peaks, at shorter elution times than for the homopolymers, are consistent with chain extension, indicating the effectiveness of PM1 and PM2 as macro-CTAs. Molecular weights of M_n = 32900 g/mol (PDI = 1.27) for PM1-*b*-PS and M_n = 58400 g/mol (PDI = 1.26) for PM2-*b*-PS were determined relative to PS standards. The absolute molecular weights of the block copolymers by GPC-MALLS are higher than the values from GPC-RI relative to PS standards, which is in accord with our GPC studies on organoboron quinolate homopolymers discussed in Section 2.1.²⁰



Figure 2-8. GPC overlays of block copolymers and corresponding macro-CTA precursors. (A) PM1-*b*-PS and PM1; (B) PM2-*b*-PS and PM2; (C) PS-*b*-PM1 and PS.

The ¹H and ¹¹B NMR spectra of both block copolymers are shown in Figure 2-9. In the ¹H NMR spectra, the signals of the PS blocks are clearly seen. The signals of the boron quinolate blocks are comparatively very weak, due to the much lower molecular weights relative to those of the PS blocks (Table 2-3), and they are somewhat obscured by overlap with signals of the PS blocks. Nevertheless, the NMe₂ group of PM2-*b*-PS and the ¹Bu group of each of the block copolymers are clearly observed in the respective ¹H NMR

spectra. Moreover, both block copolymers show one single peak at 7.6 ppm in the ¹¹B NMR, further supporting the presence of the boron quinolate blocks. The GPC and NMR analyses thus clearly demonstrate that well-defined PS-based block copolymers of fairly high molecular weight were obtained successfully.

Polymer ^a	$M_{ m n,\ GPC}^{ m b}$	PDI _{GPC} ^b	<i>M</i> _n , MALLS ^c	PDI _{MALLS} ^c	$M_{ m n,UV}^{ m b}$	m, n _{MALLS} ^{c,e}	m, n _{UV}
PM1 _m -1	5800	1.21	13500	1.23		34	
$PM1_m-b-PS_n$	32900	1.27	43300	1.18	45600	34, 290	34, 308
PM2 _m	4500	1.18	12900	1.25		25	
PM2 _m - <i>b</i> -PS _n	58400	1.26	64800	1.24	67900	25, 500	25, 528
PS _m -1	8130	1.16	9470	1.14		89	
PS _m -b-PM1 _n	16000	1.29	33000	1.21	28700	89, 60	89, 49
PM1 _m -2	8710	1.28	27600	1.22		70	
PM1 _m - <i>b</i> -PNIPAM _n	107200	1.27	f	f	224400 ^e	f	70, 1740
P(St-alt-MAh) _m	10400	1.28	4520	1.26		22	
P(St- <i>alt</i> -MAh) _m - <i>b</i> -PM1 _n	22400	1.34	f	f	19500 °	f	22, 38

Table 2-3. Summary of molecular weight data of organoboron quinolate block copolymers and the corresponding macro-CTA precursors

^a For the block copolymers, the block sequence corresponds to the polymerization sequence. ^b Determined by GPC-RI analysis. ^c Determined by GPC-MALLS analysis or triple-detection GPC (for P(St-*alt*-MAh)_m). ^d Based on UV-vis analysis and absolute molecular weight data for the homopolymer precursor ($\epsilon_{394} = 2460 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit of PM1, $\epsilon_{440} = 3710 \text{ M}^{-1} \text{ cm}^{-1}$ per repeat unit of PM2 ^e m and n refer to the degree of polymerization of the first and second block, respectively. ^f Not measured.



Figure 2-9. ¹H NMR spectra of PM1-*b*-PS and PM2-*b*-PS in CDCl₃. The corresponding ¹¹B NMR spectra are shown as insets.

An alternative route to PS-based block copolymers is to use PS as macro-CTA to control the polymerization of boron quinolate monomers as shown in Figure 2-7 (Route B). A narrow PS macro-CTA (PS-2, GPC-MALLS: $M_n = 9470$ g/mol, PDI = 1.14) was synthesized with AIBN and BDTB in bulk at 80 °C. The chain extension of the PS precursor with M1 was conducted in dioxane at 70 °C with AIBN as the initiator. The GPC analysis shows apparent chain extension to form a block copolymer (GPC-MALLS: $M_n = 33000$ g/mol, PDI = 1.21) with an average of 89 styrene and 60 boron quinolate repeat units (Figure 2-8(C)). However, small shoulder peaks on both the high and low molecular weight sides are apparent. The high molecular weight shoulder is likely a result of chain-chain coupling at the late stage of polymerization, while the low molecular weight shoulder could be due to incomplete chain extension of the PS precursor or retardation. It is well known that in the synthesis of block copolymers via RAFT polymerization, the chain transfer constant of the first block should be higher than (or at least comparable to) that of the second block.²² Based on the GPC results (Figure 2-8(A) and (C)), we conclude that the styrene and styryl-type boron quinolate monomers are

interchangeable in the block copolymer synthesis via RAFT, but Route A is preferable. This could be related to the sterically demanding structure and electron-rich nature of the boron quinolate monomer, which might impact the crossover step from styrene to boron quinolate as a monomer. Another reason for Route A to give better results is likely that the chain extension of PM1 can be performed in bulk styrene, whereas chain extension of PS with crystalline M1 requires the use of considerable amounts of dioxane as a solvent.



Figure 2-10. Synthesis routes to PM1-b-PNIPAM and P(St-alt-MAh)-b-PM1.

Encouraged by these results, we decided to pursue luminescent boron block copolymers, in which the second block provides additional functionality or responsive properties. PNIPAM and its block copolymers have drawn much interest due to their thermoresponsive behavior in water, which renders them useful as building blocks for selfassembly and smart materials.²³ A PM1-based macro-CTA (GPC-MALLS: $M_n = 27600$ g/mol, PDI = 1.28) was used to synthesize the block copolymer PM1-*b*-PNIPAM (Scheme 2-10(A)). Because DMF phase GPC is not suitable for the PM1 homopolymer, and THF phase GPC is not suitable for the high molecular weight PNIPAM block copolymer, we could not characterize the precursor and the block copolymer under the same GPC conditions. However, by using THF phase GPC for PM1 and DMF phase GPC for PM1-*b*-PNIPAM, and the same PS standards, the molecular weights and distributions were obtained (Table 2-3). The GPC curve of PM1-*b*-PNIPAM (Figure 2-11(A)) indicates well-controlled polymerization and the formation of a narrow, high molecular weight block copolymer.



Figure 2-11. GPC curves of (A) the PM1 macro-CTA (black) and PM1-*b*-PNIPAM (red), and (B) P(St-*alt*-MAh) and P(St-*alt*-MAh)-*b*-PM1. PM1, P(St-*alt*-MAh)-*b*-PM1 and P(St-*alt*-MAh) were analyzed in THF at 1.0 mL/min and PM1-*b*-PNIPAM in DMF 0.2% w/v [Bu4N]Br at 0.5 mL/min with PS calibration.



Figure 2-12. TEM image with uranyl acetate staining (A) and size distribution histogram (B) of PM1-*b*-PNIPAM micelles in water.

We explored the self-assembly of the luminescent amphiphilic PM1-*b*-PNIPAM block copolymer in water. A solution of PM1-*b*-PNIPAM in DMF (0.2 mg/mL) was dialyzed

against deionized water to remove the DMF solvent. Under these conditions, micelles with a hydrophobic PM1 core and hydrophilic PNIPAM shell are expected to form. The micelle solution was examined by TEM and DLS (Figure 2-12). The TEM image reveals the formation of quite regular spherical micelles with an average diameter of ca. 25 nm. An average $\langle D_h \rangle$ of 45 nm was determined by DLS, which is significantly larger than the size deduced from the TEM image, which is likely because of shrinkage of the PNIPAM corona upon deposition on the TEM substrate. The micelle solution shows good chemical and colloidal stability for at least 3 months.

P(St-*alt*-MAh) is a classic alternating copolymer which can be synthesized by conventional and controlled free radical polymerization. The reactive MAh repeating unit serves as a functional site for facile post-modification of the P(St-*alt*-MAh) polymer. Recently, the synthesis of P(St-*alt*-MAh) based block copolymers via RAFT has been pursued by several groups. Zhu *et al.* reported a one-pot procedure to synthesize P(St-*alt*-MAh)-*b*-PS using a high St/MAh ratio.²⁴ In the early stages of polymerization, St and MAh were incorporated in an alternating fashion into the living polymer chain. After the MAh monomer was exhausted, homopolymerization of styrene occurred, leading to a P(St-*alt*-MAh)-*b*-PS block copolymer. The Wooley group used RAFT-polymerized P(St-*alt*-MAh) to control the copolymerization of styrene and other styryl-type monomers.²⁵

We decided to pursue the synthesis of a luminescent block copolymer P(St-*alt*-MAh)-*b*-PM1, by RAFT polymerization (Figure 2-10(B)). As discussed above, RAFTpolymerized P(St-*alt*-MAh) is an effective CTA for styrene polymerization. Since our boron quinolate monomer M1 is a derivative of styrene, we chose P(St-*alt*-MAh) as macro-CTA to control the polymerization of M1. First, the copolymerization of styrene and maleic anhydride was carried out in dioxane at 70 °C for 3 hours with AIBN as the initiator and cumyl dithiobenzoate as CTA. The P(St-*alt*-MAh) precursor was analyzed by triple-detection GPC ($M_n = 4500$ g/mol, PDI = 1.26). The block copolymer P(St-*alt*-MAh)-*b*-PM1 ($M_n = 22400$ g/mol, PDI = 1.34) was then synthesized by AIBN-initiated chain extension with M1 in dioxane at 70 °C for 8 hours. The GPC results indicate successful chain extension.

The ¹H, ¹¹B and ¹³C NMR spectra of P(St-*alt*-MAh)-*b*-PM1 in CDCl₃ are shown in Figure 2-13. In the ¹H NMR, the broad signals of the PM1 block overlap with those of the P(St-*alt*-MAh) block. The ¹¹B NMR shows a single and symmetric peak at a chemical shift of 7.6 ppm, which is identical to that of the PM1-*b*-PS block copolymer. Based on the GPC results (Table 2-3), the PM1 block is relatively longer than the P(St-*alt*-MAh) block, hence the ¹³C NMR signals of the PM1 block are clearly seen. The GPC and NMR characterization suggest that a well-defined P(St-*alt*-MAh)-*b*-PM1 block copolymer was obtained successfully.



Figure 2-13. ¹H, ¹¹B and ¹³C NMR spectra of P(St-*alt*-MAh)-*b*-PM1 in CDCl₃; Q = quinolate carbon.

The copolymer P(St-*alt*-MAh)-*b*-PM1 lends itself to further functionalization by amidolysis of the maleic anhydride moieties.²⁶ To explore this possibility, we decided to react the block copolymer with 4-aminoazobenzene, which is expected to lead to decoration with photo-responsive azobenzene chromophores with simultaneous introduction of hydrophilic carboxylate groups. The post-modification was conducted in THF by addition of an excess 4-aminoazobenzene. Unreacted 4-aminoazobenzene was completely removed by precipitation in diethyl ether as confirmed by the absence of any sharp signals in the ¹H NMR spectrum. GPC analysis of the product in DMF / 0.2% M [Bu4N]Br revealed an apparent molecular weight of $M_n = 25500$ g/mol (PDI = 1.40) for the azobenzene-modified block polymer P(St-*alt*-AbMA)-*b*-PM1, which is slightly larger than that of the precursor P(St-*alt*-MAh)-*b*-PM1 ($M_n = 22400$ g/mol, Table 2-3). Due to signal overlap in the aromatic region, ¹H NMR did not allow us to clearly identify the polymer-attached azobenzene groups (Figure 2-14(A)). However, successful polymer modification is clearly evident from comparison of the UV-vis data (Figure 2-14(B)) with those of the respective building blocks and precursor polymers.



Figure 2-14. (A) ¹H and ¹¹B NMR spectra of P(St-*alt*-AbMA)-*b*-PM1 in CDCl₃. * denotes residual MeOH. (B) Comparison of the UV-vis spectra of P(St-*alt*-AbMA), P(St-*alt*-MAh)-*b*-PM1, and P(St-*alt*-AbMA)-*b*-PM1 in THF.

The formation of carboxylate groups upon ring-opening of the maleic anhydride moieties is expected to render the block copolymer P(St-*alt*-AbMA)-*b*-PM1 amphiphilic under moderately basic conditions. Thus, the self-assembly behavior of P(St-*alt*-AbMA)*b*-PM1 was first investigated in aq. NaHCO₃ (5 wt%). Dissolution in THF and subsequent dialysis against 5 wt% aq. NaHCO₃ initially resulted in a turbid solution, from which a precipitate formed within ca. 12 h. A TEM image of the freshly prepared solution revealed micrometer-sized, spindle-like structures (Figure 2-15(A)), which is consistent with formation of a semi-hydrophilic post-modified block P(St-*alt*-AbMA) that does not contain enough carboxylate groups to stabilize the hydrophobic PM1 block in water. To further enhance the solubility of the P(St-*alt*-AbMA) block, a mixture of THF/5% aq NaHCO₃ was used as solvent. In THF/5% aq. NaHCO₃ = 1:9, polydispersed spherical structures were observed (Figure 2-15(B)).



Figure 2-15. TEM images of P(St-*alt*-AbMA)-*b*-PM1 in (A) 5% NaHCO₃ aq., (B) THF/5% aq. NaHCO₃ = 1:9.

The photophysical properties of all block copolymers were examined by UV-vis and fluorescence spectroscopy in THF. A comparison of the absorption and emission spectra of the PS-based block copolymers is shown in Figure 2-16. PM1-*b*-PS shows absorption

and emission maxima at 394 and 505 nm, respectively. In contrast, the absorption and emission maxima of PM2-*b*-PS are red-shifted to 440 and 620 nm, respectively, as a result of charge transfer between the –C₆H₄NMe₂ substituent and the quinolate moiety.^{20,27} The other block copolymers, PS-*b*-PM1, PM1-*b*-PNIPAM, and P(St-*alt*-MAh)-*b*-PM1 show absorption and emission profiles that are almost identical to those of PM1-*b*-PS (Table 2-4).



Figure 2-16. UV-vis and fluorescence spectra of PM1-*b*-PS (green lines, $\lambda_{exc} = 394$ nm) and PM2-*b*-PS (red lines, $\lambda_{exc} = 440$ nm) in THF.

Block Copolymer	λ_{abs} (nm)	λ_{em} (nm)	Quantum yield
PM1-b-PS	394	505	0.23
PM2-b-PS	440	620	0.002
PS-b-PM1	394	505	0.19
PM1-b-PNIPAM	394	505	0.24
P(St-alt-MAh)-b-PM1	394	508	0.17
P(St-alt-AbMA)-b-PM1	355, 394	505	N/A ^a

Table 2-4. Photophysical data of organoboron quinolate block copolymers in THF

^a The P(St-*alt*-AbMA)-*b*-PM1 block copolymer shows almost identical emission at 505 nm when excited at 355 or 394 nm. Due to overlap of the azobenzene and boron quinolate absorption, the quantum yield of P(St-*alt*-AbMA)-*b*-PM1 was not determined.

The quantum yields of all block copolymers in THF were measured and the data are summarized in Table 2-4. The quantum yields for the PM1-based block copolymers are in the range of 0.17-0.24, while that of PM2-*b*-PS is much lower (0.002), which is related to the charge transfer process discussed above. It is noteworthy that the block copolymers with the organic blocks as precursors (PS-*b*-PM1 and P(St-*alt*-MAh)-*b*-PM1) exhibit ~30% lower quantum yields than polymers with PM1 as precursor block (PM1-*b*-PS and PM1-*b*-PNIPAM). A possible explanation is that the presence of the CTA end group favors non-radiative decay, when M1 is polymerized as the second block.²⁸

We further studied the effect of azobenzene modification in P(St-*alt*-MAh)-*b*-PM1. After attachment of the chromophore to the polymer, the absorption maximum of the azobenzene chromophore in THF is blue-shifted from $\lambda_{max} = 389$ nm to 355 nm, as a result of the electron-withdrawing effect of the amide group (Figure 2-14(B)). The absorption feature of the PM1 block at 394 nm is only seen as a shoulder band due to overlap with the azobenzene absorption, the molar extinction coefficient of which is much larger than that of the boron quinolate chromophore (4-aminoazobenzene: $\varepsilon_{389} = 14280 \text{ M}^{-1} \text{ cm}^{-1}$; M1: $\varepsilon_{394} = 3370 \text{ M}^{-1} \text{ cm}^{-1}$).

To study the photo-isomerization of P(St-*alt*-AbMA)-*b*-PM1, a polymer solution in THF was irradiated at 330~360 nm, and UV-vis spectra were recorded at different irradiation times (Figure 2-17). UV irradiation induced a decrease in absorbance at 355 nm due to trans-cis isomerization of the azobenzene chromophore. An equilibrium was reached within ~15 min, after which no further change in absorbance was observed. Upon gentle heating or irradiation with natural visible light, cis-trans isomerization

occurred and the original absorbance was reproduced. For comparison, the photoisomerization of P(St-*alt*-AbMA) was also studied, and a similar trans-cis isomerization process was observed. The relative decrease in absorbance for P(St-*alt*-AbMA)-*b*-PM1 is slightly less pronounced than that of P(St-*alt*-AbMA), possibly due to the relatively long boron quinolate block, whose absorption overlaps with that of the azobenzene groups. The emission of the boron quinolate block (excited at $\lambda_{exc} = 394$ nm) showed no change in position or intensity, which suggests that the two chromophoric systems act fully independently. Even after several hours of irradiation no decrease in emission intensity was observed indicating good photo-stability of the boron quinolate chromophore.



Figure 2-17. Absorption spectra of (A) P(St-*alt*-MAh)-*b*-PM1 and (B) P(St-*alt*-AbMA) upon irradiation with UV light (330~360 nm) in THF solution.

2.3 Luminescent Boron Quinolate Block Copolymers with Pyridine-Functionalities

Self-assembled nanostructures of block copolymers have drawn great attention due to their wide applications in controlled drug delivery, template synthesis and electronics.²⁹ Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) is one of the most ideal and widely studied models for block copolymer self-assembly, because the 4VP and St units have very similar structures, the same free volume and almost identical refractive index increments; on the other hand, the large Flory-Huggins interaction parameter between 4VP and St units makes the self-assembly of PS-*b*-P4VP fall into the strong segregation limit (SSL). In 1996, Markus Antonietti and coworkers studied the self-assembly of a series of PS-*b*-P4VP of differents block lengths in toluene by DLS and TEM. They built up the scaling relationships between the aggregation number, corona dimension and the block lengths of PS and P4VP blocks.³⁰ PS-*b*-P4VP is also important as a polymeric Lewis base³¹, pH-responsive polymer³² and H-bonding acceptor³³⁻³⁷, which has been utilized for the preparation of polymer/inorganic hybrid materials, responsive materials and supramolecular complexes.



Figure 2-18. Synthesis of pyridine-functionalized boron quinolate block copolymers.

In this section, we present two types of luminescent boron quinolate block copolymers with pyridine-functionalities. As analogs to PS-*b*-P4VP, these block copolymers take advantage of the assembly methodologies that apply to PS-*b*-P4VP for nanostructured material fabrication. We believe that the combination of pyridine functionality and

luminescent property of boron quinolate will lead to interesting applications in the areas of chemical sensors, hybrid materials and biological studies.

The synthesis of pyridine-functionalized boron quinolate block copolymers is shown in Figure 2-18. In the first method, the homopolymer PM1-2 was used for the controlled polymerization of 4VP monomer. In the second method, PS macro-CTAs were used for the controlled polymerization of a boron quinolate monomer (M3) with a pyridyl group in the 5-position of the quinoline moiety (the synthesis and characterization of M3 are given in Section 2.5). A homopolymer PM3 was also synthesized via RAFT polymerization for ¹H NMR comparison and molecular weight characterization (Section 2.5).



Figure 2-19. GPC curves of (A) PM1-2 (black) and PM1-*b*-P4VP (red), (B) PS-2 and PS-*b*-PM3-1, and (C) PS-1 and PS-*b*-PM3-2. PM1-2 was analyzed in THF at 1.0 mL/min. PM1-*b*-P4VP was analyzed in DMF with 0.2% w/v [Bu₄N]Br at 0.5 mL/min. PS-*b*-PM3-1 and PS-*b*-PM3-2 were analyzed in THF/pyridine = 95/5. PS standards were used for calibration.

The GPC curves of block copolymers and corresponding macro-CTA precursors are shown in Figure 2-19. Reasonable narrow block copolymers with apparent chain extension were achieved. The PM1 was characterized in THF, and PM1-*b*-P4VP was characterized in DMF with 0.2% w/v [Bu₄N]Br to minimize the pyridine/column interaction (Figure 2-19(A)). For M3-based block copolymers, two RAFT-polymerized

PS of different molecular weights were used as macro-CTAs. The PS precursors and block copolymers were characterized in a solvent mixture of THF/pyridine = 95/5. The GPC analysis revealed well-defined block copolymers with reasonably narrow distribution. The molecular weights of boron quinolate homopolymers usually deviate by a factor of $2\sim3$.²⁰ Therefore, the UV-Vis absorbances of the boron chromophores (determined for the corresponding boron quinolate homopolymers) were also used for absolute molecular weight analysis. The molecular weight data of homo- and block copolymers by GPC and UV-Vis are summarized in Table 2-5.

Polymer ^a	$M_{ m n, \ GPC}{}^{ m b}$	PDI_{GPC}^{b}	$M_{ m n, MALLS}^{ m c}$	$M_{ m n,UV}{}^{ m d}$	m, n _{GPC} ^e	m, $n_{\rm UV}$ ^{e, f}
PM1 _m	8710	1.28	27600		22	
PM1 _m - <i>b</i> -P4VP _n	44400	1.27	g	110640	22, 339	70, 790
PM3 _m	3420	1.28	g		7	
PS _m -2	3840	1.18	3570		35	
PS _m -b-PM3 _n -1	9990	1.23	g	17450	35, 13	32, 30
PS _m -1	8130	1.16	9470		76	
PS _m - <i>b</i> -PM3 _n -2	11440	1.25	g	13110	76, 7	89, 8

Table 2-5. Summary of molecular weight data of pyridine-functionalized boron quinolate

 block copolymers and the corresponding macro-CTA precursors

^a For the block copolymers, the block sequence corresponds to the polymerization sequence. ^b Determined by GPC-RI analysis. ^c Determined by GPC-MALLS analysis. ^d Based on UV-vis analysis and absolute molecular weight data for the homopolymer precursor. ^e m and n refer to the degree of polymerization of the first and second block, respectively. ^f m is based on the GPC-MALLS data. ^g Not measured.



Figure 2-20. ¹H NMR spectra of PM1-*b*-P4VP, PM3 and PS-*b*-PM3-1 in CDCl₃. The corresponding ¹¹B NMR spectra are shown as insets.

The ¹H and ¹¹B NMR spectra of PM1-*b*-P4VP, PM3 and PS-*b*-PM3-1 are given in Figure 2-20. The boron quinolate blocks show broad peaks in the aromatic region. Due to the much longer P4VP block, the signals of the boron quinolate block of PM1-*b*-P4VP are hardly seen. All three block copolymers show a single signal with a chemical shift of 7.6 ppm in the ¹¹B NMR.



Figure 2-21. UV-vis and fluorescence spectra of PM1-*b*-P4VP (A, $\lambda_{exc} = 394$ nm) and PS-*b*-PM3-1 (B, $\lambda_{exc} = 406$ nm) in THF.

Sample ^a	$\lambda_{abs} (nm)$	$\lambda_{em} (nm)^{b}$	Quantum yield	
M1	395	506	0.20	
PM1-b-P4VP	394	505	0.19	
PM1-b-P4VPMeOTf	310, 380	509	0.19	
M3	406	519	0.23	
PM3	406	519	0.14	
PS- <i>b</i> -PM3-1	406	519	0.20	
PS- <i>b</i> -PM3-2	406	519	0.13	
PS-b-PM3MeOTf	360, 398	499	0.09	

Table 2-6. Photophysical data of pyridine-functionalized boron quinolate polymers

Similar to the other PM1-based block copolymers, the PM1-*b*-P4VP shows absorption and emission maxima at 394 and 505 nm, respectively. M3 and the corresponding homoand block copolymers show identical absorption and emission maxima at 406 and 519 nm, respectively. Representative absorption and emission spectra of PM1-*b*-P4VP and PS-*b*-PM3-1 in THF are given in Figure 2-21. The photophysical data of both monomers

^a PM1-*b*-P4VPMeOTf and PS-*b*-PM3MeOTf were measured in DMF and the other samples were measured in THF. ^b Excitation at the absorption maxima. The excitation wavelength for PS-*b*-PM3MeOTf was 398 nm.

and the corresponding polymers are summarized in Table 2-6. The quantum efficiency of PS-*b*-PM3-1 is 0.20, which is slight lower than that of M3 (0.23). Differently, the quantum efficiencies of PM3 and PS-*b*-PM3-2 are comparatively lower (0.14 and 0.13), possibly because the chain transfer agent at the chain end acts as a fluorescence quencher and affects the quantum yield more for the polymers having shorter PM3 chain lengths.²⁸

We studied the self-assembly of pyridine-functionalized block copolymers in selective solvents. In toluene, which is a selective solvent for the PM1 block, PM1-*b*-P4VP formed vesicles instead of spherical micelles (Figure 2-22(A)), because the P4VP block is much longer than the PM1 block. The DLS measurement revealed a hydrodynamic diameter ($\langle D_h \rangle$) of 76±19 nm, which is slightly larger than what is observed by TEM observation.



Figure 2-22. TEM image (A) and number-averaged size distribution histogram (B) of PM1-*b*-P4VP vesicles in toluene.

The self-assembly of PS-*b*-PM3-1 was studied in methanol and cyclohexane. In methanol, the block copolymer formed polydisperse spherical aggregates, which are expected to have a PS core and a PM3 shell (Figure 2-23(A)). The $\langle D_h \rangle$ of the block copolymer aggregates in methanol is 168±50 nm (Figure 2-23(B)). In cyclohexane, reverse self-assembled aggregates with a PM3 core and a PS shell are expected to form. From Figure 2-23(C), we can see that the block copolymers formed small particles,

which further aggregated together to give extended branched aggregates, because cyclohexane is a medium solvent for the PS shell. The $\langle D_h \rangle$ based on DLS is 1169±147 nm, which also indicates further aggregation of the smaller particles.



Figure 2-23. TEM image (A) and number-averaged size distribution histogram (B) of PS-*b*-PM3-1 micelles in methanol; TEM image (C) and number-averaged size distribution histogram (D) of PS-*b*-PM3-1 aggregates in cyclohexane.

Pyridinium compounds are generally known as effective germicidal agents. With appropriate substituents on the pyridine ring or the nitrogen atom, pyridinium compounds possess wide applications, including cosmetics, pharmaceuticals, gene delivery and phase transfer catalysis.³⁸ The pyridine-functionalized boron quinolate block copolymers can serve as precursors for polymeric luminescent pyridinium materials for the above mentioned purposes. To this end, we pursued the quaternization of pyridine-functionalized boron quinolate block copolymers (Figure 2-24).



Figure 2-24. Quaternization of pyridine-functionalized boron quinolate block copolymers.

Methyl triflate was used as a powerful methylating reagent. The quaternization reaction was carried in chloroform and the product purified by precipitation in hexanes. To prove the feasibility, a quaternization reaction of a model compound of M3 was also performed with methyl triflate (see Section 2.5). The ¹H and ¹¹B NMR spectra of the quaternized block copolymers PM1-*b*-P4VPMeOTf and PS-*b*-PM3MeOTf are shown in Figure 2-25. Based on a comparison with P4VP homopolymer, the ¹H NMR signals of the pyridinium moieties of PM1-*b*-P4VPMeOTf are down-field shifted and the degree of quaternization is quantitative. The methyl signal of the pyridinium group appears at 4.2 ppm, providing further evidence for quaternization. Similarly, the pyridinium rings of PS-*b*-PM3MeOTf show down-field shifted peaks at 9.0 ppm, and the methyl signal of the pyridinium group appeared at 4.4 ppm. The degree of quaternization appears to be quantitative based on ¹H NMR analysis. The ¹¹B NMR signals of both quaternized block copolymers remained the same after quaternization, indicating the excellent stability of boron chromophores.


Figure 2-25. Comparison of ¹H NMR spectra of P4VP, PM1-*b*-P4VPMeOTf (A) and PS-*b*-PM3-1, PS-*b*-PM3MeOTf (B) in DMSO-*d*6 (PS-*b*-PM3-1 in CDCl₃). The corresponding ¹¹B NMR spectra are shown as insets.



Figure 2-26. UV-vis absorption and fluorescence spectra of PM1-*b*-P4VPMeOTf (A, λ_{exc} = 380 nm) and PS-*b*-PM3MeOTf (B, λ_{exc} = 398 nm) in DMF.

The photophysical data of quaternized block copolymers were acquired in a good solvent DMF (Figure 2-26, Table 2-6). New bands assigned to formation of pyridinium groups appeared at 310 and 360 nm for PM1-*b*-P4VPMeOTf and PS-*b*-PM3MeOTf. The boron chromophores of PM1-*b*-P4VPMeOTf show essentially the same absorption and emission profiles as the PM1-*b*-P4VP precursor in THF. The quaternized boron chromophores of PS-*b*-PM3MeOTf show blue-shifted absorption and emission at 398 and 499 nm, respectively, and the quantum yield is 0.09 in DMF, about half of that of the PS-*b*-PM3MeOTf exhibited good solubility in water.

The quaternization reaction is useful not only for post-modification, but also powerful for nanostructured material fabrication. The Chen group developed a quaternization crosslinking method to prepare polymeric nanoparticles (Figure 2-27).³⁹ They dissolved a PS-*b*-P4VP block copolymer and 1,4-dibromobutane crosslinker in a common solvent, DMF. The two bromoalkyl units from one crosslinker molecule react with the pyridyl units from different block copolymer chains slowly at room temperature, eventually leading to core-crosslinked polymeric nanoparticles. Due to the relatively long nonreactive PS blocks, the core-core coupling reaction was prohibited.



Figure 2-27. Scheme (A) and SEM image (B) of quaternization crosslinked PS-*b*-P4VP nanoparticles.³⁹



Figure 2-28. Photograph (A) and SEM image (B) of PM1-b-P4VP crosslinked gel.

With the expectation of different crosslinked structures, we used PM1-*b*-P4VP as block copolymer precursor with a short nonreactive PM1 block and a much longer crosslinkable P4VP block. 40 mg of block copolymer and 123 mg of 1,4-dibromobutane (molar ratio of C₄H₈Br₂/4VP = 2.0) were dissolved in 2.0 mL of DMF and stirred at room temperature. The solution became more and more viscous and gelation occurred in 6 days. Figure 2-28 (A) shows the photographs of the resulting crosslinked block copolymer gel in natural and UV light. The gel had the same color and emission as the block copolymer precursor. Different from the example of core-crosslinked PS-*b*-P4VP polymeric nanoparticles discussed above, in our case, the nonreactive PM1 block is much shorter than the P4VP block, and thus not long enough to stabilize small particles. Therefore, the extended crosslinking reaction of the P4VP blocks led to gel formation. Figure 2-28 (B) shows the surface morphology of the gel sample.

The pyridine-functionalized boron quinolate block copolymers can also act as polymeric Lewis base for polymer/inorganic hybrid material fabrication.^{31,40-42} In solution, the pyridine units can coordinate to metal cations. Depending on the coordination strength and coordination number, metal cations can serve as crosslinkers for the block copolymers and lead to a metal/block copolymer complex.

We chose ZnCl₂ as the metal cation source because of the well-known Zn/pyridine coordination.^{43,44} Experimentally, 0.05 mL of ZnCl₂ solution in methanol (c = 12.1 mg/mL) were added to 20.0 mL of a chloroform solution containing 5.0 mg of PM1-*b*-P4VP under stirring. As shown in Figure 2-29 (A), the as-formed mixture exhibited strong light scattering, indicating the formation of colloidal particles. The $\langle D_h \rangle$ of PM1*b*-P4VP/ZnCl₂ complex is 177±73 nm based on DLS. A control experiment with PM1-*b*-P4VP in chloroform/methanol mixture (v/v = 400/1) in the absence of ZnCl₂ gave $\langle D_h \rangle$ = 11.2±3.1 nm, which is a sign of single chains. Single chains are expected because the trace amount of selective methanol in the mixture is not enough for block copolymer aggregation. Therefore, we conclude that the coordination between P4VP blocks and Zn²⁺ led to the aggregation. The TEM image of PM1-*b*-P4VP/ZnCl₂ complex (Figure 2-29 (B)) shows highly branched structures with much larger feature size than the DLS result, which may be a result of further aggregation on the copper grid upon solvent evaporation. The PM1-*b*-P4VP/ZnCl₂ complex showed identical absorption and emission as the block copolymer itself.



Figure 2-29. (A) Number-averaged size distribution of PM1-*b*-P4VP/ZnCl₂ complex (red) and PM1-*b*-P4VP (black) in chloroform/methanol mixture (v/v = 400/1) (Inset: PM1-*b*-P4VP/ZnCl₂ complex showing strong light scattering); (B) TEM image of PM1-*b*-P4VP/ZnCl₂ complex (Inset: PM1-*b*-P4VP/ZnCl₂ complex under UV irradiation).

Similarly, PS-*b*-PM3-1/ZnCl₂ complex formed extended aggregates with $\langle D_h \rangle =$ 496±204 nm (Figure 2-30 (A) and (B)). To study the block length effect on the complex morphology, PS-*b*-PM3-2 with a relatively longer PS block was also used for Zn²⁺ complexation. The $\langle D_h \rangle$ of PS-*b*-PM3-2/ZnCl₂ complex was determined to be 73±27 nm (Figure 2-30 (C)). Different from the complexes with relatively longer pyridine-containing blocks, the TEM image (Figure 2-30 (D)) of PS-*b*-PM3-2/ZnCl₂ complex and a PS shell. Extended aggregates were not observed because of the presence of a relatively longer PS block.



Figure 2-30. (A) Number-averaged size distribution of PS-*b*-PM3-1/ZnCl₂ complex (red) and PS-*b*-PM3-1 (black) in chloroform/methanol mixture (v/v = 500/1); (B) TEM image of PS-*b*-PM3-1/ZnCl₂ complex; (C) Number-averaged size distribution of PS-*b*-PM3-2/ZnCl₂ complex (red) and PS-*b*-PM3-2 (black) in chloroform/methanol mixture (v/v = 400/1) (Inset: PS-*b*-PM3-2/ZnCl₂ complex showing strong light scattering); (B) TEM image of PS-*b*-PM3-2/ZnCl₂ complex (Inset: PM1-*b*-P4VP/ZnCl₂ complex under UV irradiation).

Besides the propensity for nanostructure formation, PM3-based polymers have potential as chemical sensors and responsive luminescent materials. Novel boron quinolate-pyridine-metal complex structures can be generated through coordination interaction. To explore this possibility, we chose zinc meso-tetraphenylporphyrin (ZnTPP) for the complexation with PS-*b*-PM3. Porphyrin compounds are interesting because of their excellent photochemical and photophysical properties and potential applications in the areas of sensors, electronics, photosensitized solar cells and light-emitting devices.⁴⁵ An interesting aspect is that the Q-bands of ZnTPP overlap with the emission of PM3 polymers. Energy transfer between boron quinolate and ZnTPP is therefore possible, allowing for emission tuning.

We studied the structures and photophysical properties of PS-*b*-PM3-1/ZnTPP complex in solution. Cyclohexane was used, because it is a moderately good solvent for the PS block, but a nonsolvent for PM3 block and ZnTPP. Therefore, in cyclohexane, PS-*b*-PM3-1 is expected to form aggregates of PM3/ZnTPP complex, and the PS blocks will sustain the solubility of the supramolecular assemblies.



Figure 2-31. (A)~(D) TEM images of PS-*b*-PM3-1/ZnTPP complex at the weight ratio of 0.1, 0.2, 0.5 and 1.0; (E)~(H) Number-averaged size distribution of PS-*b*-PM3-1/ZnTPP complex at the weight ratio of 0.1 ($<D_h> = 867\pm108$ nm), 0.2 ($<D_h> = 1132\pm103$ nm), 0.5 ($<D_h> = 986\pm139$ nm) and 1.0 ($<D_h> = 1189\pm151$ nm).

To PS-*b*-PM3-1 solutions in 1.0 mL of dichloromethane ($c_0 = 1.0 \text{ mg/mL}$), were added different amounts (0.4, 0.8, 2.0 and 4.0 mL) of a ZnTPP solution in dichloromethane ($c_{ZnTPP} = 0.25 \text{ mg/mL}$). The weight ratios ZnTPP/PS-*b*-PM3-1 are 0.1, 0.2, 0.5 and 1.0, respectively, corresponding to ZnTPP/pyridine molar ratios of 0.085, 0.170, 0.425 and 0.85. Cyclohexane was added dropwise to the mixture under stirring. The volume of the solution was set to be 20 mL. Dichloromethane (boiling point = 39.6 °C) was allowed to evaporate under stirring at room temperature, and then the volume of the solutions was reset to 20 mL by refilling with cyclohexane (boiling point = 80.7 °C). The

evaporation/refilling cycle was repeated 3 times. One drop of the as-formed solution was dissolved in CDCl₃ and examined by ¹H NMR; the signal of dichloromethane was absent, indicating its complete evaporation. Supramolecular co-assemblies of PS-*b*-PM3-1/ZnTPP complex were obtained.



Figure 2-32. Schematic illustration of proposed supramolecular co-assembly of PS-*b*-PM3-1/ZnTPP.

The PS-*b*-PM3-1/ZnTPP complexes were analyzed by TEM and DLS. Similar to the self-assembly of PS-*b*-PM3-1 in cyclohexane (Figure 2-23 (C)), the PS-*b*-PM3-1/ZnTPP complexes form assemblies with a PM3/ZnTPP complex core and a PS shell that further aggregate into branched structures due to the medium solubility of PS in cyclohexane (Figure 2-31 (A)~(D)). The number-averaged diameters of these supramolecular co-assemblies based on DLS measurements (Figure 2-31 (E)~(H)) are 867±108, 1132±103, 986±139 and 1189±151 nm, respectively. It should be noted that these data correspond neither to the sizes of the initial particles of PS-*b*-PM3-1/ZnTPP complexes nor the branched structures observed in TEM, but represent the statistically averaged

hydrodynamic diameters of branched aggregates in cyclohexane. The schematic illustration of supramolecular co-assembly of PS-*b*-PM3-1/ZnTPP complexes is shown in Figure 2-32.



Figure 2-33. (A) and (B) Photographs of PS-*b*-PM3-1/ZnTPP supramolecular coassembly solutions under natural light and UV irradiation at 365 nm. From left to right: ZnTPP in dichloromethane, PS-*b*-PM3-1 aggregates in cyclohexane, PS-*b*-PM3-1/ZnTPP complex solutions in cyclohexane (weight ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.085, 0.17, 0.425 and 0.85); (C) Absorption and fluorescence spectra of PS-*b*-PM3-1 self-assembly in cyclohexane (green) and ZnTPP in dichloromethane (purple); (D) and (E) Absorption and fluorescence ($\lambda_{exc} = 416$ nm) spectra of PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.1, 0.2, 0.5 and 1; molar ratios of ZnTPP/PS-*b*-PM3-1 = 0.085, 0.17, 0.425 and 0.85).

The photographs of ZnTPP solution in dichloromethane, PS-*b*-PM3-1 aggregates and PS-*b*-PM3-1/ZnTPP complex solutions in cyclohexane under natural and UV light are shown in Figure 2-33 (A) and (B). The PS-*b*-PM3-1 aggregate solution was highly greenemissive, similar to the block copolymer in THF as a good solvent. In contrast, only the orange emission from ZnTPP was observed for all the PS-*b*-PM3-1/ZnTPP complex solutions, indicating energy transfer from boron quinolate chromophores to ZnTPP

molecules. The ZnTPP, PS-b-PM3-1 and the corresponding supramolecular co-assembly solutions were further examined by UV-Vis and fluorescence measurements. In cyclohexane, PS-b-PM3-1 showed absorption and emission maxima at 416 and 518 nm, respectively. The absorption and emission spectra of ZnTPP were acquired in dichloromethane, because it is completely insoluble in cyclohexane. A very strong Soret band at 419 nm and two O-bands at 547 and 585 nm were recorded, while excitation at 547 nm led to two emission peaks at 598 and 643 nm (Figure 2-33 (C)). The absorption spectra of PS-b-PM3-1/ZnTPP complex in cyclohexane were normalized to the absorption maximum of the boron quinolate (416 nm, Figure 2-33 (D)). Although quantitative intensity analysis of the spectra was compromised by the strong light scattering of the large supramolecular aggregates (~800-1000 nm), clear red-shifts for the Q-bands to about 564 and 603 nm were observed, which is indicative of the axial coordination between ZnTPP and the pyridine units from the block copolymer.⁴⁶ The pyridine/ZnTPP axial coordination was also evidenced by the shoulder peaks between 428 and 442 nm. The emission spectra of PS-b-PM3-1/ZnTPP complex (excited at 416 nm) are given in Figure 2-33 (E). At a molar ratio of ZnTPP/pyridine = 0.085, the characteristic emission of ZnTPP was observed, indicating complete energy transfer from boron quinolate to ZnTPP. With increasing molar ratio, the emission of ZnTPP weakened and disappeared at a molar ratio of 0.85 due to the self-quenching of ZnTPP in the supramolecular assemblies. This study presents an example of supramolecular systems that incorporate two kinds of chromophores into assembled nanostructures through coordination interaction. The supramolecular co-assemblies exhibit controllable

photophysical properties by simply changing the ratio of block copolymer and the encapsulated guest chromophore.

2.4 Conclusions

We synthesized a series of well-defined luminescent boron quinolate block copolymers with controlled molecular weight and narrow distribution via RAFT polymerization. The amphiphilic PEO- and PNIPAM-based block copolymers formed spherical micelles in water. The P(St-alt-MAh)-b-PM1 served as a scaffold for post-modification. The Azobenzene-modified bock copolymer P(St-alt-AbMA)-b-PM1 showed solventdependent self-assembly in basic solutions. The pyridine-functionalized boron quinolate block copolymers PM1-b-P4VP and PS-b-PM3 acted as versatile building blocks for nanostructure formation. In selective solvents, self-assembled micelles, vesicles and extended aggregates were obtained. The quaternization of pyridine units was used to modify the block copolymers and prepare crosslinked polymeric gels. At last, the pyridine-functionalized block copolymers form supramolecular complexes with transition metal cations. In chloroform, the coordination between ZnCl₂ and block copolymers led to large aggregates or spherical micelles. The supramolecular co-assembly of PS-b-PM3-1 and ZnTPP in cyclohexane resulted in extended branched structures with controllable emission properties. Energy transfer from boron quinolate chromophores to ZnTPP was observed in these complexes. With an increase of the ZnTPP/ PS-b-PM3-1 molar ratio, self-quenching of ZnTPP was observed due to the increased local concentration of ZnTPP in the supramolecular aggregates. These luminescent boron quinolate block copolymers are powerful building blocks for nanostructures that have potential in biological and energy-related applications.

2.5 Experimental

General methods. The 499.9 MHz ¹H and 125.7 MHz ¹³C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ¹¹B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. The ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks and the ¹¹B NMR spectra externally to BF₃•Et₂O ($\delta = 0$) in C₆D₆. Elemental analyses were performed by Quantitative Technologies Inc. (Whitehouse, NJ).

GPC-RI analyses were performed in THF (1.0 mL/min) or DMF with 0.2% w/v of [Bu4N]Br (0.50 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Three styragel columns (Polymer Laboratories; two 5 µm Mix-C and one 10 µm Mix-D), which were kept in a column heater at 35 °C (THF), or a set of two polyvinylalcohol columns (Shodex Asahipak; one 5 µm GF-510 HQ and one 9 µm GF-310 HQ) at 65 °C (DMF), were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories, Varian Inc.). Multi-angle laser light scattering (GPC-MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument in-line with the GPC, using the columns specified above. A Wyatt Optilab refractive index detector operated at 690 nm was used as the concentration detector and differential refractive indices dn/dc were calculated with the Wyatt Astra software assuming 100% mass recovery. The triple

detection GPC measurement was performed using a Viscotek TDA305 Max Triple Detection SEC system by Malvern. DMF with 30 mM LiBr was used as the eluent at a temperature of 50 °C and a flow rate of 1.0 mL/min. Two Viscotek I-MBHMW-3078 mixed-bed high molecular weight columns with an exclusion limit >10 million g/mol) were used for separation. The dynamic light scattering (DLS) measurements were performed at 25.0 \pm 1 °C with a Malver Zetasizer Nano-ZS instrument, equipped with a 4 mW, 633 nm He-Ne laser and an Avalanche photodiode detector at an angle of 173°.

UV-vis absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The mass fraction of the boron quinolate block in the copolymers was determined by preparing solutions of known concentration and measuring the UV-vis absorbance at the absorption maximum of the respective boron chromophore. Assuming that the absorptivity of the individual chromophores is independent of the polymer architecture, we used the molar absorptivity of the homopolymers ($\epsilon_{394} = 2460 \text{ M}^{-1} \text{ cm}^{-1}$ per homopolymer repeat unit of PM1, $\varepsilon_{440} = 3710 \text{ M}^{-1} \text{ cm}^{-1}$ per homopolymer repeat of PM2, and $\varepsilon_{406} = 4730 \text{ M}^{-1} \text{ cm}^{-1}$ per homopolymer repeat of PM3) as the reference. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer with optically dilute solutions (A < 0.1). Anthracene was used as the standard and the quantum yield of anthracene (0.33 in THF) was adopted from the Handbook of Photochemistry.⁴⁷ Sample solutions were prepared using a microbalance $(\pm 0.1 \text{ mg})$ and volumetric glassware. The quantum yields were calculated by plotting a graph of integrated fluorescence intensity vs. absorbance of at least 4 solutions with increasing concentration. The gradient of the graph is proportional to the quantum yield.

$$\Phi_{X} = \Phi_{ST} \left(\frac{Grad_{X}}{Grad_{ST}} \right) \left(\frac{\eta_{X}^{2}}{\eta_{ST}^{2}} \right)$$

Transmission electron microscopy (TEM) was conducted on a FEI Tecnai 12 electron microscope operated at 80 kV. One drop of polymer micelle solution was cast on a copper grid with a carbon coating.

Materials. 1,4-Dioxane and THF were distilled from Na/benzophenone prior to use. Azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. Styrene was purified by passing it through a neutral alumina column and then distilled under reduced pressure. Maleic anhydride was purified by recrystallization in toluene, and N-isopropyl acrylamide (NIPAM) in a hexanes/benzene mixture. All other solvents and chemicals were commercial products and used as received without further purification. The chain transfer agents (CTAs) used in this work were synthesized according to literature procedures.^{19,21,48}

Synthesis of M1. To a solution of boron tribromide (2.07 g, 8.62 mmol) in anhydrous toluene (10 mL) was added dropwise under stirring a solution of 1-trimethylsilyl-4-*tert*-butylbenzene (1.43 g, 6.90



mmol) in toluene (10 mL) at RT. The mixture was stirred at RT overnight, all volatile components were removed under high vacuum and the residue was redissolved in CH₂Cl₂ (10 mL). Then, a solution of 4-trimethylstannylstyrene (1.84 g, 6.90 mmol) in CH₂Cl₂ (10 mL) was added slowly under stirring. After 2 h, a solution of 8-methoxyquinoline (1.10 g, 6.91 mmol) CH₂Cl₂ (10 mL) was added dropwise and the mixture was stirred for an additional hour. The reaction mixture was extracted with 3 x 50 mL of aqueous ammonium bicarbonate (10%) and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude product was recrystallized from CH₂Cl₂/ether

solvent mixture (v/v=1/2), to give **M1** as a yellow microcrystalline solid. Yield: 2.0 g, 74%. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 8.60$ (d, ³J = 5.0 Hz, 1H, Q-H2), 8.40 (d, ³J = 8.5 Hz, 1H, Q-H4), 7.66 (pst, ³J = 8.0 Hz, 1H, Q-H6), 7.62 (dd, ³J = 5.0 Hz and 8.5 Hz, 1H, Q-H3), 7.46 (d, ³J = 7.5 Hz, 2H, Ph-H2,6), 7.37 (d, ³J = 8.0 Hz, 2H, Sty-H2,6), 7.33 (d, ³J = 8.0 Hz, 2H, Ph-H3,5), 7.33 (d, ³J = 8.5 Hz, 2H, Sty-H3,5), 7.24 (d, ³J = 8.0 Hz, 1H, Q-H5), 7.18 (d, ³J = 7.5 Hz, 1H, Q-H7), 6.70 (dd, ³J = 11.0, 17.5 Hz, 1H, Vi), 5.70 (d, ³J = 17.5 Hz, 1H, Vi), 5.16 (d, ³J = 11.0 Hz, 1H, Vi), 1.30 (s, 9H, CMe₃); ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 159.1$ (Q-C8), 149.8 (Ph-C4), 143.8 (br., Ph-C1), 139.5 (Q-C2/4), 138.8 (Q-C2/4), 137.9 (Q-C9), 137.5 (vinyl-C), 136.4 (styryl-C4), 133.1 (Q-C6), 132.4 (styryl-C2,6), 132.0 (Ph-C2,6), 128.7 (Q-C10), 125.7 (styryl-C3,5), 124.7 (Ph-C3,5), 122.9 (Q-C3), 113.0 (vinyl-C), 112.3 (Q-C5), 109.9 (Q-C7), 34.6 (CMe₃), 31.6 (CMe₃), styryl-C1 not observed; ¹¹B NMR (160.386 MHz, CDCl₃) $\delta = 11.4$ (w_{1/2} = 400 Hz). Elemental analysis for C₂₇H₂₆BNO: calcd C 82.87, H 6.70, N 3.58; found C 82.60, H 6.75, N 3.49%.

Synthesis of M2. To a solution of boron tribromide (1.62 g, 6.47 mmol), in 10 mL of anhydrous toluene was added dropwise a solution of 1-trimethylsilyl-4-*tert*-butylbenzene (0.89 g, 4.31 mmol) in 10 mL anhydrous toluene at RT under stirring. The mixture was stirred overnight, followed by removing the excess boron tribromide and toluene under high vacuum. The residue was redissolved in 10 mL of dry CH_2Cl_2 . Then, a solution of 4-trimethylstannylstyrene (1.15 g, 4.31 mmol) in CH_2Cl_2 (10 mL) was added dropwise under stirring. After 2 h, a solution of 5-(4'-dimethylamino phenyl)-8-methoxyquinoline (1.20 g, 4.31 mmol) in CH_2Cl_2 (25 mL) was added dropwise and the mixture was stirred for another 2 h. The reaction mixture was worked up with 3×50 mL of aqueous

ammonium bicarbonate (10%), and the combined organic layers were dried over sodium sulfate. After rotary evaporation, the crude monomer was purified by column chromatography on silica gel with CH₂Cl₂ as the eluent. Recrystallization from CH_2Cl_2 /hexanes=1/2 (v/v) mixture gave M2 as an orange microcrystalline solid. Yield: 1.80 g, 82%. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 8.60$ (d, ³J = 4.0 Hz, 1H, Q-H2), 8.59 (overlapped, 1H, O-H4), 7.62 (d, ${}^{3}J = 8.0$ Hz, 1H, O-H6), 7.57 (dd, ${}^{3}J = 5.0$ Hz and 8.0 Hz, 1H, Q-H3), 7.51 (d, ³J = 8.0 Hz, 2H, styryl-H2,6), 7.44 (d, ³J = 8.0 Hz, 2H, Ph-H2,6), 7.4-7.3 (m, 6H, $^{\text{Q}}$ Ph-H3,5, Ph-H3,5, styrvl-H3,5), 7.22 (d, 3 J = 8.0 Hz, 1H, O-H7), 6.89 (d, ${}^{3}J = 8.5$ Hz, 2H, ${}^{Q}Ph$ -H2,6), 6.72 (dd, ${}^{3}J = 11.0$, 17.5 Hz, 1H, Vi), 5.72 (d, ${}^{3}J = 17.5$ Hz, 1H, Vi), 5.18 (d, ${}^{3}J = 11.0$ Hz, 1H, Vi), 3.05 (s, 6H, NMe₂), 1.32 (s, 9H, CMe₃); ${}^{13}C$ NMR (125.698 MHz, CDCl₃): $\delta = 157.7$ (Q-C8), 150.1 (^QPh-C1), 149.7 (Ph-C4), 139.3 (Q-C2/4), 138.3 (Q-C2/4), 138.0 (Q-C9) 137.6 (vinyl-C), 136.3 (styryl-C4), 132.6 (Q-C6), 132.5 (styryl-C2,6), 132.0 (Ph-C2,6), 130.5 (^QPh-C3,5), 127.2 (Q-C10), 126.8 (Q-C5), 126.2 (^QPh-C4), 125.7 (styryl-C3,5), 124.7 (Ph-C3,5), 122.6 (Q-C3), 113.0 (vinyl-C), 112.9 (^QPh-C2,6), 109.9 (Q-C7), 40.8 (NMe₂), 34.6 (CMe₃), 31.6 (CMe₃), n.o. (Ph-C1, styryl-C1); ¹¹B NMR (160.386 MHz, CDCl₃) δ = 11.4 (w_{1/2} = 400 Hz). Elemental analysis for C₃₅H₃₅BN₂O × 0.5(C₆H₁₄): calcd C 82.45, H 7.65, N 5.06; found C 82.01, H 7.81, N 4.97%. The amount of cocrystallized hexanes was independently confirmed by ¹H NMR integration.

Synthesis of 5-pyridyl-8-methoxy quinoline.

The 5-pyridyl-8-methoxy quinolone ligand was prepared in analogy to method by Anzenbacher (Chemistry-A European Journal, 2006, 12, 4523; JOC, 2004, 69, 1723) Under nitrogen protection, to a Schlenk tube were loaded 3.87 g (16.3 mmol) of 5bromo-8-methoxy quinolone (JOC, 1972, 37, 4078), 2.00 g (16.3 mmol) of pyridyl boronic acid, 875 mg (0.757 mmol, 5 mol%) of Pd(PPh₃)₄, 50 mL of degassed toluene, and a mixture of degassed water/EtOH = 25 mL/25 mL. The tube was sealed and heated at 100 °C for 3 days. The mixture was extracted with CH₂Cl₂. The combined CH₂Cl₂ solution was washed with water and dried over MgSO4. The crude solution was concentrated on a rotary evaporator, and subjected to silica gel column chromatography with hexanes/THF mixture as the eluent, followed by crystallization in hexanes/THF = 1/1 mixed solvent. The product was obtained as white crystals. Yield: 2.39 g, 62%. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 9.00$ (d, ³J = 4.0 Hz, 1H, Q), 8.74 (d, ³J = 5.5 Hz, 2H, Pv), 8.22 (d, ${}^{3}J = 8.5$ Hz, 1H, Q), 7.47 (d, ${}^{3}J = 8.5$ Hz, 1H, Q), 7.46 (dd, ${}^{3}J = 4.0$ Hz and 8.5 Hz, 1H, Q), 7.41 (d, ${}^{3}J = 5.5$ Hz, 2H, Py), 7.15 (d, ${}^{3}J = 8.0$ Hz, 1H, Q), 4.17 (s, 3H, Me). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 156.0$, 150.1, 149.6, 147.6, 140.4, 133.6, 129.4, 127.8, 127.1, 125.2, 122.3, 107.3, 56.4.



Figure 2-34. ¹H and ¹³C NMR spectra of 5-pyridyl-8-methoxy quinoline in CDCl₃.

Synthesis of M3. In a glove box, 1.30 g (5.17 mmol) of BBr₃ were dissolved in 15 ml of toluene in a flame-dried Schlenk flask, and cooled to -20 °C. Then, a solution of 0.89 g (4.31 mmol) of trimethysilyl-4-*tert*-butylbenzene in 15 mL of toluene at -20 °C was

added dropwise under stirring. The solution was warmed up to room temperature and stirred for 6 h. After removal of the solvent under vacuum, the solid was redissolved in 5 mL of anhydrous CH₂Cl₂. A solution containing 1.15 g (4.31 mmol) of 4trimethylstannyl styrene in 20 mL of CH₂Cl₂ was added dropwise under stirring at -20 °C. After 6 h, a solution containing 1.02 g (4.32 mmol) of 5-pyridyl-8-methoxyquinoline in 20 mL of CH₂Cl₂ was added dropwise under stirring. After 3 h, the Schlenk flask was taken out of the glove box, and warmed up to 50 °C. After another 3 h, the reaction was worked up with CH₂Cl₂/10% NH₄HCO₃ aq. and the organic extracts were dried over MgSO₄. The solution was concentrated and then subjected to column chromatography on silica gel with hexanes/ethyl acetate as the eluent. The monomer was obtained as a yellow solid. Yield: 1.22 g, 60%. ¹¹B NMR: $\delta = 11.9$ ppm (w_{1/2} = 400 Hz). ¹H NMR $(499.895 \text{ MHz}, \text{CDCl}_3)$: $\delta = 8.76 \text{ (d, }^3\text{J} = 5.5 \text{ Hz}, 2\text{H}, \text{Py-H2,6}), 8.67 \text{ (d, }^3\text{J} = 5.0 \text{ Hz}, 1\text{H},$ Q-H2), 8.55 (d, ${}^{3}J$ = 8.5 Hz, Q-H4), 7.71 (d, ${}^{3}J$ = 8.0 Hz, 1H, Q-H6), 7.67 (dd, ${}^{3}J$ = 5.0 Hz and 8.5 Hz, 1H, Q-H3), 7.47 (d, ${}^{3}J = 8.5$ Hz, 2H, Ph), 7.43 (d, ${}^{3}J = 6.0$ Hz, 2H, Py), 7.40 (d, ${}^{3}J = 8.0 \text{ Hz}$, 2H, Ph), 7.35 (d, ${}^{3}J = 8.0 \text{ Hz}$, 2H, Ph), 7.30 (d, ${}^{3}J = 8.0 \text{ Hz}$, 2H, Ph/St), 7.26 (d, ${}^{3}J = 8.0$ Hz, 1H, Q-H7), 6.71 (dd, ${}^{3}J = 11.0$, 17.5 Hz, 1H, Vi), 5.72 (d, ${}^{3}J = 17.5$ Hz, 1H, Vi), 5.18 (d, ³J = 11.0 Hz, 1H, Vi), 1.31 (s, 9H, CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 159.6$, 150.6, 150.0, 146.2, 140.0, 138.0, 137.4, 137.1 136.6, 133.9, 132.4, 132.0, 126.4, 125.7, 124.8, 124.5, 123.6, 123.2, 113.2, 110.0, 34.6, 31.6, B-C not observed. UV-Vis in THF: $\lambda_{max} = 406$ nm, $\varepsilon = 4140$ cm⁻¹ M⁻¹. Fluorescence in THF: λ_{em} $= 519 \text{ nm} (\lambda_{\text{exc}} = 406 \text{ nm}), \Phi = 23\%.$



Figure 2-35. ¹H, ¹¹B and ¹³C NMR spectra of M3 in CDCl₃.

Synthesis of model compound for M3. In a glove box, 117 mg (0.466 mmol) of BBr₃ were dissolved in 5 ml of CH₂Cl₂ in a flame-dried Schlenk flask, and cooled to -20 °C. Then, 277 mg (0.933 mmol) of trimethylstannyl-4-tert-butylbenzene in 5 mL of CH₂Cl₂ at -20 °C were added dropwise under stirring. The solution was warmed up to room temperature and stirred for 3 h. Then, a solution containing 110 mg (0.466 mmol) of 5pyridyl-8-methoxy quinoline in 5 mL of CH₂Cl₂ was added dropwise under stirring. After 2 h, the Schlenk flask was taken out of the glove box, and the crude product was subjected to column chromatography on silica gel with CH_2Cl_2 as the eluent, followed by crystallization in hexanes/CH₂Cl₂ mixture. The product was obtained as yellow crystals. Yield: 160 mg, 69%. ¹¹B NMR: δ = 11.7 ppm (w_{1/2} = 430 Hz). ¹H NMR (499.895 MHz, CDCl₃): $\delta = 8.76$ (d, ³J = 5.5 Hz, 2H, Py-H2,6), 8.70 (d, ³J = 5.0 Hz, 1H, Q-H2), 8.54 (d, ${}^{3}J = 8.5$ Hz, Q-H4), 7.70 (d, ${}^{3}J = 8.0$ Hz, 1H, Q-H6), 7.67 (dd, ${}^{3}J = 5.0$ Hz and 8.5 Hz, 1H, Q-H3), 7.43 (d, ${}^{3}J = 7.8$ Hz, 4H, Ph-H3,5), 7.43 (2H, overlapped, Ph-H3,5), 7.33 (d, 4H, Ph), 7.5-7.4 (m, 6H, ^QPh-H2,6, Py-H3,5), 7.26 (d, ³J = 8.0 Hz, 1H, Q-H7), 1.31 (s, 18H, CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 159.7$, 150.6, 149.9, 146.2, 143.4 (broad B-C), 140.0, 138.0, 136.9, 133.9, 131.9, 126.4, 124.7, 124.4, 123.5, 123.0, 109.9, 34.6, 31.6. UV-Vis in THF: $\lambda_{max} = 407$ nm, $\varepsilon = 5510$ cm⁻¹ M⁻¹. Fluorescence in THF: λ_{em} = 520 nm (λ_{exc} = 407 nm), Φ = 24%.



Figure 2-36. ¹H, ¹¹B and ¹³C NMR spectra of model compound for M3 in CDCl₃.

Quaternization of model compound of M3 with methyl triflate. To a solution containing 50.0 mg (0.107 mmol) of model compound of M3 in 2.0 mL of chloroform at 0 °C, was added dropwise a solution containing 35.0 mg (0.213 mmol) of methyl triflate in 1.0 mL of chloroform. After stirring for 2 h, the solvent was removed under vacuum and the crude product was recrystallized in CH₂Cl₂/hexanes mixture. The product was obtained as yellow needle-like crystals. Yield: 58 mg, 86%. ¹¹B NMR: $\delta = 13.0$ ppm (w_{1/2}

= 850 Hz). ¹H NMR (499.895 MHz, CDCl₃): δ = 8.73 (d, ³J = 4.9 Hz, 1H, Q), 7.32 (d, ³J = 8.0 Hz, 4H, Ph-H3,5), 7.38 (d, ³J = 8.0 Hz, 4H, Ph-H3,5), 8.83 (d, ³J = 5.0 Hz, 2H, Py-H2,6 and 1H, overlapped Q), 8.05 (d, ³J = 4.5 Hz, 2H, Py-H3,5), 7.84 (d, ³J = 8.0 Hz, 1H, Q), 7.83 (dd, not ovserved, Q-H3), 7.9-7.7 (m, 3H, Q-H3,4,6), 7.25 (d, ³J = 8.0 Hz, 1H, Q-H7), 4.48 (s, 3H, Me), 1.29 (s, 18H, CMe₃). ¹³C NMR (125.698 MHz, CDCl₃): δ = 162.5, 155.2, 150.2, 145.4, 142.6 (broad B-C), 141.1, 138.0, 136.7, 136.4, 131.9, 127.4, 126.2, 125.4, 124.9, 118.5, 110.3, 48.3, 34.6, 31.6. UV-Vis in THF: λ_{max} = 401 nm, 363 nm, ε = 13940 cm⁻¹ M⁻¹. Fluorescence in THF: λ_{em} = 498 nm (λ_{exc} = 401 nm), Φ = 44%.



Figure 2-37. ¹H, ¹¹B and ¹³C NMR spectra of quaternized model compound for M3 in CDCl₃.



Figure 2-38. Top: ¹H, ¹¹B and ¹³C NMR spectra of quaternized model compound for M3 with methyl triflate in CDCl₃; Bottom: UV-vis and fluorescence spectra of quaternized model compound for M3 in THF.

Synthesis of **PM1**. Schlenk tube filled with methyl 3-Α was benzylsulfanylthiocarbonylsulfanylpropionate (CTA1) (11.0 mg, 0.0384 mmol), M1 (500 mg, 1.28 mmol), AIBN (2.1 mg, 0.0128 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. To determine the conversion of monomer at different times, one drop of solution was taken out with a syringe at 30 min, 75 min, 150 min, 270 min and 360 min for ¹H NMR analysis (the integral ratio of the vinyl signal at 5.16 ppm and the methyl group of anisole at 3.86 ppm was used to determine the monomer conversion). The polymerization was quenched at liquid nitrogen temperature after 360 min. The polymer was purified by two precipitations into a 10-fold volume of methanol and then dried under high vacuum. GPC-RI (THF, 1 mL/min): $M_n = 5840$, PDI = 1.21. The NMR data are identical to those reported in ref. 7.

Synthesis of PM2. A Schlenk tube was filled with methyl 3benzylsulfanylthiocarbonylsulfanylpropionate (CTA1) (5.80 mg, 0.020 mmol), M2 (344 mg, 0.674 mmol), AIBN (1.11 mg, 0.00674 mmol in 1.0 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. To determine the conversion of monomer at different times, one drop of solution was taken out with a syringe at 30 min, 75 min, 150 min, 270 min and 360 min for ¹H NMR analysis (the integral ratio of the vinyl signal at 5.16 ppm and the methyl group of anisole at 3.86 ppm was used to determine the monomer conversion). The polymerization was quenched at liquid nitrogen temperature after 360 min. The polymer was purified by 2 precipitations into a 10-fold volume of hexanes/methanol=2/1 (v/v) and then dried under high vacuum. GPC-RI (THF, 1 mL/min): $M_n = 4500$, PDI = 1.18. The NMR data are identical to those reported in ref. 7.

Synthesis of PM3. In a Schlenk tube, 350 mg (0.747 mmol) of M3, 4.56 mg (0.0187 mmol) of benzyl dithiobenzoate (BDTB), 0.77 mg (0.0047 mmol) of AIBN were dissolved in 1.5 mL of anisole ([M3]/[CTA]/[AIBN] = 33.5/1/0.25). After 3 freezepump-thaw cycles, the Schlenk tube was immersed in a 70 °C oil bath for 10 h. The crude product was precipitated two times by dropwise addition of a THF solution of the polymer to a 10-fold volume of diethyl ether. The solid was collected by filtration and dried in high vacuum, affording 110 mg of a yellow powder (conversion = 30%). ¹¹B NMR: δ = 7.6 ppm (w_{1/2} = 650 Hz, CDCl₃). ¹H NMR (499.895 MHz, CDCl₃): δ = 8.9-8.0 (3H), 8.0-5.5 (14H), 2.5-1.5 (3H, backbone), 1.2 (9H, ¹Bu). ¹³C NMR (125.698 MHz, CDCl₃): δ = 159.7, 150.5, 150.2, 146.1, 143.9, 140.2, 137.6, 136.9, 133.7, 131.9, 128.3, 127.1, 126.1, 124.7, 124.4, 123.8, 122.9, 109.4, 34.6, 31.6. GPC-RI (THF/pyridine = 95/5): M_n = 3420 g/mol, PDI = 1.28. UV-Vis in THF: λ_{max} = 406 nm, ε_{406} = 4750 cm⁻¹M⁻¹. Fluorescence in THF: λ_{em} = 519 nm (λ_{exc} = 406 nm), ϕ = 14%. **Synthesis of PEO(45)**-*b*-PM1(71) (Kinetic analysis of the chain extension of CTA2 with M1). A flame-dried Schlenk tube was filled with CTA2 (45 mg, 0.020 mmol), M1 (780 mg, 2.00 mmol), AIBN (2.6 mg, 0.016 mmol in 3 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C and samples were withdrawn at predetermined times. Data from a kinetic analysis are provided in Figure 2-4.

Synthesis of PEO(440)-b-PM1. A flame-dried Schlenk tube was filled with CTA3 (360 mg, 0.0184 mmol), AIBN (1.0 mg, 0.0061 mmol), M1 (720 mg, 1.84 mmol in 4 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.60 g. The conversion of monomer based on the weight of the final product was determined be 33%. Elemental analysis to ca. for C7H7(C27H26BNO)37C4H4S3O(C2H4O)440OCH3): calcd C 66.51, H 8.07, N 1.51; found C 66.68, H 7.64, N 1.55%.

Synthesis of PEO(440)-*b*-**PM2.** A flame-dried Schlenk tube was filled with CTA3 (391 mg, 0.020 mmol), AIBN (1.1 mg, 0.0067 mmol), M2 (510.5 mg, 1.00 mmol in 2 mL of anisole) and the mixture was degassed by three freeze-pump-thaw-cycles. The polymerization was conducted at 80 °C. After 24 h, the polymerization was quenched at liquid nitrogen temperature. The polymer was purified by two precipitations into a 10-fold volume of cold ether and then dried under high vacuum. The isolated yield of the block copolymer was 0.57 g. The conversion of monomer based on the weight of the

final product was determined to be ca. 35%. Elemental analysis for C7H7(C35H35BN2O)14C4H4S3O(C2H4O)440OCH3: calcd C 61.91, H 8.51, N 1.46; found C 61.61, H 8.60, N 1.45%.

Synthesis of PS-1. To a Schlenk tube, styrene (15.62 g, 150 mmol), benzyl dithiobenzoate (BDTB) (122 mg, 0.500 mmol) and AIBN (20.6 mg, 0.125 mmol) were loaded. After 3 freeze-pump-thaw cycles, the tube was immersed for 3.5 h in an 80 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated three times by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. The PS macro-CTA was obtained as a light pink powder after drying in high vacuum. Yield: 4.10 g (26% conversion assuming quantitative recovery). GPC-RI (THF): $M_n = 8130$ g/mol, PDI = 1.16. GPC-MALLS (THF): $M_n = 9470$ g/mol.

Synthesis of PS-2. Into a Schlenk tube were loaded styrene (5.21 g, 50.0 mmol), benzyl dithiobenzoate (BDTB) (122 mg, 0.50 mmol), AIBN (41.1 mg, 0.25 mmol), and 20.0 mL of dioxane ([St]/[CTA]/[AIBN] = 100/1/0.5). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath for 3 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times from THF into a 10-fold volume of MeOH, followed by drying in high vacuum. The product was obtained as a pink powder (1.80 g). Conversion = 32%. GPC-RI (THF): M_n = 3840 g/mol, PDI = 1.18. GPC-MALLS (THF): M_n = 3570 g/mol.

Synthesis of Poly(styrene-*alt***-maleic anhydride) (P(St-***alt***-MAh)).** A Schlenk tube was loaded with styrene (1.56 g, 15.0 mmol), MAh (1.47 g, 15.0 mmol), BDTB (45.5 mg, 0.167 mmol), AIBN (3.4 mg, 0.021 mmol) and 7.0 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed for 3.0 h in a 70 °C oil bath under stirring. After

quenching in liquid nitrogen, the polymer was precipitated three times by dropwise addition of a THF solution of the polymer to a 10-fold volume of dry ether. P(St-*alt*-MAh) macro-CTA was obtained as a light pink powder after drying in high vacuum. Yield: 0.69 g (21% conversion assuming quantitative recovery). GPC-RI (DMF, 0.2% [Bu₄N]Br): M_n = 10400 g/mol, PDI = 1.28. Triple Detection GPC (DMF, 30 mM LiBr): M_n = 4500 g/mol, PDI = 1.26, dn/dc = 0.111 mL/g.

Synthesis of PM1-*b*-PS. A Schlenk tube was loaded with PM1-1 (25.0 mg, 1.85 µmol; $M_n = 13500$ g/mol by GPC-MALLS), AIBN (0.10 mg, 0.61 µmol) and styrene (0.70 mL, 6.1 mmol). After 3 freeze-pump-thaw cycles, the tube was immersed for 8.0 h in a 70 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. PM1-*b*-PS was obtained as a yellow powder after drying in high vacuum. Yield: 80 mg (9% conversion assuming quantitative recovery). GPC-RI (THF): $M_n =$ 32900 g/mol, PDI = 1.27. GPC-MALLS (THF): $M_n = 43300$ g/mol, PDI = 1.18, dn/dc = 0.201 mL/g. PM1 mass fraction by UV-Vis analysis: 0.296 (using $\varepsilon_{395} = 3370$ cm⁻¹M⁻¹).

Synthesis of PM2-*b*-PS. A Schlenk tube was loaded with PM2 (25.0 mg, 1.94 μ mol), AIBN (0.13 mg, 0.79 μ mol; $M_n = 12900$ g/mol by GPC-MALLS) and styrene (1.0 mL, 8.7 mmol). After 3 freeze-pump-thaw cycles, the tube was immersed for 8.0 h in a 70 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. PM2-*b*-PS was obtained as a red powder after drying in high vacuum. Yield: 130 mg (9% conversion assuming quantitative recovery). GPC-RI (THF): $M_n = 58400$

g/mol, PDI = 1.26. GPC-MALLS (THF): $M_n = 64800$ g/mol, PDI = 1.24, dn/dc = 0.198 mL/g. PM2 mass fraction by UV-Vis analysis: 0.190 (using $\varepsilon_{440} = 3650$ cm⁻¹M⁻¹).

Synthesis of PS-*b*-PM1. A Schlenk tube was loaded with PS-2 (50.0 mg, 6.15 µmol; $M_n = 9470$ g/mol by GPC-MALLS), AIBN (0.34 mg, 2.1 µmol), M1 (241 mg, 0.615 mmol), and 2.0 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed for 11 h in a 70 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. PS-*b*-PM1 was obtained as a yellow powder after drying in high vacuum. Yield: 145 mg (39% conversion assuming quantitative recovery). GPC-RI (THF): $M_n = 16000$ g/mol, PDI = 1.29. GPC-MALLS (THF): $M_n = 33000$ g/mol, PDI = 1.21, dn/dc = 0.206 mL/g. PM1 mass fraction by UV-Vis analysis: 0.670 (using $\varepsilon_{395} = 3370$ cm⁻¹M⁻¹).

Synthesis of PM1-*b*-PNIPAM. In a Schlenk tube, PM1-2 (45.0 mg, 1.63 µmol; M_n = 27600 g/mol by GPC-MALLS), AIBN (0.12 mg, 0.73 µmol) and NIPAM (600 mg, 5.30 mmol) were dissolved in 0.8 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed for 8.0 h in a 70 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated three times by dropwise addition of a DMF solution of the polymer to a 10-fold volume of diethyl ether. PM1-*b*-PNIPAM was obtained as a yellow powder after drying in high vacuum. Yield: 605 mg (93% conversion assuming quantitative recovery). GPC-RI (DMF / 0.2% [Bu4N]Br): M_n = 107200 g/mol, PDI = 1.27. PM1 mass fraction by UV-Vis analysis: 0.123 (using ε_{395} = 3370 cm⁻¹M⁻¹).

Synthesis of P(St-*alt*-MAh)-*b*-PM1. A Schlenk tube was loaded with P(St-*alt*-MAh) macro-CTA (30 mg, 6.7 µmol; $M_n = 4520$ g/mol by triple detection GPC), AIBN (0.38 mg, 2.3 µmol), M1 (226 mg, 0.58 mmol), and 2.0 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed for 8.0 h in a 70 °C oil bath under stirring. After quenching in liquid nitrogen, the polymer was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of diethyl ether. P(St-*alt*-MAh)-*b*-PM1 was obtained as a yellow powder after drying in high vacuum. Yield: 150 mg (53% conversion assuming quantitative recovery). GPC-RI (DMF / 0.2% [Bu₄N]Br): $M_n = 22400$ g/mol, PDI = 1.34. The absolute molecular weight was determined by UV-vis analysis assuming that $M_n = 4520$ g/mol for the first block: $M_n = 19500$ g/mol. PM1 mass fraction by UV-Vis analysis: 0.768 (using $\varepsilon_{395} = 3370$ cm⁻¹M⁻¹).

Synthesis of P(St-*alt*-AbMA)-*b*-PM1. In a Schlenk flask, P(St-*alt*-MAh)_m-*b*-PM1_n (40 mg, for n=22, m=38: 0.19 mmol MAh functional groups) and 4-aminoazobenzene (94 mg, 0.48 mmol) were dissolved in 3.0 mL of dry THF. The mixture was purged with nitrogen for 10 min and then sealed. After stirring at 80 °C for 48 h, the mixture was precipitated twice by dropwise addition of a THF solution of the polymer to a 10-fold volume of diethyl ether. The product was obtained as an orange powder after drying in high vacuum. Yield: 35 mg. GPC-RI (DMF containing 0.2% [Bu₄N]Br): $M_n = 25500$ g/mol, PDI = 1.40.

Synthesis of PM1-b-P4VP. PM1-2 (250 mg, 9.06 μ mol), AIBN (0.68 mg, 4.14 μ mol) and 4VP (2.93 g, 27.9 mmol) were dissolved in 1.0 mL of dioxane ([4VP]/[PM1-CTA]/[AIBN] = 3080/1/0.46). After 3 freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath for 8.0 h with stirring. The reaction was terminated by placing the tube

in liquid nitrogen. The polymer was precipitated three times by dropwise addition of a DMF solution of the polymer to a 10-fold volume of diethyl ether. The product was obtained as a yellow powder (1.15 g, conversion = 31%) after drying in high vacuum. GPC-RI (DMF / 0.2% [Bu₄N]Br): $M_{n, GPC}$ = 44400 g/mol, PDI = 1.27. PM1 mass fraction by UV-Vis analysis = 0.25 (using ε_{395} = 3370 cm⁻¹M⁻¹). The molecular weight was also determined by UV-vis analysis assuming that M_n = 27600 g/mol for the PM1 block: M_n , UV-Vis = 110640 g/mol.

Synthesis of PS-*b*-PM3-1. In a Schlenk tube, PS-2 (150 mg, 0.040 mmol), M3 (940 mg, 2.00 mmol), and AIBN (1.31 mg, 0.0080 mmol) were dissolved in 5.0 mL of 1,4-dioxane ([M3]/[PS-2]/[AIBN] = 50/1/0.2). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in an 80 °C oil bath for 5 h. The polymerization was quenched in liquid nitrogen. The polymer solution was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The product was obtained as a yellow powder (450 mg, conversion = 32%). GPC-RI (THF/pyridine = 95/5): M_n = 9990 g/mol, PDI = 1.23. UV-Vis in THF: λ_{max} = 406 nm. Fluorescence in THF: λ_{em} = 519 nm (λ_{exc} = 406 nm), ϕ = 0.20. Weight fraction of boron block based on UV = 0.78 (using ε_{406} = 4750 cm⁻¹M⁻¹).

Synthesis of PS-*b*-PM3-2. In a Schlenk tube, PS-1 (79 mg, 0.00832 mmol), M3 (187 mg, 0.400 mmol), AIBN (0.33 mg, 0.0020 mmol) were dissolved in 1.0 mL of 1,4-dioxane ([M3]/[PS-1]/[AIBN] = 48/1/0.24). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in a 70 °C oil bath for 8 h. The polymerization was quenched in liquid nitrogen and the product was diluted with 2 mL of THF. The polymer solution was then precipitated three times from THF into a 10-fold volume of MeOH, followed by

drying in high vacuum. The product was obtained as a yellow powder (152 mg, conversion = 39%). GPC-RI (THF/pyridine = 95/5): $M_n = 11435$ g/mol, PDI = 1.25. UV-Vis in THF: $\lambda_{max} = 406$ nm. Fluorescence in THF: $\lambda_{em} = 519$ nm ($\lambda_{exc} = 406$ nm), $\Phi = 0.13$. Weight fraction of boron block based on UV = 0.38 (using $\varepsilon_{406} = 4750$ cm⁻¹M⁻¹).

Synthesis of PM1-*b***-P4VPMeOTf.** To a solution of PM1-*b*-P4VP (50 mg, 0.36 mmol of pyridine units) in 3.0 mL of CHCl₃, were added 200 mg (1.22 mmol) of methyl triflate dropwise under stirring. A yellow suspension appeared within seconds. After stirring for 1.0 h at room temperature, the suspension was precipitated into a 10-fold volume of diethyl ether. After filtration, the product was dried in high vacuum. The product was obtained as a light yellow powder (57 mg). ¹H NMR analysis in DMSO-d6 indicated quantitative quaternization of the pyridine moieties (Py-Me appeared at 4.22 ppm. Pyridine signals shifted to 8.68 and 7.48 ppm).

Synthesis of PS-*b***-PM3MeOTf.** To a solution of PS-*b*-PM3-1 (40 mg, 0.069 mmol of pyridine units) in 3.0 mL of CHCl₃, were added 80 mg (0.49 mmol) of methyl triflate dropwise under stirring. A yellow suspension appeared within seconds. After stirring for 1.0 h at room temperature, the suspension was precipitated into a 10-fold volume of diethyl ether/hexanes (v/v = 1/1). After filtration, the product was dried in high vacuum. The product was obtained as a yellow powder (38 mg). ¹H NMR analysis indicated ca. 100 % quaternization of the pyridine moieties.

Self-assembly of PEO(440)-*b*-PM1, PEO(440)-*b*-PM2. The block copolymer under investigation (2.5 mg) was dissolved in THF as a common solvent (5.0 mL), and deionized water was added dropwise under magnetic stirring. The final concentration of

the polymer was 0.01 mg/mL. Then, the solution was dialyzed against deionized water for 3 days to remove THF.

Self-assembly of PM1-*b*-PNIPAM in Water. 2.0 mg of block copolymer were dissolved in 10.0 mL of DMF. The block copolymer solution in DMF was loaded in a dialysis tube (cut-off molecular weight = 6~8 kDa) and dialyzed against ~1 L of deionized water for 3 days to remove DMF.

Self-assembly of P(St-*alt***-AbMA)**-*b*-**PM1 in basic solutions.** Two solutions of P(St*alt*-AbMA)-*b*-PM1 in THF were prepared at a concentration of 0.5 mg/mL. To one of the solutions was added 5% aq. NaHCO₃ dropwise under stirring. The final ratio of THF/5% aq. NaHCO₃ was set to be 1:9. The second polymer solution was dialyzed against 5% aq. NaHCO₃ to completely remove the THF solvent.

Self-assembly of PM1-*b***-P4VP in toluene.** 1.9 mg of block copolymer were dissolved in 1.9 mL of dichloromethane. 10.0 mL of toluene were added to the block copolymer solution dropwise under magnetic stirring. The dichloromethane solvent was allowed to evaporate slowly at room temperature under stirring for 72 h.

Self-assembly of PS-*b***-PM3-1 in methanol.** 3.0 mg of block copolymer were dissolved in 3.0 mL of dichloromethane. 30.0 mL of methanol were added to the block copolymer solution dropwise under magnetic stirring. The dichloromethane solvent was allowed to evaporate slowly at room temperature under stirring for 72 h.

Self-assembly of PS-b-PM3-1 in cyclohexane. 1.0 mg of block copolymer was dissolved in 1.0 mL of dichloromethane. 20.0 mL of cyclohexane were added to the block copolymer solution dropwise under magnetic stirring. The dichloromethane solvent was allowed to evaporate slowly at room temperature under stirring for 72 h.

Quaternization crosslinking induced gelation of PM1-*b***-P4VP in DMF.** 40 mg of block copolymer (0.288 mmol of pyridine units) were dissolved in 2.0 mL of DMF, followed by addition of 123 mg (0.576 mmol) of 1,4-dibromobutane. The mixture was stirred at room temperature and gelation occurred in 6 days.

Co-assembly of PM1-*b***-P4VP/ZnCl₂.** 5.0 mg of block copolymer was dissolved in 20.0 mL of CHCl₃ under stirring. 0.05 mL of ZnCl₂ stock solution in MeOH (c = 12.1 mg/mL) was added under stirring.

Co-assembly of PS-*b***-PM3-1/ZnCl₂.** 5.0 mg of block copolymer were dissolved in 20.0 mL of CHCl₃ under stirring. 0.04 mL of ZnCl₂ stock solution in MeOH (c = 10.0 mg/mL) was added under stirring.

Co-assembly of PS-*b***-PM3-1/ZnTPP.** 4.0 mg of block copolymer were dissolved in 4.0 mL of dichloromethane. The block copolymer solution was divided equally into 4 vials. To the block copolymers solutions, were added 0.4 mL, 0.8 mL, 2.0 mL and 4.0 mL of ZnTPP solution in dichloroform (c = 0.25 mg/mL), respectively. Cyclohexane was added to the above mixtures dropwise under stirring. The volume of the solutions was set to be 20 mL. Dichloromethane (boiling point = 39.6 °C) was allowed to evaporate under stirring at room temperature for 24 h, and then the volumes of solutions were reset to 20 mL by refilling with cyclohexane (boiling point = 80.7 °C). The evaporation/refilling cycle was repeated for 3 times to completely remove dichloromethane from the mixture.

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Chapter 3 Luminescent Boron Quinolate Star Polymers ^[a]

Living polymerization techniques have been widely applied to the synthesis of polymers with complex architectures, including block, graft, hyperbranched and star polymers.¹ Star polymers are especially attractive because of their well-defined core-shell structure that allows for controlled incorporation of functional groups into the nano-sized core and/or shell regions. The latter is critical in applications ranging from nanocontainers for encapsulation and drug delivery vehicles, catalysis, optoelectronics, to coatings.²⁻⁵ In the case of chromophore-functionalized star polymers and dendrimers, precise architectural control can be exploited for effective site isolation, which is important for lightharvesting, oxygen sensing, bioimaging, and photovoltaic devices.⁶⁻⁹ The "core-first" method uses a polyvalent chromophoric small molecule as the initiator to grow a polymer shell.⁶ An alternative is to prepare core-crosslinked star polymers (CCSs) via the "armfirst" approach, in which a pre-synthesized linear polymer initiator or chain transfer agent is used to control the polymerization of a crosslinker (multifunctional monomer).^{3,10} This latter approach is advantageous, because a relatively large core fraction containing multiple chromophores can be realized and the size can be controlled by using low polydispersity arm precursors of designed molecular weight.

Luminescent organoboron polymers, on the other hand, have recently received much attention as a result of their proven utility as emissive materials, chemical sensors, and bioimaging agents. However, efforts at achieving architectural control are still in their infancy and only a few examples of nanostructures obtained by block copolymer [a] This chapter is adapted from a journal publication (ref. 34) self-assembly have been reported.¹¹⁻¹³ Moreover, most of the luminescent boron polymers reported thus far are not compatible with aqueous media and the disassembly of micellar structures occurs in common organic solvents. In this chapter, we introduce a new and expeditious approach to core cross-linked organoboron nanostructures that involves the synthesis of the first organoboron star polymers by arm-first RAFT polymerization (Figure 3-1) and demonstrate that well-defined core-shell structures can indeed be realized. We also apply the boron star polymers as building blocks for the aqueous self-assembly of luminescent super-aggregates and explore the formation of charged nanostructures using post-functionalization methods.



Figure 3-1. Synthesis of organoboron star polymers via arm-first RAFT polymerization in the presence of crosslinker **1**.

3.1 Results and Discussion

In spite of the fact that the crosslinker can be used to easily incorporate functionality into the core of star polymers, the variety of crosslinkers utilized remains limited mostly to divinylbenzene, bifunctional acrylates and acrylamides.¹⁴ Compound **1** was chosen as a functional boron-containing crosslinker because of the facile formation, high stability,

and strong and tunable luminescence of boron quinolate heterocycles.¹⁵⁻¹⁸ The crosslinker **1** was prepared by treatment of B(OMe)₃ with two equiv of StMgCl (St = styryl), followed by *in-situ* reaction of the St₂B(OMe) intermediate with 8-hydroxyquinoline (Figure 3-2). Purification by column chromatography followed by recrystallization from CH₂Cl₂/hexanes gave **1** as a luminescent crystalline solid in 55% yield.



Figure 3-2. Synthesis of crosslinker 1. 8-HQ = 8-hydroxyquinoline.



Figure 3-3. (A) ¹¹B NMR spectrum of **1**; (B) Molecular structure of **1** (ORTEP, 50% probability). Selected bond lengths (Å) and angles (deg): B1-C1 1.609(2), B1-C9 1.605(2), B1-N1 1.637(2), B1-O1 1.523(1), O(1)-B(1)-C(9) 110.52(10), O(1)-B(1)-C(1) 111.06(10), C(1)-B(1)-C(9) 116.28(10), O(1)-B(1)-N(1) 98.95(9), C(9)-B(1)-N(1) 110.56(9), C(1)-B(1)-N(1) 108.06(9); (C) Absorption and emission spectra of **1** in THF.

The ¹¹B NMR (Figure 3-3(A)) of **1** shows a single peak at 11.5 ppm as expected for tetracoordinate boron, and the ¹H and ¹³C NMR spectra (Figure 3-11) establish the composition and high purity of the crosslinker. A single crystal X-ray structure further confirms successful formation of the desired boron heterocycle and its functionalization

with two polymerizable styryl groups (Figure 3-3 (B)). The B-N distance of 1.637(2) Å and the N-B-O angle of 98.95(9)° are in the range typically observed for diarylboron quinolate complexes.¹⁸ In THF, the crosslinker forms a yellow solution with $\lambda_{max} = 395$ nm and displays strong green emission at 505 nm with a quantum yield of 22% (Figure 3-3(C)).

To incorporate crosslinker **1** into star polymers various living polymerization techniques can be explored, however, controlled free radical polymerization methods are attractive because of the generally mild reaction conditions and good tolerance of trace impurities.^{3,4,19-21} We decided to pursue the polymerization of **1** by RAFT,^{5,22} which is renowned for its exceptionally high functional group tolerance. In the presence of linear polymers macro-CTAs, arm-first RAFT polymerization of **1** was expected to lead to star polymers with crosslinked organoboron cores as shown in Figure 3-1.^{23,24}



Figure 3-4. GPC-RI overlays of (A) the isolated, crude, and linear arm precursors of PS star polymer (THF), (B) PNIPAM, PNIPAM-*b*-PS and P4VP star polymer (DMF/0.2% w/w [Bu₄N]Br).

In a proof-of-concept study, we first explored the synthesis of star polymers from a narrow PS macro-CTA (PS-1, $M_n = 9470$ g/mol, PDI = 1.14) as arm precursor. The reaction was carried out in dioxane at 80 °C for 12 h with a molar ratio of [1]/[PS-1]/[AIBN] = 24/1/0.1. The GPC overlay of the PS precursor, the crude product, and the isolated star polymer is shown in Figure 3-4 (A). The GPC curve for the isolated product

reveals a monomodal distribution of high molecular weight and low dispersity (M_n = 73800 g/mol, PDI = 1.21), indicative of successful star formation. The absolute molecular weight of the isolated PS star polymer was determined by GPC with multi-angle laser light scattering (MALLS) detection to be M_n = 271000 g/mol. The variation between the GPC-RI and GPC-MALLS results is due, in part, to the architecture of the star polymer, which is more compact in solution than the respective linear PS.²⁵ NMR characterization (Figure 3-5) further supports the structure of the PS star polymer. The ¹¹B NMR shows a single peak at 7.3 ppm, confirming the presence of the boron crosslinker. The quinolate signals are significantly broadened and hardly seen in the ¹H and ¹³C NMR spectra, as expected for the highly rigid environment of the crosslinked core. Thus, GPC, MALLS and NMR characterization demonstrate the successful synthesis of narrow PS star polymers with a crosslinked boron quinolate core.



Figure 3-5. ¹H, ¹¹B and ¹³C NMR spectra of PS star polymer in CDCl₃.

Encouraged by these results, we next investigated the preparation of luminescent star polymers with functional arms. High molecular weight star polymers with PNIPAM, PNIPAM-*b*-PS and P4VP arms were prepared by reaction with crosslinker **1**. The PNIPAM-*b*-PS precursor was synthesized by chain extension of PNIPAM with St, which places the chain transfer agent at the PS-end. Hence, a star architecture with the hydrophilic PNIPAM block at the periphery is expected. A relatively long PS block was chosen to favour amphiphilic self-assembly of the resulting star polymer (*vide infra*). The GPC curves of the isolated star polymers are shown in Figure 3-4 (B) and the molecular weight data are summarized in Table 3-1.

Sample	$M_{\rm n, GPC}$ (kg/mol)	PDI ^a	M _{n, MALLS} (kg/mol)	<i>frac</i> _{core} ^b	$f_{\rm arm}^{\rm c}$
PS-1	8.1	1.16	9.5		
PS star	73.8	1.21	271	0.51	14
PNIPAM-1	8.8	1.18	11.2		
PNIPAM star	146	1.32	334	0.32	20
P4VP	11.1	1.32	15.2		
P4VP star	294	1.46	320	0.16	18
PNIPAM-2	6.8	1.17	7.8		
PNIPAM-b-PS	57.9	1.24	75.8		
PNIPAM-b-PS star	729	1.19	5046	0.11	59

 Table 3-1. Summary of structural parameters of star polymers

^a Polydispersity index (PDI = M_w/M_n) based on GPC-RI detection. ^b Mass fraction of the core determined by comparison of Abs₃₉₅ of the star polymer with that of a linear boron quinolate polymer used as standard. ^c Average number of arms based on GPC-MALLS data.

The geometry of star polymers is typically characterized by assessment of the mass fraction of the core (*frac*_{core}) and the average number of arms (f_{arm}) present. Due to the crosslinked core structure, ¹H NMR integration can not be used to determine *frac*_{core}. Therefore, the calculation of *frac*_{core} and *f*_{arm} is usually based on the assumption that (1)

the crosslinker molecules consumed in the reaction add equally to all the arm precursors or (2) that all of the crosslinker molecules are incorporated into the final star polymer and none are present in the linear byproducts.¹⁰ However, in practice, both assumptions are not accurate. Fortunately, we can take advantage of the fact that the chromophoric core of the stars absorbs strongly at 395 nm, where the arms do not show any absorption, to conveniently determine *frac*_{core} according to Eq. 3-1. Based on *frac*_{core} and the absolute molecular weights of the star polymers and the respective arm precursors, *f*_{arm} was then calculated according to Eq. 3-2. The structural parameters of all the star polymers and the corresponding arm precursors are summarized in Table 3-1. The *frac*_{core} decreases from the PS to the PNIPAM and P4VP stars, which is related to a combination of increasing arm incorporation and the larger molecular weight of the P4VP arm precursor.^{10,26} For the PNIPAM-*b*-PS star polymer, *frac*_{core} makes up only 11%, consistent with the high molecular weight and relatively large number of arms present.

$$frac_{core} = \frac{Abs_{star} \times Conc_{stan}}{Conc_{star} \times Abs_{stan}} = \frac{Abs_{star}}{Conc_{star} \times 6.265}$$
(3-1)
$$f_{arm} = \frac{M_{n,star} \times (1 - frac_{core})}{M_{n,arm}}$$
(3-2)

To further investigate the star architectures, we acquired DLS data and also directly imaged the PS and PNIPAM-*b*-PS star polymers by TEM. According to the TEM data both star polymers adopt a spherical shape, but the PNIPAM-*b*-PS stars ($D_{\text{TEM}} = 37 \text{ nm}$; Figure 3-6 (B)) are apparently larger than the PS stars ($D_{\text{TEM}} = 17 \text{ nm}$; Figure 3-6 (A)). This again is consistent with the fact that the molecular weight of the PNIPAM-*b*-PS is much higher than that of the PS arm precursor. In comparison, DLS gave number-

average diameters of $\langle D_{h,app} \rangle = 15$ nm for the PS stars and $\langle D_{h,app} \rangle = 64$ nm for the PNIPAM-*b*-PS stars using DMF as a good solvent for both blocks. The relatively larger diameter of the PNIPAM-*b*-PS stars obtained by DLS is likely the result of a more extended structure in solution and partial collapse of the arms after deposition onto the TEM grid. Interestingly, a core-shell structure is clearly evident for the PNIPAM-*b*-PS stars, which we attribute to more effective staining of the core containing the boron quinolate crosslinker. The apparent hydrodynamic diameters of the PNIPAM and P4VP star polymers are $\langle D_{h,app} \rangle = 18$ and 22 nm, respectively, and thus slightly larger than that for the PS stars.



Figure 3-6. TEM images of (A) PS and (B) PNIPAM-*b*-PS star polymers with crosslinked organoboron quinolate cores. The samples were deposited from CHCl₃ solution and stained with RuO₄ vapour.

As a result of chromophore incorporation into the core, all the star polymers are obtained as light yellow powdery solids that form green luminescent solutions. They show absorption and emission maxima at ca. 395 and 505 nm, respectively, which are similar to those of the respective linear polymer²⁵ (Table 3-2), indicating that despite the confinement in the core of the star polymer architectures, chromophore-chromophore complex (or exciplex) formation is not favourable. The fluorescence quantum yields

range from 0.06-0.18, which is slightly lower than that of the crosslinker **1** (0.22). A possible reason is the high local concentration of boron chromophores in the core of the star polymers, which might facilitate self-quenching to some extent. Another contributing factor could be the incorporation of sulphur from the chain transfer agents, which might lead to heavy atom quenching effects. Differences in the core compactness and polarity of the different arms could play a role as well.

Sample	λ _{abs} (nm)	$\lambda_{em} (nm)^{b}$	Quantum efficiency ^c
Crosslinker 1	395	505	0.22
PS star	395	505	0.064
PNIPAM star	394	506	0.11
PNIPAM-b-PS	395	505	0.18
star			
P4VP star	395	505	0.12
P4VP-Cz star	332 ^d , 346 ^d , 390	505	0.089

Table 3-2. Photophysical data of crosslinker 1 and star polymers in THF

^a Measurements in THF, except for the P4VP and P4VP-Cz stars which were investigated in CHCl₃. ^b The excitation wavelength is 395 nm for the crosslinker and all the star polymers. ^c Anthracene (quantum yield = 0.33 in THF) was used as standard. ^d Carbazole-centered absorption bands.

Self-assembly of functional star polymers provides a convenient method to construct nano-aggregates containing different functionalities. However, compared to the extensive studies on the self-assembly of block copolymers, reports on the self-assembly of star polymers remain rare and fluorescent stars have so far not been explored in this respect.²⁷⁻³⁰ We studied the self-assembly of the amphiphilic luminescent organoboron PNIPAM-*b*-PS star polymers in water. The star polymer solution in THF, which is a good solvent for PNIPAM and PS, was dialyzed against deionized water. In water, the stars

form larger aggregates, as indicated by strong scattering of light. According to TEM analysis (Figure 3-7 (A)), the star polymers form large vesicle-like aggregates with an average diameter of $D_{\text{TEM}} = 97$ nm based on 60 randomly chosen particles. The intensity-averaged hydrodynamic diameter $\langle D_{h,app} \rangle$ was determined by DLS to be 108 nm (Figure 3-7 (B)). The proposed mechanism for self-assembly is illustrated in Figure 3-7 (C). In water, the hydrophobic inner PS shell of the star is expected to shrink toward the crosslinked core, forming a hydrophobic layer. As the outer hydrophilic PNIPAM shell is designed to be much smaller than the PS inner shell, and not large enough to efficiently stabilize the particles in water, different star polymers aggregate to reduce the hydrophobic PS/water interface.



Figure 3-7. (A) TEM image of PNIPAM-*b*-PS star polymer assemblies deposited from water and stained with iodine vapour. (B) Intensity-averaged size distribution of aggregates of PNIPAM-*b*-PS star polymers in water; inset: photograph of an aqueous solution excited at 365 nm with a handheld UV lamp. (C) Proposed self-assembly mechanism in water.

The size of the particles and luminescence of the aggregate solutions did not change significantly over a period of at least 6 months under ambient conditions, indicating good colloidal and chemical stability. Moreover, self-assembly did not affect the luminescence as the aggregates obtained from the PNIPAM-*b*-PS star polymers in water show green emission (inset of Figure 3-7 (B)) similar to that of the unaggregated star polymers in THF as a good solvent. Another interesting aspect is that the stability of the boron quinolate core was further enhanced in the self-assembled aggregates of the PNIPAM-*b*-PS star polymer. When the PNIPAM star polymer was dissolved in strong base (0.1 M NaOH), the luminescence disappeared within ca. 12 h, indicating that the boron quinolate chromophores decomposed under these harsh conditions. In contrast, over the same period of time, the luminescence of the PNIPAM-*b*-PS star polymer in NaOH did not change significantly, suggesting that the long hydrophobic PS block acts as an effective barrier and isolates the boron quinolate moieties from the base (Figure 3-8).



Figure 3-8. Fluorescence spectra of (left) PNIPAM star polymer before and after addition of NaOH solution; (right) PNIPAM-b-PS star polymer before and after addition of NaOH solution.



Figure 3-9. (A) Schematic illustration of the functionalization of luminescent P4VP star polymers with carbazole chromophores; (B) ¹H NMR spectra of P4VP (red) and P4VP-Cz (black) star polymers in DMSO-d6.



Figure 3-10. UV-vis (A) and fluorescence (B) spectra of P4VP-Cz star polymers in DMF at different excitation wavelengths, and comparison to spectra obtained for the (C) P4VP star polymer and (D) *N*-(4'-bromobutyl)carbazole.

Finally, we explored the quaternization of the pyridine groups in the P4VP star polymers as a means of generating charged luminescent nanostructures and at the same time to introduce additional functionality to the outer shell of the star polymers (Figure 3-9 (A)). Reaction with an excess of *N*-(4-bromobutyl) carbazole, indeed resulted in quaternization of ca. 50% of the pyridine unit based on ¹H NMR integration (Figure 3-9 (B)). The introduction of the carbazole chromophores was also evident in the absorption spectra of the resulting quaternized stars (Figure 3-10). However, only a single emission band at $\lambda_{em} = 505$ nm ($\phi = 9\%$ at $\lambda_{exc} = 390$ nm) was present, which we attribute to selective pyridinium-based quenching of the carbazole fluorophores in the shell (for *N*-(4-bromobutyl)carbazole $\lambda_{em} = 370$ nm, $\phi = 59\%$), but not the boron fluorophore in the core. Upon quaternization, the carbazole-modified P4VP star polymers became soluble in water and, similar to natural proteins, the charged star polymers precipitate in the presence of an excess of inorganic salt, such as NaI, NaBF₄, Bu₄NBr and K₂CO₃ due to effective screening of the charges.

3.2 Conclusions

Arm-first RAFT polymerization has in the past been plagued by high polydispersity, contamination with unincorporated linear species and star-star coupling, and only recently have a few examples of well-defined star polymers emerged.^{23,24,31-33} In this chapter, we have successfully applied arm-first RAFT polymerization to prepare the first examples of luminescent organoboron star polymers. Their spherical star structure and low polydispersity were confirmed by GPC, MALLS, DLS and TEM analysis. The star polymers are stable in water and the amphiphilic PNIPAM-b-PS star polymer undergoes self-assembly into even larger luminescent super-aggregates. Our approach offers a convenient and novel means of using (hydrophobic) organoboron chromophores in water as a medium, which is highly desirable and advantageous for potential applications as new luminescent materials and in bioimaging. Moreover, the modular synthesis allows us to readily tune the luminescence of the nanostructures either by variation of the crosslinker or by introduction of additional functionality into the arms. The latter was successfully demonstrated in the facile decoration of the P4VP stars with carbazole moieties. The pyridyl groups also lend themselves to binding of metal complexes and further studies in this respect are now in progress. These well-defined luminescent boron quinolate star polymers are expected to prove useful in biological and energy-related applications.

3.3 Experimental

General methods. The 499.9 MHz ¹H and 125.7 MHz ¹³C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ¹¹B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. The ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks and the ¹¹B NMR spectra externally to BF₃•Et₂O ($\delta = 0$) in C₆D₆. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

GPC analyses were performed in THF (1.0 mL/min) or DMF with 0.2% w/v Bu4NBr (0.50 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Three styragel columns (Polymer Laboratories; two 5 µm Mixed-C and one 5 µm Mixed-D), which were kept in a column heater at 35 °C, were used for separation in THF. For separation in DMF/0.2% Bu4NBr either a set of two polyvinylalcohol columns (Shodex Asahipak 9 µm GF-710 HQ and 5 µm GF-510 HQ) or a set of two styragel columns (Polymer Laboratories; one 10 µm Mixed-B and one 5 µm Mixed-C) was used at 65 °C. The columns were calibrated with polystyrene standards (Polymer Laboratories). Multiangle laser light scattering (MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument in-line with the GPC; a Wyatt Optilab T-rEX refractive index detector operated at 658 nm was used as the concentration detector for in-line GPC-MALLS measurements; differential refractive indices (dn/dc) were calculated from in-line GPC-MALLS detection using the Wyatt Astra software assuming 100% mass recovery or literature data were used as specified.

UV-visible absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse Fluorescence spectrophotometer with optically dilute solutions (A<0.1). Anthracene was used as the standard and the quantum yield of anthracene (0.33 in THF) was adopted from the Handbook of Photochemistry (S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker Inc., New York, 1993.). Sample solutions were prepared using a microbalance (\pm 0.1 mg) and volumetric glassware. The quantum yield was calculated from a graph of integrated fluorescence intensity vs. absorbance of at least 4 solutions with increasing concentration. The gradient of the graph is proportional to the quantum yield.

Transmission electron microscopy (TEM) characterization was conducted on a FEI Tecnai 12 electron microscope operated at 80 kV. The star polymer solution in chloroform was cast on a copper grid with a carbon coating (no formvar), and stained by RuO4 vapor for 10 min in a sealed container. To stain the star polymer aggregates, one drop of micelle solution in water was cast on a copper grid. The water was allowed to evaporate, and the sample was stained by exposure to iodine vapor for 30 min.

Dynamic light scattering (DLS) was carried out on a Wyatt Dawn EOS instrument that was modified with a Wyatt QELS attachment. Data were collected either in-line or in batch mode using an avalanche photodiode and an optical fiber. The in-line GPC-QELS data are given as number-average hydrodyanmic diameters. For batch mode measurements, the data was processed using the Wyatt QELS software (regularization analysis, results are given as intensity-average hydrodynamic diameters). **Materials.** THF and 1,4-dioxane were distilled from Na/benzophenone prior to use. Dichloromethane (DCM) was dried over CaH₂, followed by vacuum transfer. Azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. Styrene (St) and 4-vinyl pyridine (4VP) were purified by passing the liquid through a neutral alumina column and then distilled under reduced pressure. N-isopropyl acrylamide (NIPAM) was crystallized in hexanes/benzene mixture. The chain transfer agents (Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo, S. H. Thang, *Macromolecules* **2003**, *36*, 2256-2272; M. H. Stenzel, T. P. Davis, A. G. Fane, *J. Mater. Chem.* **2003**, *13*, 2090-2097) and *N*-(4'-bromobutyl)carbazole (C. Barrett, B. Choudhury, A. Natansohn, P. Rochon, *Macromolecules* **1998**, *31*, 4845-4851) used in this chapter were synthesized according to reported procedures. All the other solvents and chemicals were used without further purification.

Synthesis of distyrylboron quinolate (Crosslinker 1). Method 1. To a flame-dried 3neck flask containing 6.42 g (0.264 mol) of magnesium, were added 300 mL of THF and 1.0 mL of 1,2-dibromoethane. After stirring for 5 min, 33.3 g (0.24 mol) of 4chlorostyrene were added via an addition funnel. The reaction mixture was stirred at 55 °C for 2 h. The styryl magnesium chloride solution was then added via canula to trimethoxy borane (10.4 g, 0.100 mol) in 30 mL of THF. The reaction mixture was stirred at 45 °C for 1 h, followed by the addition of 14.5 g (0.100 mol) of 8-hydroxy quinoline under nitrogen protection. After stirring for another 6 h at 45 °C, an aqueous solution of [NH4][HCO₃] was added and the product was extracted into DCM. The crude product was purified by silica gel column chromatography with DCM as the eluent and then crystallized from DCM/hexanes mixture to give a yellow microcrystalline solid (17.1 g, 55%). Method 2. In a glove box, 2.35 g (9.37 mmol) of BBr₃ were dissolved in 10 mL of DCM in a Schlenk flask. A solution of 4-trimethylstannyl styrene (5.00 g, 18.73 mmol) in 20 mL of DCM was added dropwise to the BBr3 solution. The reaction mixture was stirred at room temperature for 4 h, then 1.49 g (9.37 mmol) of 8-methoxy quinoline solution in 10 mL of DCM were added. After another 2 h of stirring, the reaction mixture was worked up with 10% aqueous [NH4][HCO3] (3×50 mL). The organic phase was separated and dried over Na₂SO₄. The crude product was purified by column chromatography on silica gel with DCM as the eluent, and crystallized in a 1/2 mixture of DCM/ether. The product was obtained in the form of yellow crystals (1.73 g, 51%). ¹¹B NMR (160.380 MHz, CDCl₃): δ = 11.3 (w_{1/2} = 430); ¹H NMR (499.893 MHz, CDCl₃): δ = 8.58 (d, ${}^{3}J = 5.0$ Hz, 1H, Q-H2), 8.43 (d, ${}^{3}J = 8.0$ Hz, Q-H4), 7.68 (pst, ${}^{3}J = 8.0$ Hz, 1H, Q-H6), 7.64 (dd, ${}^{3}J = 5.0$ Hz and 8.5 Hz, 1H, Q-H3), 7.42 (d, ${}^{3}J = 8.0$ Hz, 4H, Ph-H2,6), 7.34 (d, ${}^{3}J$ = 8.0 Hz, 4H, Ph-H3,5), 7.25 (d, ${}^{3}J$ = 8.5 Hz, 1H, Q-H5), 7.20 (d, ${}^{3}J$ = 7.5 Hz, 1H, Q-H7), 6.70 (dd, ${}^{3}J = 11.0$ Hz, 18.0 Hz, 2H, vinyl-H), 5.67 (d, ${}^{3}J = 18.0$ Hz, 2H, vinyl-H), 5.18 (d, ${}^{3}J = 11.0$ Hz, 2H, vinyl-H); ${}^{13}C$ (125.698 MHz, CDCl₃): $\delta = 158.9$, 147.0, 139.4, 139.0, 137.7, 137.4, 136.5, 133.1, 132.4, 128.6, 125.7, 123.0, 113.1, 112.5, 109.9; UV-Vis (THF, 3.0 x 10^{-5} M): $\lambda_{max} = 395$ nm ($\varepsilon = 3200$); fluorescence (THF, 3.0 x 10^{-5} M): $\lambda_{em,max} = 505$ nm, $\Phi = 0.22$ ($\lambda_{exc} = 395$ nm). High resolution MALDI-MS: Calcd for C₂₅H₁₉NBO: 360.1559; obsvd: 360.1574.



Figure 3-11. ¹H, ¹¹B and ¹³C NMR spectra of crosslinker 1 in CDCl₃.

Synthesis of poly(*N*-isopropyl acrylamide) macro-CTA (PNIPAM-1). Into a Schlenk tube were loaded NIPAM (3.53 g, 31.2 mmol), 3-benzylsulfanylthiocarbonylsulfanyl propionate (59.6 mg, 0.208 mmol), AIBN (3.42 mg, 20.8 µmol, stock solution in dioxane), and 12 mL of dioxane. After 3 freeze-pump-thaw cycles, the tube was immersed in a 60 °C oil bath and kept stirring for 3 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired PNIPAM-1 was obtained as a pink powder (1.15 g, 33%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu4NBr): $M_n = 8800$ g/mol, PDI = 1.18. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu4NBr): $M_n = 11230$ g/mol, PDI = 1.11, dn/dc = 0.074 mL/g.

Synthesis of poly(*N***-isopropyl acrylamide) macro-CTA (PNIPAM-2).** Into a Schlenk tube were loaded NIPAM (4.52 g, 40.0 mmol), benzyl dithiobenzoate (BDTB) (98 mg, 0.40 mmol), AIBN (13.1 mg, 80 μmol), and 4.0 mL of dioxane. After 3 freeze-pump-

thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 20 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired PNIPAM-2 was obtained as a pink powder (1.62 g, 34%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu₄NBr): $M_n = 6800$ g/mol, PDI = 1.17. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu₄NBr): $M_n = 7840$ g/mol, PDI = 1.08, dn/dc = 0.075 mL/g.

Synthesis of P4VP. Into a Schlenk tube were loaded 4-vinyl pyridine (15.5 g, 147 mmol), benzyl dithiobenzoate (BDTB) (120 mg, 0.491 mmol), AIBN (16.1 mg, 98.2 μ mol), and 1.0 mL of dioxane. After three freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether, followed by drying in high vacuum. The desired P4VP macro-CTA was obtained as a pink powder (6.70 g, 42%). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu4NBr): $M_n = 11100$ g/mol, PDI = 1.32. GPC-MALLS (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu4NBr): $M_n = 11100$ g/mol, PDI = 1.200 g/mol, PDI = 1.09, dn/dc = 0.143 mL/g.

Synthesis of PNIPAM-*b***-PS.** Into a Schlenk tube were loaded 50 mg of PNIPAM-CTA2, AIBN (13.1 mg, 80 μmol), 3.0 mL of styrene and 1.0 mL of dioxane. After three freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of methanol, followed by drying in high vacuum. The desired of PNIPAM-*b*-PS macro-CTA was obtained as light pink

powder (0.70 g). GPC-RI (styragel columns, THF): $M_n = 57900$ g/mol, PDI = 1.24; GPC-MALLS (styragel columns, DMF with 0.2 % (w/v) Bu₄NBr): $M_n = 75800$ g/mol, PDI = 1.18, dn/dc = 0.149 mL/g.

Synthesis of PS star polymer. In a Schlenk tube, PS-1 (547 mg), distyrylboron quinolate (500 mg, 1.38 mmol), and AIBN (0.94 mg, 5.72 µmol; stock solution in dioxane) were dissolved in 6.0 mL of dioxane ([crosslinker]/[PS-1]/[AIBN] = 24/1/0.10). After three freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated into a 10-fold volume of methanol. The precipitated polymer was fractionated twice in THF/methanol. The isolated material was dried in high vacuum to give the product as a yellow powder (740 mg). GPC-RI (styragel columns, THF): $M_n = 73800$ g/mol, PDI = 1.21. GPC-MALLS (styragel columns, THF): $M_n = 271000$ g/mol, PDI = 1.38, dn/dc = 0.169 mL/g.

Synthesis of PNIPAM star polymer. In a Schlenk tube, PNIPAM-1 (400 mg), distyrylboron quinolate (289 mg, 0.80 mmol), and AIBN (1.09 mg, 6.67 µmol; stock solution in dioxane) were dissolved in 10.0 mL of dioxane ([crosslinker]/[PNIPAM-1/[AIBN] = 16/1/0.13). After three freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath under stirring for 12 h. The reaction was terminated by placing the tube The polymer was in liquid nitrogen. then fractionated three times in dichloromethane/ether. The isolated material was dried in high vacuum to give the product as a yellow powder (240 mg). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu₄NBr): $M_n = 146000$ g/mol, PDI = 1.32. GPC-MALLS (styragel columns, DMF with 0.2 % (w/v) Bu₄NBr): 334400 g/mol, PDI = 1.80, dn/dc = 0.106 mL/g.

Synthesis of P4VP star polymer. In a Schlenk tube, P4VP (300 mg), distyrylboron quinolate (233 mg, 0.645 mmol), and AIBN (0.589 mg, 3.58 µmol; stock solution in dioxane) were dissolved in 3.0 mL of dioxane and 1.0 mL of DMF ([crosslinker]/[P4VP]/[AIBN] = 33/1/0.18). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath under stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then fractionated in methanol/ether 3 times. The isolated polymer was dried in high vacuum to give the product as 180 mg of yellow powder. GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) Bu4NBr): M_n = 294000 g/mol, PDI = 1.46. GPC-MALLS (styragel columns, DMF with 1 % (v/v) pyridine): M_n = 320000 g/mol, PDI = 1.98, dn/dc = 0.143 mL/g.

Synthesis of PNIPAM-*b*-PS star polymer. In a Schlenk tube, PNIPAM-*b*-PS (175 mg), distyrylboron quinolate (33 mg, 0.183 mmol), and AIBN (0.167 mg, 1.02 μ mol; stock solution in dioxane) were dissolved in 1.0 mL of dioxane ([crosslinker]/[PNIPAM-*b*-PS]/[AIBN] = 79/1/0.44). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The crude product was then fractionated in THF/ether twice. The isolated polymer was dried in high vacuum to give the product as a yellow powder (135 mg). GPC-RI (polyvinylalcohol columns, DMF with 0.2 % (w/v) TBAB): M_n = 729000 g/mol, PDI = 1.40, dn/dc = 0.127 mL/g.



Figure 3-12. GPC overlays of PNIPAM, P4VP, and PNIPAM-*b*-PS star polymers and their corresponding arm precursors.

Self-assembly of PNIPAM-*b*-PS star polymer. The PNIPAM-*b*-PS star polymer (1.2 mg) was dissolved in 6.0 mL of THF. The star polymer solution was loaded into dialysis tubing (cut-off molecular weight = 6000~8000) and dialyzed against ~1L of deionized water for 3 days. The THF solvent was completely removed by changing water 5 times.

Stability studies of PNIPAM and PNIPAM-*b*-PS star polymers in strongly basic water. The PNIPAM star polymer was dissolved in water (c = 0.2 mg/mL) and NaOH was added ($c_{\text{NaOH}} = 0.1 \text{ M}$). Similarly, NaOH was added to a solution of PNIPAM-*b*-PS star polymer in water ($c_{\text{NaOH}} = 0.1 \text{ M}$). For both samples, fluorescence spectra were taken before and 12 h after NaOH addition.

Carbazole modification of P4VP star polymer (Synthesis of P4VP-Cz star). In a vial, P4VP star polymer (40 mg) was dissolved in 4.0 mL of DMF, followed by addition of 230 mg of *N*-(4'-bromobutyl)carbazole. Nitrogen was bubbled through the tube for 5 min and the tube was sealed. After stirring at 45 °C for 2 days, the polymer solution was

precipitated in ether three times, and then dried under high vacuum to give the product as a light yellow solid (56 mg).

Solubility test of P4VP-Cz star polymer in water. The P4VP-Cz star polymer was dissolved in water at 0.1 mg/mL. A chosen inorganic salt (NaI, NaBF₄, Bu₄NBr or K₂CO₃) was dissolved in the star polymer solution ($c_{salt} = 0.1$ M). A flocky precipitate was observed within minutes after addition.

Determination of the mass fraction of the core (*frac*_{core}) of star polymers from the UV-vis absorption at 395 nm using a linear boron quinolate polymer as standard. The *frac*_{core} of the star polymers containing a crosslinked boron quinolate core is calculated based on comparison of the absorption at $\lambda_{abs} = 395$ nm with that of a linear boron quinolate polymer ($M_{n, GPC} = 8710$ g/mol, PDI = 1.28, $M_{n, MALLS} = 27550$ g/mol) as standard.



Figure 3-13. The structure of the linear boron quinolate polymer standard and calibration curve for the absorbance of the linear boron quinolate polymer at $\lambda_{abs} = 395$ nm used for the estimation of the mass fraction of the core (*frac*_{core}) of star polymers.

Assuming that the boron quinolate chromophores in the linear polymer and the crosslinked core of the star polymers have a similar absorptivity ε at $\lambda_{abs} = 395$ nm, and

given that the arms of the star polymers show no absorbance at this wavelength, the *frac*_{core} of star polymers is given by:

$$frac_{core} = \frac{Abs_{star} \times Conc_{stan}}{Conc_{star} \times Abs_{stan}} = \frac{Abs_{star}}{Conc_{star} \times 6.265}$$

where *Abs*_{star}, *Abs*_{stan}, *Conc*_{star} and *Conc*_{stan} are the absorbance of the star polymer and standard, and the concentration of the star polymer and standard, respectively. The calculated *frac*_{core} of the star polymers are listed in Table 3-1.

Determination of the average number of arms (f_{arm}) of star polymers. From the *frac*_{core} of the star polymers and the absolute molecular weights of the star polymers and arm precursors, we can calculate the average number of arms (f_{arm}) of the star polymers using the formula,

$$f_{arm} = \frac{M_{n,star} \times (1 - frac_{core})}{M_{n,arm}}$$

where $M_{n,star}$ and $M_{n,arm}$ are the absolute molecular weights of the star polymers and arm precursors, respectively.

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Chapter 4 Luminescent Tricoordinate Boron Block Copolymers

In the last two chapters, we introduced a series of luminescent organoboron quinolate block copolymers and star polymers that serve as versatile building blocks for supramolecular nanostructures. The bidentate quinolate ligands render these polymers excellent stability that is crucial for luminescent polymers in practical applications, such as chemical sensors and electronic devices. Meanwhile, a selection of methods can be applied to functionalize the 5-position of quinolate ligands and provide for variation of the photophysical properties and methodologies of material fabrication.

Different from tetracoordinate boron chromophores, tricoordinate boron compounds and polymers are known as Lewis acids and possess empty p-orbitals that can interact with electron-donating species, which usually results in color and luminescence changes. These phenomena have been utilized to detect potentially toxic anions, such as fluoride and cyanide anions, as well as neutral Lewis bases.¹ However, a large number of tricoordinate boron compounds suffer from instability of the labile boron center. To overcome this disadvantage, bulky ligands have been used to stabilize the tricoordinate boron compounds with carefully selected ligands have been proved to be promising candidates for functional materials.¹ On the other hand, despite of the universal processability and fabrication properties, polyolefins with tricoordinate boron functionalities remain rare in the literature. In this chapter, we will introduce novel block copolymers with two types of tricoordinate boron functionalities: borinic acid groups and bismesityl boranes. The advantages of these block copolymers include high

luminescence, excellent stability, as well as the potential for nanostructure formation. They are also studied for fluoride detection.

4.1 Borinic Acid Block Copolymers

Taking advantage of their glucose-binding properties, boronic acid-functionalized polymeric materials are expected to serve as candidates for sugar-related disease diagnosis and therapy.² To this end, various boronic acid block copolymers and their sugar-binding behavior were studied by different research groups.³⁻⁷ On the other hand, as weak polyelectrolytes of switchable solubility and charge state, boronic acid polymers can also be utilized as building blocks for stimuli-responsive self-assembled materials.^{8,9} In a notable recent example, the Sumerlin group reported the supramolecular co-assembly of boronic acid block copolymers and multifunctional diol molecules. In aqueous solution, the inter-polymer crosslinking between the boronic acid blocks and diols led to dynamic star polymer structures, which dissociated upon addition of monofunctional diol.¹⁰

Compared to the extensive studies on boronic acid compounds and polymers, borinic acids have been mostly ignored, in spite of their easy synthesis and excellent stability.¹¹ With a general structure of RR'BOH, borinic acids are weak organic acids that possess diverse structures and properties when R and R' are varied. In this section, we report the first examples of borinic acid block copolymers (BABCs) that share the features of strong luminescence and H-bonding induced supramolecular assembly. A novel borinic acid monomer was synthesized and converted to well-defined narrow block copolymers with strong luminescence and excellent stability via RAFT polymerization. The BABCs were employed as H-bonding donors for supramolecular co-assemblies with poly(4-

vinylpyridine) (P4VP) as a H-bonding acceptor, and as precursor to a BABC/silica composite material.



Figure 4-1. Synthesis of borinic acid monomer and corresponding block copolymers.

We designed a borinic acid compound with a styryl group and explored the synthesis of the first BABCs (Figure 4-1). The borinic acid monomer (M4) was obtained with high purity by Stille coupling of styryltrimethyltin and iodophenyl triisopropylphenyl borinic acid in 81% yield. As shown in Figure 4-2, the ¹H NMR of borinic acid monomer BA reveals the presence of a vinyl group in the region from 5.2 to 7.0 ppm and the –OH group at 5.82 ppm. The signal of the methyl groups in ortho-position to B at 1.21 ppm is

broadened due to the hindered rotation about the bulky isopropyl groups. The ¹¹B NMR shows a single broad peak around 49 ppm, indicating the tricoordinate boron structure.

For the block copolymer synthesis, RAFT polymerization of BA was carried out in the presence of PS-1 and PNIPAM-3 as macro chain transfer agents. The ¹H and ¹¹B NMR spectra of PS-b-PBA and PNIPAM-b-PBA are shown in Figure 4-2. Compared to the monomer, the ¹¹B NMR of both block copolymers shifted upfield to 43 ppm. The borinic acid groups showed broad signals in the ¹H NMR at the same chemical shift as the monomer. For PS-b-PBA, a new broad peak appeared at 3.75 ppm. This peak is assigned to methyl borinic ester groups, which must have formed during the precipitation in methanol. According to the ¹H NMR integration at 3.75 (-OMe) and 5.82 (-OH) ppm, about 30% of the BOH groups underwent esterification. Attempts at purification by precipitation into hexanes rather than MeOH led to large losses due to the high solubility of the polymer. To the contrary, the signal of ester was absent in the ¹H NMR of PNIPAM-b-PBA, because PNIPAM-b-PBA could be readily purified by precipitation in diethyl ether. The GPC graphs in Figure 4-3 show single symmetric peaks upon chain extension, indicating well controlled polymerization. The molecular weight data are summarized in Table 4-1. The degree of polymerization was also determined by ¹H NMR integration and found to be comparable to the GPC results. BABCs with fairly high molecular weights and reasonably narrow distribution were successfully synthesized.



Figure 4-3. ¹H and ¹¹B NMR spectra of borinic acid monomer and BABCs in CDCl₃.



Figure 4-3. GPC overlays of (A) PS-1 (black) and PS-*b*-PBA (blue) in THF, and (B) PNIPAM-3 (black) and PNIPAM-*b*-PBA (blue) in DMF with 0.2% (w/w) of Bu₄NBr.

Polymer ^{<i>a</i>}	$M_{ m n,GPC}$	PDI _{GPC}	$M_{ m n,MALLS}$	m, n _{GPC} ^b	m / n _{NMR} ^c
PS _m -1	8130	1.16	9470	89	89 ^e
PS _m - <i>b</i> -PBA _n	16880	1.08	20400	89, 27	89 ^e / 24
PNIPAM _m -3	9630	1.09	d	82	63 ^f
PNIPAM _m -b-PBA _n	27020	1.26	d	82, 42	63 ^f / 35

Table 4-1. Summary of molecular weights of BABCs and CTAs.

^{*a*} m and n refer to the degree of polymerization of the first and second block, respectively. ^{*b*} Determined by GPC-MALLS (PSm-*b*-PBA_n) or GPC-RI (PNIPAM_m-*b*-PBA_n PNIPAM_m-*b*-PBA_n). ^{*c*} Based on ¹H NMR integration (aromatic region 6.18~7.22 ppm for PSm-*b*-PBA_n, 4.0 and 2.9 ppm for PNIPAM_m-*b*-PBA_n). ^{*d*} Not measured. ^{*e*} Based on GPC-MALLS. ^{*f*} Based on ¹H NMR end group analysis of PNIPAM.



Figure 4-4. Absorption (A) and emission (B) spectra of borinic acid monomer (black) and PS-*b*-PBA (blue); (C) photographs of PS-*b*-PBA in THF solution and as a solid under UV irradiation.

A valuable property of both the borinic acid monomer and the BABCs lies in their strong luminescence under UV irradiation. The photophysical data of the monomer and BABCs are given in Figure 4-4 and Table 4-2. The borinic acid monomer shows absorption and emission maxima at 294 and 345 nm, respectively, with a high quantum efficiency of 0.82 in THF. The BABCs show almost identical blue-shifted absorptions at ca. 280 nm due to the conversion of the vinyl group during polymerization. The emission spectra of the BABCs are similar to that of the monomer but somewhat flattened and broadened in shape, and the quantum efficiency is reduced to ~0.37, possibly due to the neighboring group effect of boron chromophores along the polymer chain.

Sample	$\lambda_{abs} (nm)$	$\epsilon (cm^{-1}M^{-1})$	$\lambda_{em} (nm)^{b}$	$arPhi_{ m F}$
Monomer	294	26290	345	0.82
PS-b-PBA	280	28080 ^a	~330-360	0.36
PNIPAM-b-PBA	282	29750 ^a	~330-360	0.38

Table 4-2. Photophysical properties of borinic acid monomer and BABCs in THF

^{*a*} The molar extinction coefficient of the borinic acid unit of BABCs was estimated according to the block ratio derived from the ¹H NMR integration ; ^{*b*} All samples were excited at the corresponding $\lambda_{abs.}$

Having accomplished the synthesis of well-defined BABCs, we next investigated applications as building blocks for supramolecular nanostructures and hybrid material synthesis. Non-covalent interactions, such as H-bonding, inclusion complexation, metal coordination, electrostatic interaction and biorecognition, have been extensively used to generate supramolecular nanostructures.¹²⁻¹⁴ H-bonding interactions draw particular attention because of their important role in the storage and expression of life information, as well as the striking utility in the programmable assembly of nanostructures with welldefined shape, size and functions. For example, the Ikkala group studied the supramolecular nanostructures of block copolymer/amphiphile complexes through Hbonding in the bulk state.^{15,16} Representative systems are PS-b-P4VP/pentadecylphenol(PDP) and nonadecylphenol(NDP) complexes, in which the phenol small molecules bind to the P4VP block through H-bonding, forming combshaped supramolecules. By tuning the block length ratio of PS and P4VP blocks, the phase separation of the supramolecules leads to hierarchical structures, including lamellar-within-spherical, lamellar-within-cylinder, lamellar-within-lamellar, cylinderwithin-lamellar and spherical-within-lamellar. The supramolecular H-bonding coassembly of PS-b-P4VP/acid compounds has been reported by Chen and co-workers.¹⁷⁻²⁰ In the good solvent chloroform, the H-bonding between acids and the P4VP block led to comb-like supramolecules. Meanwhile, the reduced solubility of the P4VP/acid complex drove the formation of nanostructures, such as spherical micelles and hollow spheres.

These examples demonstrate that P4VP is an effective H-bonding acceptor for supramolecular nanostructures. The –OH groups of BABCs show a chemical shift at ~5.8 ppm, which is a reflection of the weak acidity that is close to that of phenol compounds. Therefore, we expected the BABCs to be promising as H-donors for luminescent supramolecular nanostructures.

The supramolecular co-assembly of BABCs and P4VP homopolymer was carried out in chloroform. Upon addition of a P4VP solution in chloroform into a solution of the respective BABC under stirring, features of opalescence due to polymeric colloids appeared immediately. The DLS characterization results for PS-*b*-PBA/P4VP and PNIPAM-*b*-PBA/P4VP supramolecular micelles are given in Figure 4-5 (A). The sizes of supramolecular micelles are larger than those of the single chains of PS-*b*-PBA ($<D_h>$ = 3.8±0.8 nm), PNIPAM-*b*-PBA ($<D_h>$ = 4.5±1.2 nm) and P4VP ($<D_h>$ = 8.5±1.2 nm), indicating that all polymer chains were involved in the supramolecular micelles. The size of PS-*b*-PBA/P4VP assembly ($<D_h>$ = 26.5±8.2 nm) is much smaller than that of PNIPAM-*b*-PBA/P4VP assembly ($<D_h>$ = 215±90 nm), possibly because the block length ratio of PS/PBA (m/n = 3.3) is larger than that of PNIPAM/PBA (m/n = 1.8), Another reason could be that about 30% of the borinic acid groups in PS-*b*-PBA formed methyl esters that are not available for H-bonding interaction. The BABC/P4VP

assemblies present spherical structures. The size of the PS-*b*-PBA/P4VP aggregates based on TEM is close to the DLS result, while the size of PNIPAM-*b*-PBA/P4VP aggregates is smaller than the DLS result, likely because the core of the aggregates in chloroform is highly swollen, but shrinks upon solvent evaporation on the copper grid. Similar to the BABC solutions, the supramolecular assemblies are highly luminescent.



Figure 4-5. (A) Size distribution of PS-*b*-PBA/P4VP (green solid, $\langle D_h \rangle = 26.5\pm8.2$ nm) and PNIPAM-*b*-PBA/P4VP (purple solid, $\langle D_h \rangle = 215\pm90$ nm) supramolecular micelles, and PS-*b*-PBA (green dash, $\langle D_h \rangle = 3.8\pm0.8$ nm), PNIPAM-*b*-PBA (purple dash, $\langle D_h \rangle = 4.5\pm1.2$ nm), P4VP (red dash, $\langle D_h \rangle = 8.5\pm1.2$ nm) single chains in chloroform; TEM images of PS-*b*-PBA/P4VP (B) and PNIPAM-*b*-PBA/P4VP (C) supramolecular micelles; (D) schematic illustration of H-bonding induced supramolecular micelle formation.

It should be noted that as Lewis bases, pyridines can form complexes with tricoordinate borane compounds. To confirm that the supramolecular co-assembly of BABCs and P4VP results from H-bonding, rather than Lewis acid/base interaction, we acquired the ¹H and ¹¹B NMR spectra of a mixture of borinic acid monomer and 4-¹Bu-pyridine in CDCl₃ (Figure 4-6). The proton signal of the –OH group completely disappeared, which is a sign of H-bonding. Meanwhile, the mixture showed an identical ¹¹B NMR signal as the monomer by itself, indicating the absence of significant Lewis acid/base interaction. We attribute this to the bulk of the triisopropylphenyl group and the π -electron-donating nature of the –OH group that lower the Lewis acidity of the borane moiety. The proposed mechanism of H-bonding induced supramolecular co-assembly of BABC/P4VP is illustrated in Figure 4-5 (D). Other functional building blocks for supramolecular co-assembly with BABCs. These results hence offer a new design principle for boron-functionalized polymer-based nanostructures and luminescent materials.



Figure 4-6. ¹H and ¹¹B NMR spectra of BA monomer/4-^tBu pyridine mixture in CDCl₃.



Figure 4-7. TEM images and size distribution of PNIPAM-*b*-PBA vesicles (A) and PNIPAM-*b*-PBA/silica composite (B); (C) photographs of PNIPAM-*b*-PBA vesicles and PNIPAM-*b*-PBA/silica composite, under UV-irradiation (365 nm hand-held UV lamp); (D) Absorption and emission spectra of PNIPAM-*b*-PBA vesicles in water; (E) Absorption and emission spectra of PNIPAM-*b*-PBA/silica composite in water.

The amphiphilic self-assembly of PNIPAM-*b*-PBA was studied in water and the resulting aggregates were used as nanoreactors for inorganic material synthesis. Water was added dropwise to a PNIPAM-*b*-PBA solution in THF under stirring. After dialysis against water, the self-assembly was examined by TEM and DLS. Vesicles were observed in the TEM image (Figure 4-7 (A)). Due to the softness of the polymeric material, the thin-walled vesicles were broken and fused together on the copper grid. DLS characterization revealed a size of $\langle D_h \rangle = 173\pm57$ nm. A sol-gel reaction was attempted within the vesicles to synthesize a BABC/silica composite material. The hydrophobic tetraethyl orthosilicate (TEOS) precursor was added during vesicle formation. Then, triethyl amine was added to catalyze the sol-gel reaction, followed by dialysis to remove the triethyl amine. The TEM image in Figure 4-7 (B) shows the
BABC/silica composite with what appears to be a hollow structure. The size of the nanocomposite structures based on DLS is $\langle D_h \rangle = 242\pm133$ nm, which is larger and more polydispersed than the vesicles. The photophysical data of vesicles and borinic acid block copolymer/silica composite were also examined (Figure 4-7 (C)-(E)). The emission of the vesicles is similar to that of the block copolymer in the good solvent THF, but significantly weakened, presumably due to chromophore aggregation in the wall of the vesicles. Interestingly, a weak and broad green-emissive band was observed in the BABC/silica composite, possibly due to the interaction between the borinic acid moieties and silica.

4.2 Triarylborane-Functionalized Polymers

Triarylborane compounds and polymers have been utilized as chemical sensors for potentially toxic anions, such as fluoride and cyanide.^{1,21-24} However, anion sensing based on triarylboranes in highly polar organic solvents and aqueous media still remains a great challenge because of the large hydration enthalpy of anions such as F⁻ and CN⁻, and the instability of triaryl boranes, which limits the practical application.²² In this section, we describe novel tricoordinate boron-functionalized polymers and their use as anion sensors. Dimesitylphenylborane was selected as binding site because of its excellent stability due to the hindered boron center. At the same time, the bulky mesityl groups provide selectivity of the anion binding, so that only small or linear anions, such as fluoride and cyanide, can form Lewis acid/base complexes with the boron center. We synthesized a series of well-defined homo-, block and block-random copolymers via RAFT polymerization and used them for fluoride sensing studies. In this work, for the first time,

we explored the chain architecture effect on fluoride sensing. Secondly, a dual responsive fluoride sensor in the polar solvent DMF was developed that is based on the self-assembly of block copolymers. Moreover, a positively charged block-random copolymer was synthesized by post-modification and enhanced fluoride sensing in aqueous media (DMF/water = 9/1 (w/w)) was realized.



PNIPAM-b-P(M5-ran-4VPMeOTf)

Figure 4-8. Synthesis of dimesitylboron monomer and corresponding homo- and block copolymers.



Figure 4-9. ¹H and ¹¹B NMR spectra of M5, PM5, PNIPAM-*b*-PM5, PNIPAM-*b*-P(M5*ran*-4VP) in CDCl₃ and NIPAM-*b*-P(M5-*ran*-4VPMeOTf) in DMSO-*d*6.

We designed a dimesityl boron compound with a styryl group (M5) and explored the synthesis of homo- and block copolymers (Figure 4-8). M5 was obtained with high purity by Stille coupling of styryltrimethyltin and iodophenyl dimesityl borane in 72% yield. As shown in Figure 4-9, the ¹H NMR of M5 reveals the presence of the vinyl group in the region from 5.31 to 6.78 ppm. The signal of the meta protons and methyls of the mesityl groups appear at 6.86, 2.34 and 2.07 ppm, respectively. The ¹¹B NMR shows a single broad peak around 74 ppm, indicating the tricoordinate boron structure.

For the polymer synthesis, RAFT polymerizations of M5 were carried out in the presence of benzyl dithiobenzoate and PNIPAM-3 as macro chain transfer agent. 4VP was also used as a comonomer to synthesize PNIPAM-b-P(M5-ran-4VP) for the incorporation of pyridine functionalities (Figure 4-8). The ¹H and ¹¹B NMR spectra of the homo- and block copolymers are shown in Figure 4-9. Compared to the monomer, the ¹¹B NMR signal of all polymers shifted upfield to 65 ppm, and the signals of the mesityl groups are clearly seen in the ¹H NMR spectra, indicating the stability of the boron chromophore during polymerization. The tertiary protons of the isopropyl groups of the PNIPAM block are found at 4.1 ppm, and the aromatic protons of the 4VP units of PNIPAM-b-P(M5-ran-4VP) appeared at 8.3 and 6.4 ppm. Taking into consideration the earlier work by Gabbai and coworkers,^{25,26} we postulated that positive charges along the polymer chain may enhance the fluoride binding ability of the boron sites. Therefore, the pyridine moieties in PNIPAM-b-P(M5-ran-4VP) were quaternized to introduce positive pyridinium units. Methyl triflate was used as a strong methylation agent and the quaternization was carried in chloroform. The ¹H NMR spectrum of PNIPAM-*b*-P(M5ran-4VPMeOTf) in DMSO-d6 shows the signals of pyridinium units at 8.7 and 7.5 ppm,

and the boron chromophores and PNIPAM block remained intact. The post-modified block copolymer shows only a weak peak around 62 ppm in the ¹¹B NMR due to the reduced weight fraction of boron chromophores after post-modification.



Figure 4-10. GPC traces of (A) PM5 in THF at 1.0 mL/min; (B) PNIPAM-3 in DMF/pyridine = 99/1 (v/v) at 0.5 mL/min; (C) PNIPAM-*b*-PM5 in chloroform at 1.0 mL/min; (D) PNIPAM-*b*-P(M5-*ran*-4VP) in DMF/pyridine = 99/1 (v/v) at 0.5 mL/min.

The GPC traces of PM5, PNIPAM-3, PNIPAM-*b*-PM5 and PNIPAM-*b*-P(M5-*ran*-4VP) are shown in Figure 4-10, and the molecular weights are summarized in Table 4-3. The PM5 homopolymer is soluble in organic solvents such as chloroform and THF, and not soluble in hexanes, ether, methanol or DMF. The GPC of PM5 was characterized in THF (Figure 4-10 (A)). Fairly narrow polymer (PDI = 1.25) with M_n = 9770 g/mol was synthesized, indicating that benzyl dithiobenzoate is an effective CTA for M5. The GPC trace of the PNIPAM-3 precursor (7380 g/mol based on ¹H NMR end group analysis) for the two block copolymers was acquired in DMF/pyridine = 1/1 (v/v). For PNIPAM-*b*-PM5, neither DMF nor THF was suitable for GPC characterization, because PM5 is not soluble in DMF and PNIPAM has strong interaction with the GPC column in THF. Fortunately, the attempt in chloroform gave a narrow GPC trace without tailing (Figure 4-10 (C)), which indicates that well-defined block copolymer with fairly high molecular weight (degree of polymerization, m and n) based on GPC is relative to PS standard. Thus, we also

estimated m and n by ¹H NMR integration (Table 4-3). PNIPAM-*b*-P(M5-*ran*-4VP) is well soluble in DMF, because the fraction of M5 units in the second block was low (0.13 based on ¹H NMR integration) and randomly embedded between the 4VP units. Therefore, we were able to characterize PNIPAM-*b*-P(M5-*ran*-4VP) in DMF/pyridine = 1/1 (v/v) (Figure 4-10 (D)). The mole fractions of M5 (x) and 4VP (y) were also estimated to be 0.13 and 0.87 according to ¹H NMR integration, which are close to the feed ratio (1/9).

Table 4-3. Summary of molecular weights of dimesityl boron polymers.

Polymer ^{<i>a</i>}	$M_{ m n,\ GPC}$	PDIGPC	m, ngpc ^b	m, n _{NMR} ^c
PM5m	9770	1.25	22	d
PNIPAM-3 _m	9630	1.09	82	63 ^f
PNIPAM _m -b-PM5 _n	57470	1.20	82, 111	63, 159
PNIPAM _m - b -P(M5 _x - ran -4VP _y) _n ^{e}	25520	1.33	е	63, 173 ^e

^{*a*} m and n refer to the degree of polymerization of the first and second block, respectively. ^{*b*} Determined by GPC-RI. ^{*c*} Based on ¹H NMR integration. ^{*d*} Not estimated due to overlap of the end group and repeating units. ^{*e*} x and y refer to the molar fractions of M5 and 4VP units in the second block, respectively. For PNIPAM_m-*b*-P(M5_x-*ran*-4VP_y)_n, n can not be determined by GPC, because the molar ratio of x/y is unknown. Thus, m, n, x and y were estimated by ¹H NMR integration to be 63, 173, 0.13 and 0.87, respectively. ^{*f*} from ¹H NMR end group analysis.



Figure 4-11. Absorption and emission spectra of PM5 in THF.

The monomer M5 and corresponding dimesityl boron-functionalized polymers are strongly emissive in the UV region. As a representative example, the absorption and emission spectra of PM5 are given in Figure 4-11, and the photophysical data of M5 and the polymers are summarized in Table 4-4. Similar to the M5 monomer, PM5 homopolymer shows absorption and emission maxima at 330 and 385 nm. The quantum vield of PM5 is 0.22, which is lower than that of M5 (0.52), possibly because of the neighboring group effect of boron chromophores along the polymer chain (bimolecular quenching), and the quenching effect of the CTA end groups. This end group effect would be less pronounced for PNIPAM-b-PM5 considering the much higher molecular weight, and consequently a higher quantum yield is observed for the latter. The absorption and emission of PNIPAM-b-PM5 is otherwise identical to that of PM5 homopolymer, while PNIPAM-b-P(M5-ran-4VP) shows ~10 nm red-shifted emission. We attribute this slight shift to the presence of the 4VP comonomer units, which might affect the polarity of the borane environment. The quaternized block-random copolymer PNIPAM-b-P(M5-ran-4VPMeOTf) is insoluble in THF. Thus, the photophysical properties of PNIPAM-b-P(M5-ran-4VPMeOTf) was studied in DMF. Comparing to the other polymers and monomer in THF, PNIPAM-b-P(M5-ran-4VPMeOTf) shows similar absoption maximum at 332 nm and a largely red-shifted emission maximum at 423 nm.

Sample	$\lambda_{abs} (nm)$	λ_{em} (nm) ^{<i>a</i>}	${\it P}_{ m F}$
M5	334	385	0.52
PM5	330	385	0.22
PNIPAM- <i>b</i> -PM5	329	384	0.30
PNIPAM-b-P(M5-ran-4VP)	329	394	0.20
PNIPAM-b-P(M5-ran-4VPMeOTf) ^b	332	423	0.08

Table 4-4. Photophysical properties of dimesityl boron-functionalized monomer and polymers in THF.

^{*a*} All samples were excited at the corresponding λ_{abs} ; ^{*b*} Measured in DMF.

With well-defined dimesityl phenyl boron-functionalized polymers in hand, we examined their application as chemical sensors for fluoride anions. First, we compared the fluoride binding behavior of M5, PM5, PNIPAM-*b*-PM5 and PNIPAM-*b*-P(M5-*ran*-4VP) in THF. The absorption and emission spectra of the monomer and polymers upon titration with tetrabutylammonium fluoride (TBAF) in THF are shown in Figure 4-12. All measurements were performed under ambient conditions in the presence of air, but using freshly distilled THF.



Figure 4-12. Absorption (A) and emission (B) spectra of M5 upon titration with TBAF in THF ([B] = 7.07×10^{-6} M, [F⁻] = 3.30×10^{-4} M, $0 \sim 1.35$ equiv., step = 0.27 equiv.); Absorption (C) and emission (D) spectra of PM5 upon titration with TBAF in THF ([B] = 9.32×10^{-6} M, [F⁻] = 3.30×10^{-4} M, $0 \sim 1.23$ equiv., step = 0.175 equiv.); Absorption (E) and emission (F) spectra of PNIPAM-*b*-PM5 upon titration with TBAF in THF ([B] = 1.43×10^{-5} M, [F⁻] = 2.20×10^{-4} M, $0 \sim 1.24$ equiv., step = 0.12 equiv.); Absorption (G) and emission (H) spectra of PNIPAM-*b*-P(M5-*ran*-4VP) upon titration with TBAF in THF ([B] = 9.87×10^{-6} M, [F⁻] = 2.20×10^{-4} M, $0 \sim 1.48$ equiv., step = 0.185 equiv.). [B] and [F⁻] correspond to the boron chromophore and F⁻ concentration, respectively.

For the titration of M5, as shown in Figure 4-12 (A), a binding constant of $\lg\beta = 7.3$ was determined. The absorption band at 334 nm decreased gradually with the addition of TBAF, and a higher energy band at 308 nm developed, which is ascribed to the fluoroborate complex. In the emission spectrum (Figure 4-12 (B)), the intensity of the borane band decreased gradually with TBAF addition, giving way to a broad and weak emission band. ^[a]

The homopolymer PM5 showed an identical binding constant ($lg\beta = 7.3$). The new absorption band of the borate complex appeared at 276 nm, which is different from that of M5 (308 nm), because the backbone of PM5 is saturated (Figure 4-12 (C)). More interestingly, amplified fluorescence quenching was observed in the emission spectrum (Figure 4-12 (D)). Addition of only 0.175 equiv. of TBAF led to about 60% fluorescence quenching, and the emission was almost completely quchened at 0.7 equiv. of TBAF addition. The titration results for the PNIPAM-b-PM5 block copolymer (Figure 4-12 (E) and (F)) are essentially the same as for PM5, because the PNIPAM block is inert. Again, a large binding constant of $\lg\beta = 7.3$ and amplified quenching were observed. Usually, the amplified quenching phenomenon is observed in conjugated polymer structures, in which electronic communication between repeating units extends through the polymer chain, and one bound site can affect the electronic structure of neighboring units.²⁷ The effect we observe here is likely due to effective exciton migration along the polymer chain to lower energy quenching sites.²⁸ To further confirm this interpretation, a titration study for the PNIPAM-b-P(M5-ran-4VP) block-random copolymer was performed (Figure 4-12 (G) and (H)).

[a] Complete quenching is expected. The residual long wavelength emission may be due topartial degradation of the fluoroborate product in the presence of exygen.

In this case, the designed low mole fraction of boron chromophores (0.13 based on ¹H NMR integration) in the second block leads to "dilution" of the chromophores by the 4VP comonomer units. As a result, almost no amplified quenching was observed and the titration behavior of the block-random copolymer is close to that of the monomer, due to the site-isolation of boron chromophores in the polymer chain. Meanwhile, a slightly lower binding constant $lg\beta = 6.9$ was observed, which is still comparable to that for PM5 and PNIPAM-*b*-PM5.



Figure 4-13. Absorption (A) and emission (B) spectra of PNIPAM-*b*-P(M5-*ran*-4VPMeOTf) upon titration with TBAF in DMF ([B] = 1.69×10^{-5} M, $0 \sim 1.4$ equiv., step = 0.14 equiv.); Absorption (C) and emission (D) spectra of PNIPAM-*b*-P(M5-*ran*-4VP) upon titration with TBAF in DMF ([B] = 1.59×10^{-5} M, $0 \sim 1.6$ equiv., step = 0.16 equiv.). [F⁻] = 2.20×10^{-4} M. [B] and [F⁻] correspond to the boron chromophore and F⁻ concentration, respectively.

To date, anion sensing studies based on organoborane compounds and polymers have mainly been performed in low polarity organic solvents.¹ Sensitive anion detection in polar solvents, especially in aqueous media is highly desirable for practical applications. However, due to the competition of solvent molecules, the binding between boron and F in polar solvents (especially aqueous media) tends to be very weak. To overcome this issue, the Gabbaï group reported a series of positively charged borane compounds, in which electrostatic interactions with F⁻ enhance the binding to the boron center in polar solvents and aqueous media.^{21,25,29,30} To take advantage of this concept in our polymers, we quaternized PNIPAM-b-P(M5-ran-4VP) and then compared the F⁻ binding behavior of PNIPAM-b-P(M5-ran-4VPMeOTf) and PNIPAM-b-P(M5-ran-4VP) in DMF. The absorption and emission spectra upon TBAF titration are given in Figure 4-13. From Figure 4-13 (A) and (B), we can see that in DMF, the F⁻ binding behavior of positively charged PNIPAM-b-P(M5-ran-4VPMeOTf) is similar to the F⁻ binding of neutral PNIPAM-b-P(M5-ran-4VP) in THF in that addition of 1.25 equiv. of TBAF led to almost complete saturation of boron with a large binding constant of $lg\beta = 6.6$ and no amplified quenching was observed. Differently, the unquaternized precursor PNIPAM-b-P(M5-ran-4VP) showed comparatively weak binding in DMF with a one order lower $\lg\beta = 5.5$. Upon addition of 1.6 equiv. of TBAF solution, unbound boron chromophores were still present and the solution remained luminescent. These results indicate that in the polar solvent DMF, the positive pyridinium moieties enhance the F⁻ binding.

In DMF, the binding of PNIPAM-*b*-PM5 to F⁻ is expected to be similarly weak as PNIPAM-*b*-P(M5-*ran*-4VP) due to the lack of electrostatic interactions. However, PNIPAM-*b*-PM5 may exhibit amplified quenching as in THF. Moreover, DMF is a selective solvent for the PNIPAM block of PNIPAM-*b*-PM5, and self-assembled nanostructures are expected instead of molecularly dissolved polymer chains. The F⁻ binding to the boron-containing block may therefore lead to the disassembly of

aggregates as a second response. Therefore, we decided to also study the F⁻ binding of PNIPAM-*b*-PM5 in DMF.



Figure 4-14. (A) Photographs of PNIPAM-*b*-PM5 micelles before and after addition of 1.1 equiv. of TBAF in natural light (top) and UV irradiation (bottom); (B) Size distribution of PNIPAM-*b*-PM5 in THF (black, $\langle D_h \rangle = 9.2\pm2.7$ nm), micelles in DMF (blue, $\langle D_h \rangle = 93\pm24$ nm) and block copolymer/F⁻ complex in DMF upon TBAF addition (red, $\langle D_h \rangle = 10.5\pm3.0$ nm), (C) TEM images of PNIPAM-*b*-PM5 micelles in DMF; (D) absorption and (E) emission spectra of PNIPAM-*b*-PM5 upon titration with TBAF in DMF ([B] = 1.44×10^{-5} M, [F⁻] = 2.20×10^{-4} M, $0 \sim 1.6$ equiv., step = 0.16 equiv., $1.6 \sim 4.0$ equiv., step = 0.8 equiv.). [B] and [F⁻] correspond to the boron chromophore and F⁻ concentration, respectively.

The PNIPAM-*b*-PM5 micelle solution was prepared by adding DMF into the block copolymer solution in THF. The final concentration of block copolymer was 0.25 mg/g in DMF/THF = 19/1 (w/w). The self-assembled micelles solution was used for F⁻ binding study. Interestingly, upon addition of ~1.1 equiv. of TBAF solution, the opalescence of block copolymer micelles disappeared immediately and the solution turned completely clear (Figure 4-14, top). We characterized the block copolymer solution in the good

solvent THF, and the micelles in DMF before and after addition of TBAF (Figure 4-14 (B)). In THF, the block copolymer exists as single chains with $\langle D_h \rangle = 9.2\pm2.7$ nm. In DMF, the block copolymer forms micelles with a PM5 core and a PNIPAM shell with $\langle D_h \rangle = 93\pm24$ nm. The micellar structure was also characterized by TEM (Figure 4-14 (C)). Upon addition of TBAF solution in THF, the DLS characterization revealed a significantly reduced size of $\langle D_h \rangle = 10.5\pm3.0$ nm, which is close to that in the good solvent THF, indicating the dissociation of micelles into single chains. In a control experiment, the same amount of THF was added without TBAF, and no micelle dissociation was observed. This suggests that after F⁻ binding, the charged boron-containing block turned soluble in DMF and led to the micelle dissociation.

At the same time, the F⁻ binding gave rise to fluorescence quenching (Figure 4-14(A), bottom). The absorption and emission of diluted PNIPAM-b-PM5 micelle solution upon addition of TBAF solution is given in Figure 4-14(D) and (E). Indeed, the F⁻ binding in DMF is much weaker than that in THF, and 4.0 equiv. of TBAF addition only quenched about 50% of the absorbance of the tricoordinate boron (Figure 4-14 (D)). Although the titration spectra were seriously affected by the light scattering of the micellar aggregates and the titration was not complete due to the very weak F⁻ binding, the binding constant could be roughly estimated to be 4.2, which is about three orders lower than that of the block copolymer in THF. However, the block copolymer maintained the amplified quenching in DMF, so that 2.4 equiv. of TBAF almost completely quenched the emission of the polymers (Figure 4-14 (E)). The DLS characterizations and the titration studies demonstrate that in DMF, even the relatively weaker anion binding is sufficient to result in micelle dissociation and simultaneous amplified fluorescence quenching. PNIPAM-*b*-

PM5 thus serves as the first dual responsive chemical sensor for F^- in the polar solvent DMF.



Figure 4-15. Absorption (A) and emission (B) spectra of PNIPAM-*b*-P(M5-*ran*-4VPMeOTf) upon titration with TBAF in DMF/water = 9/1 (w/w) ([B] = 1.38×10^{-5} M, 0~2.1 equiv., step = 0.21 equiv.); Absorption (C) and emission (D) spectra of PNIPAM*b*-PM5 upon titration with TBAF in DMF/water = 9/1 (w/w) ([B] = 1.45×10^{-5} M, 0~5.0 equiv., step = 1.0 equiv., and 20.0 equiv.); Absorption (E) and emission (F) spectra of PNIPAM-*b*-P(M5-*ran*-4VP) upon titration with TBAF in THF ([B] = 1.96×10^{-5} M, 0~4.35 equiv., step = 0.87 equiv., and 5.89 equiv.). [F⁻] = 2.20×10^{-4} M. [B] and [F⁻] correspond to the boron chromophore and F⁻ concentration, respectively.

At last, we attempted the F⁻ sensing in DMF/water =9/1 (w/w) with the quaternized polymer PNIPAM-*b*-P(M5-*ran*-4VPMeOTf). As shown in Figure 4-15 (A) and (B), thanks to the positive pyridinium units, the binding between F⁻ and the boron chromophores was enhanced by electrostatic interactions. About 1.66 equiv. of TBAF addition led to saturation of the boron chromophores and almost complete quenching. The fitted binding constant lg β is 6.7, which is almost identical to that of PNIPAM-*b*-P(M5-*ran*-4VPMeOTf) in DMF. Differently, without electrostatic interactions, the F⁻ binding of PNIPAM-*b*-PM5 and PNIPAM-*b*-P(M5-*ran*-4VP) is so weak in DMF/water = 9/1 (w/w), that even a large excess of F⁻ leads to only partial complexation (Figure 4-15(C)~(F)).



Figure 4-16. TEM images of PNIPAM-*b*-PM5 (A) and PNIPAM-*b*-P(M5-*ran*-4VP) (B) aggregates in water; Size distribution of PNIPAM-*b*-PM5 ((C) $\langle D_h \rangle = 455\pm133$ nm) and PNIPAM-*b*-P(M5-*ran*-4VP) ((D) $\langle D_h \rangle = 1154\pm285$ nm) aggregates in water.

The self-assembly of amphiphilic block copolymers PNIPAM-*b*-PM5 and PNIPAM-*b*-P(M5-*ran*-4VP) in water was also studied. Water was added dropwise to the block

copolymer solutions in THF under stirring. After dialysis against water, the self-assembly was examined by TEM and DLS. Both block copolymers formed large spherical aggregates (Figure 4-16 (A) and (B)). The sizes of these aggregates based on DLS analysis are 455±133 and 1154±285 nm, respectively.

4.3 Conclusions

We developed two tricoordinate boron monomers that exhibit excellent stability and strong luminescence, and synthesized a series of narrow block copolymers with welldefined architecture and controlled molecular weights. The borinic acid block copolymers serve as building blocks for H-bonding induced luminescent supramolecular nanostructures and polymer/inorganic hybrid material preparation. The dimesityl phenyl boron-functionalized polymers were used as effective chemical sensors for F⁻. Systematic studies demonstrate that: (1) The distribution of boron chromophores along the polymer backbone affects the F⁻ binding response. In THF, PM5 homopolymer and PNIPAM-b-PM5 block copolymer showed amplified quenching due to through-space interactions of neighboring boron chromophores; (2) The PNIPAM-b-PM5 block copolymer acts as a dual responsive chemical sensor for F⁻ in the polar solvent DMF. F⁻ binding gave rise to sharp responses of reduced light scattering and fluorescence quenching, which can be easily visualized by naked eye; (3) Positive charges in the polymer chains can effectively enhance the F⁻ binding in the highly polar solvent DMF and DMF/water = 9/1 (w/w) solvent mixture. These results have significant impact on the practical applications of luminescent boron-containing polymers for toxic anion sensing in aqueous solution.

4.4 Experimental

General methods. The 499.9 MHz ¹H and 125.7 MHz ¹³C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 160.4 MHz ¹¹B NMR spectra were recorded with a boron-free probe using boron-free quartz NMR tubes. The ¹H and ¹³C NMR spectra were referenced internally to the solvent peaks and the ¹¹B NMR spectra externally to BF₃•Et₂O ($\delta = 0$) in C₆D₆. Elemental analyses were performed by Quantitative Technologies Inc. (Whitehouse, NJ).

GPC-RI analyses were performed in THF (1.0 mL/min) or DMF with 0.2% w/v of [Bu₄N]Br (0.50 mL/min) using a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. Three styragel columns (Polymer Laboratories; two 5 µm Mix-C and one 10 µm Mix-D), which were kept in a column heater at 35 °C (THF), or a set of two styragel columns (Polymer Laboratories; one 5 µm Mixed-B and one 5 µm Mixed-C) at 65 °C (DMF), were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories, Varian Inc.). Multi-angle laser light scattering (GPC-MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument in-line with the GPC, using the columns specified above. A Wyatt Optilab refractive index detector operated at 690 nm was used as the concentration detector and differential refractive indices dn/dc were calculated with the Wyatt Astra software assuming 100% mass recovery. The dynamic light scattering (DLS) measurements were performed at 25.0±1 °C with a Malvern Zetasizer Nano-ZS instrument, equipped with a 4 mW, 633 nm He-Ne laser and an Avalanche photodiode detector at an angle of 173°.

UV-vis absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer with optically dilute solutions (A<0.1). Anthracene was used as the standard and the quantum yield of anthracene (0.33 in THF) was adopted from the Handbook of Photochemistry (S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker Inc., New York, 1993.). Sample solutions were prepared using a microbalance (\pm 0.1 mg) and volumetric glassware. The quantum yields were calculated by plotting a graph of integrated fluorescence intensity vs. absorbance of at least 4 solutions with increasing concentration. The gradient of the graph is proportional to the quantum yield.

Binding constants β_{1n} are given in units of M⁻ⁿ. All the constants are determined using from the HyperquadTM program. The [B] for the block copolymers for titration studies was estimated using the absorptivity of the homopolymer PM5 ($\epsilon = 30000 \text{ cm}^{-1} \text{ M}^{-1}$ per repeating unit), rather than the NMR or GPC data.

Transmission electron microscopy (TEM) was conducted on a FE.I Tecnai 12 electron microscope operated at 80 kV. One drop of polymer micelle solution was cast on a copper grid with a carbon coating.

Materials. 1,4-Dioxane and THF were distilled from Na/benzophenone prior to use. Azobisisobutyronitrile (AIBN) initiator was recrystallized in methanol. Styrene was purified by passing it through a neutral alumina column and then distilled under reduced pressure. N-isopropyl acrylamide (NIPAM) was purified by recrystallization in a hexanes/benzene mixture. All other solvents and chemicals were used without further purification. The chain transfer agent (CTA) used in this work was synthesized according to literature procedure.

Synthesis of triisopropylphenyl dimethoxy borane. The triisopropylphenyl dimethoxy borane was prepared according to Heteroatom Chem., 1992, 3, 275. To a flame-dried 3-neck flask containing 1.27 g (53.0 mmol) of Mg turnings and 40 mL of dry THF, was added 0.1 mL of 1, 2-dibromoethane. After stirring for 5 min, 10.0 g (35.3 mmol) of TipBr was added dropwise through an addition funnel. Then the reaction was refluxed for 3 h. The above Grignard reagent solution was added dropwise at 0 °C to a solution of B(OMe)₃ (4.04 g, 38.9 mmol) in 10 ml of dry THF. The reaction mixture was warmed up to room temperature slowly and stirred overnight. All volatile compounds were removed under high vacuum, then the solid residue was transferred into a round bottom flask and distilled at 110 °C under reduced pressure. The product (5.77 g, 20.9 mmol) was obtained as a colorless liquid. Yield: 59%. ¹H NMR (499.895 MHz, *d*-benzene): $\delta = 6.99$ (s, 2H), 3.49 (s, 6H), 2.82 (3H, overlapped), 1.31 (d, ³J = 6.8 Hz, 12H), 1.25 (d, 6H). ¹¹B NMR (160.386 MHz, d-benzene) $\delta = 31.5$. ¹³C NMR (125.698 MHz, *d*-benzene): $\delta = 151.1$, 150.0, 149.4, 122.8, 120.7, 52.5, 36.1, 35.4, 25.1, 24.7, B-C not observed.



Figure 4-17. ¹H, ¹¹B and ¹³C NMR spectra of triisopropylphenyl dimethoxy borane in *d*-benzene.

Synthesis of iodophenyl triisopropylphenyl borinic acid.



To a solution of 1,4-diiodobenzene (3.30 g, 10.0 mmol) in 100 mL THF were added 6.5 mL of 1.6 M *n*-BuLi in hexanes (10.4 mmol) dropwise at -78 °C. After stirring at this temperature for 1 h, a solution of TipB(OMe)₂ (2.76 g, 10.0 mmol) in 20 mL of THF was

added dropwise. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched by addition of 100 mL of water, and then extracted with CH₂Cl₂. The solvent was removed on a rotary evaporator. The crude product was crystallized in hexanes, giving 2.4 g of white crystals. Yield: 55%. ¹H NMR (499.895 MHz, CDCl₃): δ = 7.77 (d, ³J = 8.0 Hz, 2H), 7.53 (d, ³J = 8.0 Hz, 2H), 7.05 (s, 2H), 5.87 (s, 1H), 2.94 (septet, ³J = 7.0 Hz, 1H), 2.64 (septet, ³J = 7.0 Hz, 2H), 1.31 (d, ³J = 7.hz0 Hz, 6H), 1.18 (broad, 12H). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 48.9 (w_{1/2} = 600 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 150.7, 149.9, 137.2, 137.1, 120.7, 100.1, 35.1, 34.6, 24.8 (broad), 24.2, B-C not observed.



Figure 4-18. ¹H, ¹¹B and ¹³C NMR spectra of iodophenyl triisopropylphenyl borinic acid in CDCl₃.

Synthesis of borinic acid monomer (M4). To a Schlenk tube containing a solution of iodophenyl triisopropylphenyl borinic acid (2.00 g, 4.61 mmol) and 4-trimethylstannyl styrene (2.58 g, 9.66 mmol) in 10 mL of THF, a catalyst solution in 10 mL of THF consisting of 148 mg (0.16 mmol, 3 mol%) of Pd₂(dba)₃ and 260 mg (1.29 mmol) of 'Bu₃P was added. The mixture was heated to 55 °C for 4 h. After workup with CH₂Cl₂/water, the crude product was subjected to column chromotography on silica gel with hexanes/CH₂Cl₂ mixture as the eluent. Precipitation into hexanes and drying in high vacuum gave the product as a white powder (1.54 g). Yield: 85%. ¹H NMR (499.895 MHz, CDCl₃): δ = 7.89 (d, ³J = 8.0 Hz, 2H), 7.64 (overlap, 4H), 7.51 (d, ³J = 8.5 Hz, 2H), 7.07 (s, 2H), 6.78 (dd, ³J = 17.5 and 11.0 Hz, 1H), 5.82 (d, ³J = 18.0 Hz, 1H), 5.82 (s, 1H), 5.30 (d, ³J = 11.0 Hz, 1H), 2.96 (septet, ³J = 8.0 Hz, 1H), 2.73 (septet, ³J = 8.0 Hz, 2H), 1.33 (d, ³J = 7.0 Hz, 6H), 1.21 (broad, 12H). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 49 (w₁₂ = 1500 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 150.8, 149.7, 144.0, 140.5, 137.2, 136.6, 136.2, 127.5, 126.9, 126.5, 120.6, 114.3, 35.1, 34.6, 24.9 (broad), 24.3, B-C not found.



Figure 4-19. ¹³C NMR spectrum of borinic acid monomer in CDCl₃.

Synthesis of PNIPAM-3. Into a Schlenk tube were loaded NIPAM (9.04 g, 80.0 mmol), benzyl dithiobenzoate (BDTB) (200 mg, 0.80 mmol), AIBN (26.2 mg, 0.16 mmol), and 20.0 mL of dioxane ([NIPAM]/[CTA]/[AIBN] = 100/1/0.2). After 3 freeze-pump-thaw cycles, the tube was immersed in a 70 °C oil bath and kept stirring for 24 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated three times into a 10-fold volume of diethyl ether. After drying in high vacuum, 3.06 g (conversion = 32%) of PNIPAM-3 was obtained as a pink powder. GPC-RI (DMF with 0.2% TBAB): $M_{n, GPC-RI} = 9630$ g/mol, PDI = 1.09, mGPC = 82.

Synthesis of PS-*b***-PBA.** The synthesis of PS-1 ($M_{n, GPC-RI} = 7380 \text{ g/mol}$, PDI = 1.21, $M_{n, GPC-MALLS} = 9500 \text{ g/mol}$) was reported previously. For the block copolymer synthesis, 207 mg (0.0218 mmol) of PS-1, 300 mg (0.759 mmol) of borane monomer, and 0.36 mg (0.00219 mmol) of AIBN were dissolved in 2.3 mL of 1,4-dioxane in a Schlenk tube ([M4]/[PS-1]/[AIBN] = 35/1/0.1). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in an 80 °C oil bath for 12 h. The polymerization was quenched by immersing the tube in liquid nitrogen and the mixture was then diluted with 3 mL of THF. The polymer solution was precipitated three into a 10-fold volume of MeOH, and then reprecipitated two more times from THF into MeOH. After drying in high vacuum, the product was obtained as a light pink powder (405 mg, conversion = 66%). ¹H NMR integration indicates a copolymer structure with 30% B-OMe and 70% B-OH units. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 7.8$, 7.5, 6.2~7.2 (overlapped aromatic protons), 5.8 (B-OH), 3.8 (B-OMe), 2.9 (para- C-H of both borinic acid and ester), 2.7 (otho- C-H of borinic acid), 2.6 (otho- C-H of borinic ester), 0.7~2.3 (overlapped), 1.3, 1.2. ¹¹B NMR (160.386 MHz, CDCl₃): $\delta = 42.4$ (w_{1/2} = 2900 Hz). ¹³C NMR (125.698 MHz, CDCl₃): $\delta =$

150.3, 149.2, 145.5 (broad), 143.6, 136.8, 136.6, 136.0, 133.6, 127.3~129.0 (overlapped) 126.8 (broad), 125.4~126.4 (overlapped), 120.3, 56.1 (B-OMe), 46-40 (PS backbone), 35.1, 34.5, 24.8, 24.3. GPC-RI (THF): $M_n = 16880$ g/mol, PDI = 1.08. MALLS: $M_n =$ 20400 g/mol, dn/dc = 0.203 mL/g. m_{GPC} = 71, n_{GPC} = 23; m_{MALLS} = 89, n_{MALLS} = 27. m/n = 3.7 based on ¹H NMR integration (using peaks at 7.75 ppm and 7.2-6.2 ppm as reference).



Figure 4-20. ¹³C NMR spectrum of PS-*b*-PBA in CDCl₃.

Synthesis of PNIPAM-*b*-PBA. 72 mg (0.0075 mmol based on GPC-RI) of PNIPAM-3, 220 mg (0.556 mmol) of borane monomer, and 0.74 mg (0.0045 mmol) of AIBN were dissolved in 2.0 mL of 1,4-dioxane in a Schlenk tube ([M4]/[PNIPAM-3]/[AIBN] = 74/1/0.6). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in an 80 °C oil bath for 5 h. The polymerization was quenched by immersing the tube in liquid nitrogen. The polymer solution was precipitated into a 10-fold volume of MeOH, and then reprecipitated 2 more times from THF into MeOH. After drying in high vacuum, the

product was obtained as a light pink powder (185 mg, conversion = 51%). ¹H NMR (499.895 MHz, CDCl₃): δ = 7.8, 7.5, 6.2~7.2 (overlapped aromatic and amide protons), 5.9, 4.0, 2.9, 2.7, 1.4~2.4 (overlapped), 1.3, 1.2. ¹¹B NMR (160.386 MHz, CDCl₃) δ = 43. ¹³C NMR (125.698 MHz, CDCl₃): δ = 174.3 (C=O), 150.8, 149.4, 146.4~144.4 (broad), 144.0, 138.1, 136.0, 135.7, 128.3 (broad), 126.9 (broad), 126.2, 120.5, 42.7, 41.5, 35.0, 34.5, 24.8 (broad), 24.2, 22.8. GPC-RI (DMF with 0.2% TBAB): M_n = 27020 g/mol, PDI = 1.26. m_{GPC} = 82, n_{GPC} = 42. m/n = 1.8 based on ¹H NMR integration (using peaks at 4.0 ppm and 2.9 ppm as reference).



Figure 4-21. ¹³C NMR spectrum of PNIPAM-*b*-PBA in CDCl₃.

H-bonding induced supramolecular co-assembly of PS-*b***-PBA/P4VP:** To a solution of PS-*b*-PBA (3.0 mg) in 5.0 mL of chloroform, was added 0.5 mg of P4VP homopolymer in 1.0 mL of chloroform under stirring. The as-formed solution was used directly for characterization.

H-bonding induced supramolecular co-assembly of PNIPAM-b-PBA/P4VP: To a

solution of PNIPAM-*b*-PBA (3.0 mg) in 5.0 mL of chloroform, was added 0.5 mg of P4VP homopolymer in 1.0 mL of chloroform under stirring. The as-formed solution was used directly for characterization.



Figure 4-22. Photographs of PS-*b*-PBA/P4VPA (left) and PNIPAM-*b*-PBA/P4VP (right) supramolecular aggregate solutions in chloroform.

Self–assembly of PNIPAM-*b***-PBA in water.** To 3.0 mL of block copolymer solution in THF (c = 1.0 mg/mL), were added 12.0 mL of deionized water dropwise under stirring. The polymer solution was then dialyzed against deionized water for 3 days.

Silica synthesis within PNIPAM-*b***-PBA vesicle nanoreactors.** To a THF solution containing 2.0 mg of PNIPAM-*b*-PBA and 2.0 mg of TEOS, were added 30 mL of water dropwise under stirring. Then, 0.2 mL of triethyl amine were added. The solution was stirred for 5 h, followed by dialysis against deionized water.

Synthesis of M5. To a Schlenk tube containing 2.00 g (4.42 mmol) of dimesityl iodophenyl borane and 1.77 g (6.63 mmol) of 4-trimethyltin styrene in 10 mL of THF, a catalyst solution containing 162 mg (0.177 mmol, 4 mol%) of Pd₂(dba)₃ and 286 mg (1.41 mmol) of ^tBu₃P in 5.0 mL of THF was added. The tube was sealed and heated at 50 °C for 12 h. After workup with DCM/water, the crude product was subjected to silica gel column with hexanes/DCM mixture. The isolated pure fractions were combined and dried in high vacuum, affording 1.37 g of white powder. Yield: 72%. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 7.65$ (d, ³J = 8.3 Hz, 2H), 7.61 (appears as s, 4H), 7.51 (d, ³J = 8.3 Hz, 2H), 6.86 (s, 4H), 6.78 (dd, ³J = 17.6 and 10.9 Hz, 1H), 5.83 (d, ³J = 17.6 Hz, 1H), 5.31 (d, ³J = 10.9 Hz, 1H), 2.34 (s, 6H), 2.07 (s, 12H). ¹¹B NMR (160.386 MHz, CDCl₃) $\delta = 74$ (w_{1/2} = 1500 Hz). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 144.7$ (broad), 144.0, 141.9 (broad), 141.0, 140.2, 138.8, 137.3, 136.6, 128.4, 127.5, 126.9, 126.5, 114.3, 23.7, 21.4. UV-Vis in THF: $\lambda_{max} = 334$ nm, $\varepsilon = 48410$ cm⁻¹ M⁻¹. Fluorescence in THF: $\lambda_{em} = 385$ nm ($\lambda_{exc} = 334$ nm), $\Phi = 52\%$.



Figure 4-23. ¹³C NMR spectrum of M5 in CDCl₃.

Synthesis of PM5. In a Schlenk tube, 350 mg (0.817 mmol) of M5, 4.00 mg (0.0163 mmol) of benzyl dithiobenzoate (BDTB), 0.54 mg (0.0033 mmol) of AIBN were dissolved in 1.0 mL of 1,4-dioxane ([M5]/[CTA]/[AIBN] = 50/1/0.2). After 3 freeze-pump-thaw cycles, the Schlenk tube was immersed in an 80 °C oil bath for 5 h. The crude

product was precipitated two times by dropwise addition of a THF solution of the polymer to a 10-fold volume of methanol. The filtered solid was dried in high vacuum, affording a light pink powder (184 mg, conversion = 51%). ¹H NMR (499.895 MHz, CDCl₃): δ = 7.4, 7.3, 7.1, 6.7, 6.6, 6.4 (aromatic protons), 2.3, 1.9, 1.1~2.7 (broad, overlapped backbone). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 65 (w_{1/2} = 3700 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 145.1 (broad), 144.5, 144.1, 141.9, 140.9, 138.7, 138.1 (broad), 137.2, 128.4, 127.0, 126.3, 40.5 (broad), 23.6, 21.4. GPC-RI (THF): *M*_n = 9770 g/mol, PDI = 1.25, m_{GPC} = 22. UV-Vis in THF: λ_{max} = 330 nm. Fluorescence in THF: λ_{em} = 384 nm (λ_{exc} = 330 nm), ϕ = 0.22.



Figure 4-24. ¹³C NMR spectrum of PM5 in CDCl₃.

Synthesis of PNIPAM-*b*-PM5. Into a Schlenk tube were loaded PNIPAM-3 (120 mg, 7380 g/mol based on ¹H NMR end group analysis, 0.0163 mmol), M5 (1286 mg, 3.00 mmol), AIBN (1.64 mg, 0.010 mmol), and 4.0 mL of dioxane (([M5]/[PNIPAM-

3]/[AIBN] = 184/1/0.61). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 5 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was precipitated into a 10-fold volume of diethyl ether and then two more times from THF into a 10-fold volume of hexanes. After drying in high vacuum, 770 mg of block copolymer was obtained as a pink powder (conversion = 51%). ¹H NMR (499.895 MHz, CDCl₃): δ = 7.5, 7.4, 7.2, 6.8, 6.6, 6.4 (aromatic protons), 4.1, 2.2, 1.9, 1.2, 1.1~2.7 (broad, overlapped backbone). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 66 (w_{1/2} = 3400 Hz). ¹³C NMR (125.698 MHz, CDCl₃): δ = 174.4, 145.1 (broad), 144.5, 144.1, 141.9, 140.9, 138.7, 138.1 (broad), 137.2, 128.4, 127.0, 126.3, 46.4 (broad), 44.3 (broad), 42.6 (broad), 41.5, 40.5 (broad), 23.7, 22.8, 21.4. GPC-RI (chloroform): M_n = 57470 g/mol, PDI = 1.20, m_{GPC} = 82, n_{GPC} = 111. UV-Vis in THF: λ_{max} = 329 nm. Fluorescence in THF: λ_{em} = 384 nm (λ_{exc} = 329 nm), ϕ = 0.30. m/n = 0.40 based on ¹H NMR integration (using peaks at 4.1 ppm and 2.2 ppm as reference).



Figure 4-25. ¹³C NMR spectrum of PNIPAM-*b*-PM5 in CDCl₃.

Synthesis of PNIPAM-b-P(M5-ran-4VP). Into a Schlenk tube were loaded PNIPAM-3 (360 mg, 7380 g/mol based on ¹H NMR end group analysis, 0.0488 mmol), 4-vinvl pyridine (1.70 g, 16.2 mmol), M5 (771 mg, 1.80 mmol), AIBN (2.96 mg, 0.018 mmol), and 3.0 mL of THF ([4VP]/[M5]/[PNIPAM-3]/[AIBN] = 332/36.9/1/0.369). After 3 freeze-pump-thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 3 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated 3 times into a 10-fold volume of diethyl ether. After drying in high vacuum, 1.33 g (conversion = 39%) of block copolymer were obtained as a pink powder. ¹H NMR (499.895 MHz, CDCl₃): $\delta = 8.3$ (Py), 6.4 (Py), 6.2~7.8 (overlapped aromatic protons), 4.0 (PNIPAM) 3.3 (water), 2.2, 1.9, 1.1~2.7 (broad overlapped backbone). ¹¹B NMR (160.386 MHz, CDCl₃) δ = 70 ppm (w_{1/2} = 3300 Hz). ¹³C NMR (125.698 MHz, CDCl₃): $\delta = 174.4$, 152.2 (Py, broad), 150.1 (Py), 144.9, 143.4, 141.9, 140.9, 139.2, 138.7, 137.2 (broad), 128.4, 127.3 (broad), 126.3, 122.6 (Py), 44.9 (broad), 44.1 (broad), 43.5 (broad), 42.4 (broad), 41.4, 40.3 (broad), 38.1~31.1 (broad), 23.7, 22.8, 21.4. GPC-RI (DMF/pyridine = 99/1): $M_n = 25507$ g/mol, PDI = 1.33. UV-Vis in THF: $\lambda_{max} = 329$ nm. Fluorescence: $\lambda_{exc} = 329$ nm, $\lambda_{em} = 394$ nm, $\Phi = 0.20$. $x_{4VP} = 0.866$, $y_{M6} = 0.134$, m/n = 0.364 (using peaks at 8.3, 4.0 and 2.2 ppm as reference).



Figure 4-26. ¹³C NMR spectrum of PNIPAM-*b*-P(M5-*ran*-4VP) in CDCl₃.

Synthesis of PNIPAM-*b*-P(M5-*ran*-4VPMeOTf). To 40 mg of PNIPAM-*b*-P(M5-*ran*-4VP) solution in 3.0 mL of CHCl₃, was added 300 mg (1.83 mmol, largely in excess) of methyl triflate dropwise under stirring. A yellow suspension appeared within seconds. After stirring for 1.0 h at room temperature, the suspension was precipitated into a 10-fold volume of diethyl ether. After filtration, the product was dried in high vacuum. The product was obtained as a light yellow powder (45 mg). ¹H NMR (499.895 MHz, DMSO-d6): $\delta = 8.7$ (Py), 7.6, 7.5 (Py) 7.4-7.1, 6.9 (Mesityl C-H), 6.6, 4.2 (Py-Me), 3.8 (PNIPAM C-H) 2.3, 2.0 (Meesityl Me), 2.0~1.2 (backbone protons), 1.0 (PNIPAM Me). ¹¹B NMR (160.386 MHz, DMSO-d6) $\delta = 62$ ppm.

Self-assembly of PNIPAM-*b***-PM5 in water.** To 5.0 mL block copolymer solution in 1.0 g of THF, were added 19.0 g of DMF dropwise under stirring. The polymer solution was then characterized by DLS and TEM.

Self-assembly of PNIPAM-*b***-PM5 in water.** To 2.0 mL block copolymer solution in THF (c = 1.0 mg/mL), were added 18.0 mL of deionized water dropwise under stirring. The polymer solution was then dialyzed against deionized water for 3 days.

Self-assembly of PNIPAM-*b***-P(M5-***ran***-4VP) in water.** To 2.0 mL block copolymer solution in THF (c = 1.0 mg/mL), were added 18.0 mL of deionized water dropwise under stirring. The polymer solution was then dialyzed against deionized water for 3 days.

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List of Publications

Publications at Rutgers University:

- 1. "Fluoride Anion Sensing Based on Triarylborane Polymers", in preparation.
- 2. "Novel Luminescent Borinic Acid Block Copolymers as Building Blocks for Supramolecular Assemblies", in preparation.
- 3. "Pyridine-Functionalized Luminescent Organoboron Quinolate Block Copolymers for Nanostructure Fabrication", in preparation.
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Curriculum Vitae

Birth: September 22, 1982, in Shenyang, Liaoning, China

Education:

Ph.D., Chemistry, Rutgers University-Newark Campus
Advisor: Dr. Frieder Jäkle
M. Sc., Macromolecular Science, Fudan University
Advisor: Dr. Daoyong Chen
B. Eng., Polymer Materials and Engineering, Zhejiang University
Advisor: Dr. Hongzheng Chen

Honors and Awards:

2012	ACS POLY travel award
2012	Graduate Student Excellence Award of Rutgers
2008	Excellent Graduate of Fudan University
2007	Dow Chemical Scholarship
2007	Scholarship of Fudan University
2005	Excellent Graduate of Zhejiang University
2002~2004	Scholarship of Zhejiang University