Synthesis, Self-Assembly, and Formation of Al^{3+} Complex Micelles for Diblock Copolymer of 2-((8-Hydroxyquinolin-5-yl)methoxy)ethyl Methacrylate and Styrene

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ABSTRACT: Living/controlled polymerization of 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) was achieved by reversible addition−fragmentation chain transfer (RAFT) polymerization with 2-cyanoprop-2-yl dithiobenzoate (CPDB) as the RAFT agent and 2,2′-azoisobutyronitrile (AIBN) as the initiator in THF at 65 °C. The resulting PHQHEMA was used as a macro-RAFT agent in the RAFT polymerization of styrene to give diblock copolymer PHQHEMA-*b*-PS. The obtained diblock copolymer could self-assemble into nanosized micelles in a solvent mixture of toluene (Tol, selective solvent for block of polystyrene, nonsolvent for block of PHQHEMA) and THF (common solvent). The diameter and shape of the micelles were dependent on the molecular weights of the copolymers and the solvent compositions. The diameter of micelle increased with increasing molecular weight of the block copolymers and Tol content in the solvent mixture. Spherical micelles with a diameter in the range between 30 and 60 nm were formed under a Tol/THF ratio of 5:5 or 6:4, but, when the Tol/THF ratio increased to 8:2, the micelles changed from spherical structures to wormlike structures. Then, the formed micelles were used as nanoreactors to complex with triethylaluminum to give luminescent micelles with ionic cross-linking cores containing tris(8-hydroquinolinato)aluminum (Alq_3). The luminescent micelles could be redispersed in the solvents of polystyrene after drying. The emission spectra showed that the Alq_3 moieties acted as independent chromophores in the micelles.

Introduction

Since the first report of an organic light emitting diode (OLED) using Alq_3 as the emitting layer by Tang and Vanslyke,[1] Alq_3 has become one of the most famous materials for emission and electron-transporting layer in OLED because of its high stability, good emission, and electron-transporting properties. In recent years, the incorporation of Alq_3 into organic polymer by covalent bond has attached much attention because of the combination of good luminescence properties of Alq_3 and excellent processing properties of organic polymers. Two basic strategies for the synthesis of Alq_3-containing polymers have been reported: (1) Attachment of Alq_3 to a preformed polymer backbone containing 8-hydroxyquinoline moieties. These preformed polymers include main-chain-type 8-quinolinol polymers, such as poly(quinolinol)[2] and poly(aryleneethynylene)-type polymers containing 8-quinolinol units in the main chain,[3] and polymers containing pendent 8-hydroxyquinoline moieties, such as poly(arylene ether),[4] copolymers of 7-allyl- or 7-(2-methylvinyl)-functionalized derivatives of 8-hydroquinoline with styrene,[5] functionalized polystyrene,[6] and copolymers of methacrylates having 8-hydroxyquinoline moieties.[7−9] Usually, Alq_3-containing polymers were obtained by the reaction of these preformed polymers with Al^{3+}, for example, triethylaluminum ($AlEt_3$), in the presence of a large excess of 8-hydroxyquinoline. Because of the inevitable ionic cross-linking, the resulting Alq_3-containing polymer was branched and even cross-linked. Therefore, the Alq_3 content was limited to obtain soluble polymers. To increase the solubility of the resulting polymer, Takayama[7] synthesized a methacrylate monomer using 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline as the staring material. Because of the introduction of the 7-(4-ethyl-1-methyloctyl) group, the content of Alq_3 could be up to 42 wt %. To avoid cross-linking, di(8-hydroxyquinoline) aluminum chelate can be used instead of $AlEt_3$ in the coordinating reaction.[2,3,8,9] (2) Polymerization of an Alq_3-containing monomer. Meyers et al.[10,11] reported the synthesis of an Alq_3 side-chain functionalized norbornene polymer via ring-opening metathesis polymerization of an Alq_3-functionalized norbornene monomer. In this strategy, any cross-linking can be eliminated; additionally, the polymer structure can be controlled and altered by the use of comonomers to tune the polymeric properties. Lu et al.[12] reported the synthesis of tris[5-(2-methacryloylethyloxymethyl)-8-quinolinato]aluminum and its homo- and copolymers with Alq_3 as the cross-links; the feasibility of generating patterns by the homopolymers was also investigated via photopolymerization.

In this Article, we investigated the synthesis of Alq_3-containing polymer by an approach of metalation of self-assembly micelles of a diblock copolymer bearing pendent 8-hydroxyquinoline moieties. The obtained Alq_3-containing polymer is in the form of luminescent micelle with Alq_3 covalently attached in the core. Several luminescent micelles formed by self-assembly of diblock copolymers containing luminescent metal complex as side groups have been reported, including complexes of iridium(III),[13] ruthenium(II),[14,15] rhenium(I),[16,17] and europium(III).[18] These luminescent micelles may find promising applications in multicomponent systems for photoinduced charge separation processes,[13] luminescence probes for sensing,[14,17] catalysis,[15] light harvesting,[15] nanostructured and ordered fluorescent thin film for luminescence and display devices,[18] and so on. Most of them were prepared from preformed diblock copolymers containing metal complexes.[13−17] An exception was prepared with preformed micelles of polystyrene-*b*-poly(4-vinylpyridine) in selective solvent as nanoreactors to complex with Eu(III) in the presence of 1,10-phenanthroline as cooperative ligand[18] in which the luminescent metal complexes were located in the shell of the micelles.

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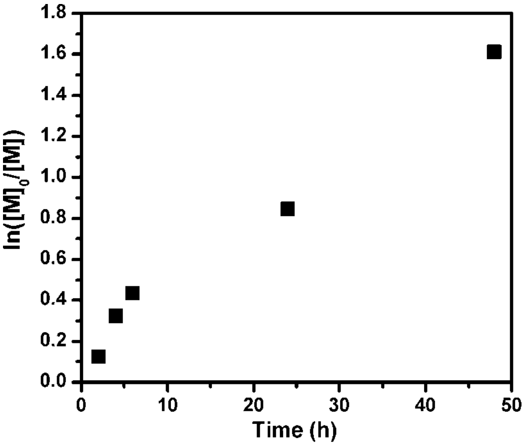

Figure 1. Semilogarithmic kinetic plot for 2-cyanoprop-2-yl dithiobenzoate (CPDB)-mediated RAFT polymerization of 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) at 65 °C in tetrahydrofuran: [HQHEMA] = 1 mol·L^{-1}; [CPDB] = 0.01 mol·L^{-1}; [CPDB]/[AIBN] 3:1.

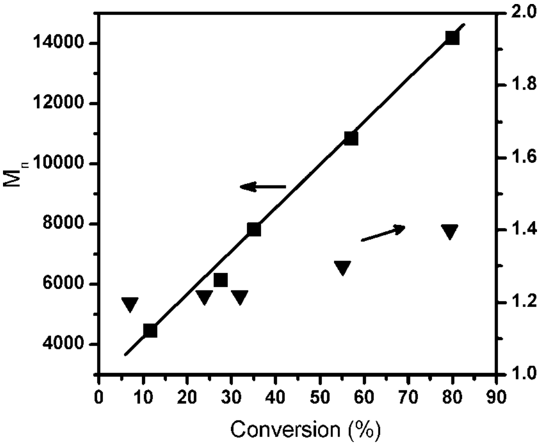

Figure 2. Evolution of the number-average molecular weight (M_n) and the polydispersity index (PDI) with monomer conversion in the CPDB-mediated RAFT polymerization of HQHEMA at 65 °C in tetrahydrofuran: [HQHEMA] = 1 mol·L^{-1}; [CPDB] = 0.01 mol·L^{-1}; [CPDB]/[AIBN] 3:1.

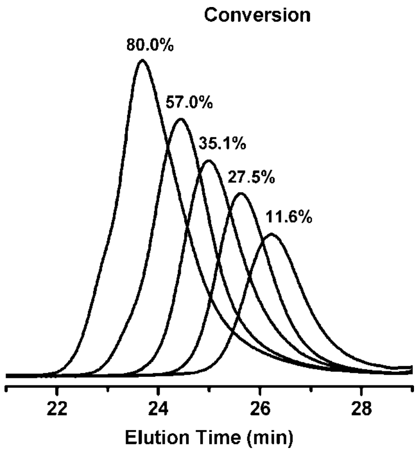

Figure 3. GPC curves of the polymers under different monomer conversions in the CPDB-mediated RAFT polymerization of HQHEMA at 65 °C in tetrahydrofuran: [HQHEMA] = 1 mol·L^{-1}; [CPDB] = 0.01 mol·L^{-1}; [CPDB]/[AIBN] 3:1.

Here we report the preparation of luminescent micelles with an Alq$_3$-containing core by a nanoreactor strategy. First, diblock copolymers of HQHEMA and styrene were synthesized by living polymerization. Then, micelles with PS shell and PHQHEMA core were obtained by the self-assembly of the obtained diblock copolymer in a mixture of THF (common solvent) and Tol (selective solvent for block of PS, nonsolvent for block of PHQHEMA). The resulting micelles were used as nanoreactors to react with AlEt$_3$ to give luminescent micelles with an Alq$_3$-containing core. Advantageously, by this strategy, possible cross-linking reactions during the synthesis of preformed diblock copolymers containing metal complexes can be avoided; meanwhile, the resulting luminescent micelles can be stabilized by ionic cross-linking in consequence of the complex reaction, and the stabilization of the micelles is necessary for the applications on the basis of such supramolecular structures to form objects with nanoscale dimensions.[19]

Table 1. Recipes and Results for the Synthesis of Block Copolymers of HQHEMA and Styrene[a]

	PHQHEMA					block copolymer			
run	wt (g)	M_n	DP$_n$[b]	PDI	reaction time (h)	wt (g)	M_n	DP$_n$ of PS[b]	PDI
BCP1	0.11	7800	27	1.22	28	0.23	14 400	63	1.23
BCP2	0.20	8430	30	1.14	24	0.31	12 880	43	1.19
BCP3	0.26	10 400	37	1.19	32	0.49	19 400	86	1.22

[a] [PHQHEMA]/[St]/[AIBN] 3:450:1; [St] = 1.0 mol·L^{-1}; 65 °C; solvent: tetrahydrofuran. [b] DP$_n$ values were calculated on the basis of GPC results.

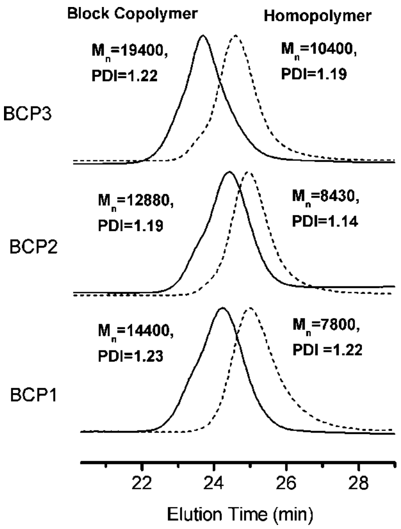

Figure 4. GPC curves of the diblock copolymers synthesized by the RAFT polymerization of styrene with PHQHEMA as macro-RAFT agent and AIBN as initiator in tetrahydrofuran at 65 °C. [PHQHEMA]/[St]/[AIBN] 3:450:1; [St] = 1.0 mol·L^{-1}.

Although the synthesis and radical polymerization of HQHEMA have been reported to obtain Alq$_3$-containing polymers,[7−9] there is no report of living polymerization of HQHEMA. Therefore, the living/controlled polymerization of HQHEMA was investigated first. Considering the presence of the 8-hydroxyquinoline moiety, reversible addition−fragmentation chain transfer (RAFT) polymerization was selected to investigate the living polymerization of HQHEMA because of its versatility to monomers and tolerance to functional groups.

Experimental Section

Materials. 8-Hydroquinoline (99%), 2-hydroxyethyl methacrylate (98%), magnesium turnings (>99.9%), and triethylaluminium solution (0.6 M in heptane, was diluted to 0.06 M before use) were all purchased from Acros Organics. Paraformaldehyde (AR, Guangdong Guanghua Chemical Factory) was used as received. Styrene (AR, Guangzhou Chemical Reagent Factory) was passed through a neutral alumina column to remove the radical inhibitor and was

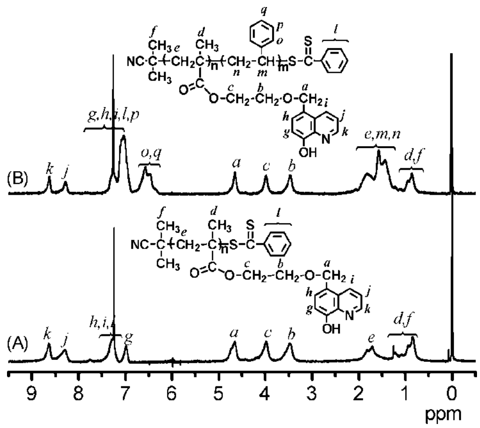

Figure 5. ^1H NMR spectra of (A) corresponding macro-RAFT agent and (B) PHQHEMA$_{27}$-*b*-PS$_{63}$ in $CDCl_3$.

Table 2. Diameters and Dispersities of the Micelles Formed by Self-Assembly of PHQHEMA-*b*-PS in Toluene−Tetrahydrofuran Solvent System

		30°		90°	
block copolymer	THF/Tol (v/v)	eff. diam (nm)	poly	eff. diam (nm)	poly
PHQHEMA$_{27}$-*b*-PS$_{63}$	5:5	41	0.115	40	0.283
	4:6	47	0.208	48	0.168
	2:8	142	0.129	77	0.548
PHQHEMA$_{30}$-*b*-PS$_{43}$	5:5	31	0.124	31	0.124
	4:6	35	0.143	36	0.168
	2:8	120	0.184	54	0.194
PHQHEMA$_{37}$-*b*-PS$_{86}$	5:5	56	0.241	56	0.504
	4:6	61	0.214	60	0.217
	2:8	190	0.267	98	0.300

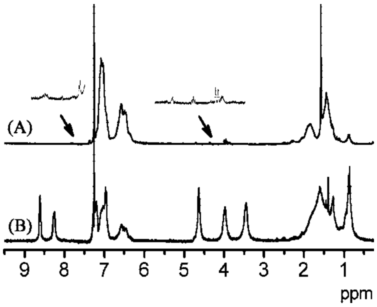

Figure 7. Comparison of the ^1H NMR spectrum of Al^{3+} complex micelles with the corresponding block copolymer PHQHEMA$_{37}$-*b*-PS$_{86}$ in $CDCl_3$.

then freshly distilled over CaH_2 before use. Dried THF was freshly distilled from sodium and benzophenone before use. 2,2′-Azoisobutyronitrile (AIBN, Sinopharm Chemical Reagent, 98%) was recrystallized twice from ethanol prior to use. 2-Cyanoprop-2-yl dithiobenzoate (CPDB)[20] and HQHEMA[8] were synthesized according to literature procedures. Other reagents were all reagent grade materials purified by standard methods if needed.

Measurements and Instrumentation. ^1H NMR spectra were recorded on a Mercury-Plus 300 NMR spectrometer (Varian) in $CDCl_3$ with tetramethylsilane as an internal standard. The molecular weight and polydispersity index (PDI) were determined by a Waters-Breeze GPC in THF at room temperature on polystyrene gel columns (Waters styragel HR1, HR3, HR4) connected with a refractive index detector (RI-2417) using polystyrene standards for calibration. Preparative GPC experiments were performed on a Waters 600 controller equipped with an Ultrastyragel column (Waters, WAT 025862) and a refractive index detector (RI2000P, Schambeck SFD GmbH). Emission spectra were recorded on an RF-5301PC fluorescence spectrophotometer. Dynamic laser scattering (DLS) measurements were carried out on a dynamic/static laser scattering system (Brooken Haven BI-200SM) with a wavelength of 514.5 nm at 25 °C. Transmission electron microscopy (TEM) images were recorded on a JEM-100CX II electron microscope operating at 100 kV. We prepared the samples by casting a drop of the solution on TEM copper grids and quickly wicking away the excess solution. The grids were left to air-dry in a fume hood. The grids were stained with 0.3% solution of phosphotungstic acid and dried under vacuum.

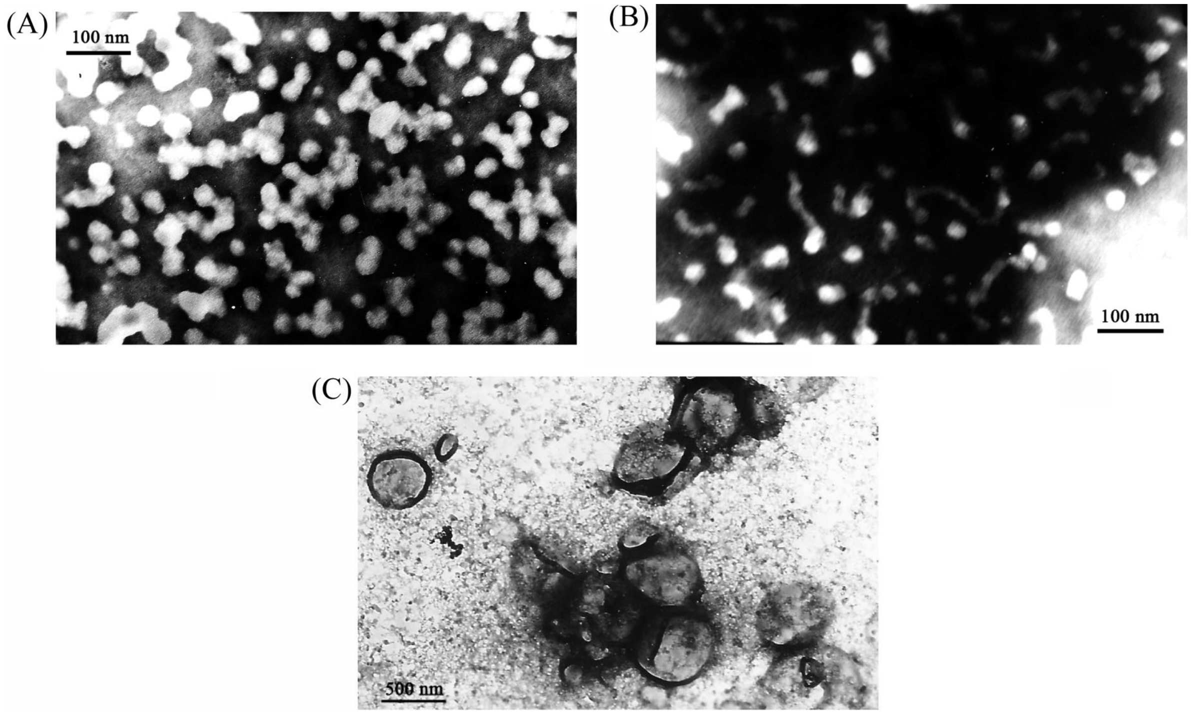

Figure 6. TEM images of the micelles of PHQHEMA$_{37}$-*b*-PS$_{86}$ under different THF/Tol ratio (A and B) and the corresponding Al^{3+} complex micelles: (A) THF/Tol 5:5; (B) THF/Tol 2:8; (C) complex micelles formed in THF/Tol 5:5.

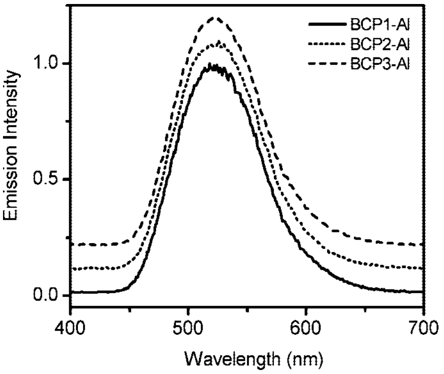

Figure 8. Normalized fluorescence spectra of Al^{3+} complex micelles in a solvent mixture of THF/Tol (5:5) (offset for clarity, $\lambda_{ex} = 393$ nm): BCP1, PHQHEMA$_{27}$-*b*-PS$_{63}$; BCP2, PHQHEMA$_{30}$-*b*-PS$_{43}$; BCP3, PHQHEMA$_{37}$-*b*-PS$_{86}$.

General Procedures of Syntheses

Reversible Addition−Fragmentation Chain Transfer Polymerization of HQHEMA. For a typical polymerization process, a stock solution in THF (15 mL) comprising HQHEMA (4.30 g, 15 mmol), AIBN (8.2 mg, 0.05 mmol), and CPDB (33.1 mg, 0.15 mmol) was prepared in a N_2-filled dry glovebox. Aliquots (2.0 mL) were removed and transferred to ampules, degassed with three freeze−pump−thaw cycles, sealed, and heated at 65 °C. After the predetermined intervals, the sealed ampules were cooled in an ice bath, and the reaction mixtures were diluted with THF and then poured in a large amount of ether. The precipitated polymers were collected by filtration, washed with ether, and dried to constant weight under vacuum at 50 °C. The overall monomer conversions were gravimetrically determined.

General Procedure for the Synthesis of Diblock Copolymer. PHQHEMA obtained by RAFT polymerization of HQHEMA described above was used as a macro-RAFT agent for the synthesis of diblock copolymer and was purified by preparative GPC to cut off the shoulder peak resulting from termination before use to obtain optimal results. PHQHEMA was dissolved in a THF solution of styrene (St, 1 mol·L^{-1}) and AIBN in a dry ampule in a N_2-filled dry glovebox. The molar ratio of PHQHEMA/St/AIBN was set to 3:450:1. Then, the resulting solution was degassed by three freeze−pump−thaw cycles, sealed, and heated at 65 °C. After the desired reaction time, the sealed tube was cooled in an ice bath, and the reaction mixture was diluted with THF and then poured in a large amount of petroleum ether. The precipitated polymer was collected by filtration, washed with petroleum ether, and dried to constant weight under vacuum at 40 °C.

Self-Assembly of Diblock Copolymer in Selective Solvent. A typical procedure for the self-assembly of the diblock copolymers is given as follows: To a solution of 9 mg of block copolymer in 4 mL of THF was added 6 mL of Tol dropwise with 5 s between drops under vigorous stirring at room temperature. The resulting mixture was left to stand overnight before further characterization.

Complexation of Self-Assembly Micelles with Triethylaluminium. The complexation reactions were carried out in a N_2-filled glovebox. A typical procedure for the complexation reaction is given as follows: To a micellar solution of 9 mg of PHQHEMA$_{27}$-*b*-PS$_{63}$ in 10 mL of THF/Tol mixture (THF/Tol 5:5) obtained as above was added 9.6 μL of 0.06 M $AlEt_3$ solution ($^1/_3$ equivalent of HQHEMA in the block copolymer). The resulting mixture was stirred overnight at room temperature. Then, the mother solution was filtrated before further characterization.

Results and Discussion

Reversible Addition−Fragmentation Chain Transfer Polymerization of HQHEMA. The key to a successful RAFT polymerization is the choice of an appropriate RAFT agent. CPDB was chosen as the RAFT agent because it has been reported to be a good RAFT agent for various (meth)acrylates[21−26] and styrenic monomers.[24,27,28] The molar ratio of CPDB/AIBN was set to three as in many reported cases of CPDB.[22−24,26,29] Thus, the RAFT polymerizations of HQHEMA were carried out in THF ([HQHEMA] = 1 mol·L^{-1}) with CPDB as the RAFT agent and AIBN as the initiator at 65 °C.

The plot of $\ln([M]_0/[M])$ versus the polymerization time is shown in Figure 1. In the initial polymerization stage (before 8 h), the polymerization nearly follows first-order kinetics, but the kinetics deviates from linearity as the reaction proceeds. This retardation can be attributed to decreased radical concentration because of the depletion of AIBN[30] because AIBN has a half life of ca. 10 h at 65 °C.

The evolution of the number-average molecular weight (M_n) and PDI with monomer conversion is shown in Figure 2. The molecular weights of the polymers linearly increase with the monomer conversions. The PDIs of the polymers are relatively narrow at low conversions (PDI $\leq$ 1.3 with conversion below 57%) and increase slightly at high conversions (PDI = 1.4 with 80% conversion). These results indicate the living/controlled nature of the RAFT polymerization of HQHEMA. However, at high conversion (80%), a relatively small shoulder peak can be observed at high molecular weight of the GPC curve (Figure 3). This population is familiar in RAFT polymerizations of, for example, methacrylate derivatives[22,23,25,31] and is often attributed to the coupling reactions by the combination of propagating radicals.

Synthesis of PHQHEMA-*b*-PS Diblock Copolymer. PHQHEMA-*b*-PS diblock copolymers were synthesized by a two-step polymerization. The first block was isolated and purified after its RAFT polymerization and was then used as a macro-RAFT agent in the RAFT polymerization of the second block. To obtain an optimal blocking efficiency and a narrow polydispersity diblock copolymer, the macro-RAFT agent should have a high transfer constant in the subsequent polymerization step to give the second block;[27] therefore, the RAFT polymerization of the monomer that corresponds to the more stabilized and sterically hindered propagating radical should be performed first. From a general point of view, a block polymerization should begin with the methacrylate monomers, followed by the styrenic monomers.[32]

Therefore, the synthesis of PHQHEMA-*b*-PS diblock copolymer was carried out with PHQHEMA, which was obtained by the RAFT polymerization, as a macro-RAFT agent for the polymerization of styrene with AIBN as the initiator in THF ([St] = 1.0 mol·L^{-1}) at 65 °C. To obtain optimal results, the PHQHEMA macro-RAFT agents were purified by preparative GPC to remove the shoulder peak before use. The molar ratio of PHQHEMA/St/AIBN was set as 3:450:1.

The recipes and results for the synthesis of diblock copolymers are shown in Table 1. The GPC curves of the diblock copolymers are shown in Figure 4. The shift toward high molecular weight of the GPC curves and the rather low PDIs of the products indicates the successful formation of the diblock copolymers. However, shoulder peaks can be observed at high molecular weight of the GPC curves, which can be attributed to the termination.

The ^{1}H NMR spectra of a diblock copolymer (Figure 5B) and the corresponding macro-RAFT agent (Figure 5A) are shown in Figure 5. Obviously, the ^{1}H NMR spectrum of the block copolymer is a sum of those of PHQHEMA block and PS block.

Self-Assembly of PHQHEMA-*b*-PS Diblock Copolymer. In PHQHEMA-*b*-PS diblock copolymer, the two blocks possess different solubilities. For example, both blocks are soluble in THF and chloroform; PS is also soluble in Tol, whereas PHQHEMA is not. Therefore, the block copolymer can be expected to self-assemble in THF/Tol and form micelles with PHQHEMA block as the core and PS block as the shell. Therefore, we investigated the self-assembly of the block copolymer by adding Tol dropwise to a solution of the block copolymer in THF until a final concentration of 9:10 mg/mL with varying THF/Tol volume ratio. No turbidity could be observed until the volume ratio of Tol/THF increased to 5:5. Dynamic light scattering (DLS) and TEM were used to investigate the self-assembly of the block copolymer. The DLS correlation functions were collected at two angles: 30 and 90°. The obtained diameters and dispersities of the micelles are reported in Table 2. Under the THF/Tol ratio of 5:5 and 4:6, the DLS results of all three diblock copolymers show essentially the same diameter at the two angles, indicating that spherical micelles were formed. The diameters are in the range between 30 and 60 nm and increase with increasing molecular weight of the block copolymers and Tol content in the solvent mixture. The formation of spherical micelles can be confirmed by the TEM investigations. A typical TEM image of the formed spherical micelles is shown in Figure 6A. While under the THF/Tol ratio of 2:8, the diameters obtained at the two angles are different, indicating that the formed micelles were not spherical. Combined with the investigation of TEM, wormlike micelles were formed. A typical TEM image of the wormlike micelles is shown in Figure 6B.

Formation of Al^{3+} Complex Micelles. It has been reported that micelles formed by amphiphilic block copolymer, in which one block has affinity for metal salts whereas the other block has affinity for the liquid medium, can trap metal salts in the core if the core has the ability to entrap metal salts by complexation or association and the shell can provide stabilization.[33] Metalation of such micelles can be performed by simple mixing of the micellar solution with the desired metal salts.[34−36]

As described above, the PHQHEMA-*b*-PS micelle formed in the THF/Tol mixture has a core containing 8-hydroxyquinoline moieties that can complex with Al^{3+} to form luminescent Alq$_3$, and the PS shell can provide affinity for the solvents. Therefore, these micelles can be used as nanoreactors in which 8-hydroxyquinoline moieties complex with Al^{3+} to form Alq$_3$-containing luminescent micelles. We carried out the metalation by mixing the micellar solution with AlEt$_3$ solution. The formed Al^{3+} complex micelles were investigated by DLS and TEM. The DLS correlation functions were collected at 30 and 90°. The obtained diameters at the two angles are the same. The diameters of the Al^{3+} complex micelles (obtained at 90°) are 421, 380, and 552 nm for PHQHEMA$_{27}$-*b*-PS$_{63}$−Al, PHQHEMA$_{30}$-*b*-PS$_{43}$−Al, and PHQHEMA$_{37}$-*b*-PS$_{86}$−Al, respectively. A typical TEM image of the Al^{3+} complex micelles is shown in Figure 6C.

Similar to the block copolymer precursor, the diameter of the formed Al^{3+} complex micelles increases with increasing molecular weight of the copolymer. But the diameter is much larger than that of the precursor micelles, ranging from about 380 to 550 nm. The large diameter indicates that these complex micelles may be large compound micelles,[14,37] which may have resulted from intermicellar chain exchange during the complexation reaction. After drying, the formed Al^{3+} complex micelles could be redispersed in the common solvents of PS such as THF, dichloromethane, and so on. Tyndall phenomenon could be observed in these dispersions, indicating that the micelles were restored. To investigate the core−shell structure of the formed Al^{3+} complex micelle, we carried out an ^{1}H NMR study by redispersing the dry micelles in CDCl$_3$. The comparison of the ^{1}H NMR spectrum of the Al^{3+} complex micelles with the corresponding block copolymer is shown in Figure 7. It can be observed that the peaks corresponding to the PHQHEMA block almost disappeared in the spectrum of Al^{3+} complex micelles, whereas the signals corresponding to the PS block are still strong, indicating that PHQHEMA blocks are located in the core of the micelles and PS blocks construct the corona. Because of the stabilization induced by ionic cross-linking in the core due to the formation of Alq$_3$ and the solubility of the PS shell, Al^{3+} complex micelles can be redispersed in the solvents of PS after drying.

The fluorescence spectra of Al^{3+} complex micelles in Tol/THF are shown in Figure 8.

The emission spectra show essentially the same profiles with emission maxima at about 520 nm that are almost identical to that of Alq$_3$. The results indicate that the Alq$_3$ moieties act as independent chromophores in the micelles, and the fluorescence properties of the Alq$_3$ moieties were not significantly affected by the polymer backbone and size of the micelles.

Conclusions

Living/controlled polymerization of HQHEMA was achieved by RAFT polymerization for the first time, and the first example of HQHEMA-containing block copolymer, PHQHEMA-*b*-PS, was synthesized by the RAFT polymerization of styrene with PHQHEMA as a macro-RAFT agent. The obtained diblock copolymer could self-assemble into nanosized micelles in the solvent mixture of THF/Tol that were used as nanoreactors to complex with AlEt$_3$ to give luminescent micelles with Alq$_3$-containing cores. Advantageously, the resulting luminescent micelles were stabilized by ionic cross-linking in consequence of the complex reaction and could be redispersed in the solvents of PS after drying. These results will contribute to the design and synthesis of polymeric luminescent nano-objects containing covalently attached luminescent metal complex.

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