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Colored Single-Chain Polymeric Nanoparticles via Intramolecular Copper Phthalocyanines Formation

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We have synthesized single-chain polymeric nanoparticles through the intramolecular formation of copper phthalocyanines from polystyrene-*co*-poly[4-((4-vinylbenzyl)oxy)phthalonitrile] under diluted conditions. Linear copolymer precursors carrying phthalonitrile pendant groups were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization followed by intramolecular macrocyclization reactions to form Cu-metallated phthalocyanines, which concurrently enabled single chain nanoparticle formation. The preparation of copper phthalocyanines within a single chain nanoparticle was confirmed using FT-IR and UV/Vis spectroscopy. The intramolecular chain collapse was characterized by SEC and AFM.

Introduction

Functional polymeric nanoparticles have attracted attention over the past decade as intriguing soft matter building blocks in the emerging field of nanomedicine, nanolithography and nanoelectronics.[1-2] Historically, these nanomaterials were prepared using micro- or miniemulsion polymerization techniques and the self-assembly of amphiphilic block copolymers in the sub 100 nm size range.[3-5] Recently, the development of a single-chain collapsed intramolecular cross-linking method allows for sub 20 nm-sized single-chain polymeric nanoparticles (SCPNs) via diverse cross-linking strategies.[6-28] In particular, the use of controlled radical polymerization has proven to be a versatile synthetic approach for preparing a wide range of linear polymer precursors with a precise molar mass and diverse coupling chemistry. Facile synthetic access to these linear copolymers enabled the preparation of well-defined and size-controlled nanoparticles by controlling the molecular weight of the starting copolymers and the composition of the cross-linkable functional units.

More recently, the preparation of novel functional SCPNs has been investigated for expanding the use of these materials for application in biotechnology and microelectronics. Representative examples of functional SCPNs include enzyme-mimetic SCPN mimicking natural folding systems such as proteins,[29-30] fluorescent particles induced by intramolecular aggregation for chemosensing materials,[31] SCPNs for MRI contrast agents via intramolecular crosslinking with dialkyne crosslinkers complexed by Gd(III) ion[32] and conductive hybrid SCPNs incorporated electroactive polythiophenes by sequential ATRP and oxidative polymerization.[33] However, the development of methods to prepare SCPNs with photoactive inclusions remains an exciting opportunity for creating novel synthetic strategies toward these materials.

Herein, we report the synthesis and characterization of new functional SCPNs with copper phthalocyanine (CuPc) functional groups. CuPcs are well known organometallic chromophores with a two-dimensional and 18 π electrons conjugated structure. Due to their optical and electrical properties, CuPcs have been extensively investigated as photoactive molecules for light-emitting devices, dye-sensitized solar cells and photosensitizers for photodynamic therapy.[34-36] Despite these earlier studies, the synthesis of soluble CuPcs on the molecular level has remained as a challenge due to their aggregation properties, resulting from their strong π-π interactions within these aromatic units.[37] Various peripheral substitutions[38-40] and polymers[41-43] have been introduced to overcome this challenge. Therefore, the SCPN as a new polymeric platform to incorporate CuPc affords a facile approach to solubilize CuPcs in various organic solvents and enable facile control of CuPc containing SCPN dissolution characteristics by simple variation of comonomers.

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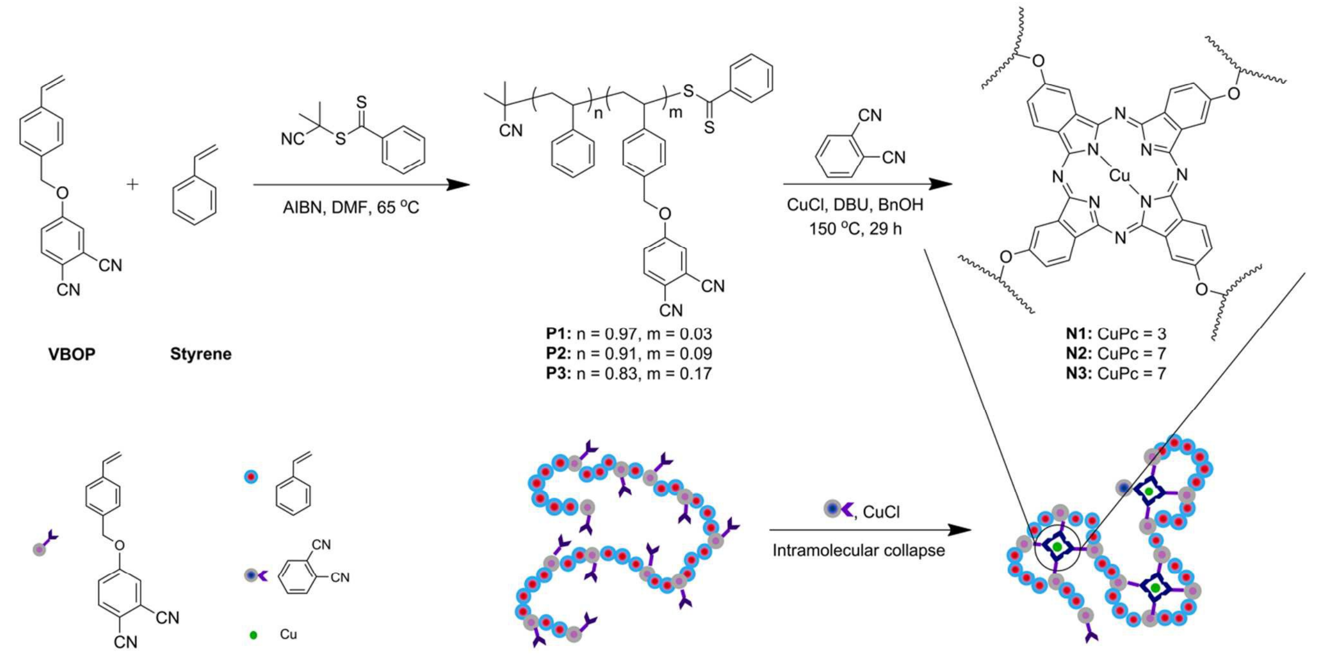

Scheme 1 Synthesis of polymeric nanoparticles containing copper phthalocyanines.

Experimental

Materials and instruments

Styrene (Junsei, 99.5%) and 4-vinylbenzyl chloride (VBC, TCI, >90%) were passed through basic alumina column to remove the inhibitor and stabilizer. CuCl (Aldrich, 98%) was purified by stirring with glacial acetic acid, followed by filtration and washing the solid three times with ethanol and twice with diethyl ether. The solid was dried under vacuum for a day. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Junsei, 98%) was recrystallized in methanol and dried under vacuum. *N*,*N*-Dimethylformamide (DMF, Junsei, 99.8%) was distilled to remove water. Phthalonitrile (PN, TCI, 99%), 4-hydroxyphthalonitrile (HPN, TCI, 97%), potassium carbonate (K_2CO_3, Aldrich, >99.0%), 2-cyano-2-propyl benzodithioate (CPDB, Aldrich, >97%), tetrahydrofuran (THF, J. T. Baker, 100%), 1,8-diazabicycloundec-7-ene (DBU, Aldrich, 98%), benzyl alcohol (Aldrich, >99%) and all of the other solvents were used as received.

Molecular weights (M_n) and the polydipersity index (M_w/M_n) were determined using size exclusion chromatography (SEC) run THF and a mobile phase and calibrated with polystyrene standards on instrument equipped with an Agilent 1100 pump, RID detector, UV detector and PSS SDV (5 µm, 10^5, 10^3, 10^2 Å 8.0 X 300.0 mm) columns. Electrospray mass-spectrum was recorded with a Bruker Ultra High Resolution ESI Q-TOF MS/MS Compact System. ^{1}H NMR spectra were obtained on a Varian Unity Inova 500 spectrometer (500 MHz) at room temperature using $CDCl_3$ as the solvent. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer. The samples for FT-IR measurement were prepared by dropping the SCPN solution (c = 1 mg/mL) onto a KBr window and removing THF using a dryer. The optical properties of the single-chain nanoparticles were measured by Optizen 3220UV UV-Vis spectroscopy. The concentration of samples for Uv-Vis was 1 mg/mL and THF was used as a solvent. Inductively coupled plasma mass spectrometer was used to determine the CuPc content in the SCPN. Sample for measurement was decomposed with a 60% nitric acid. After filtration, nitric acid was evaporated and the residues were diluted by 10 mL of 1% nitric acid solution. Copper content was measured by an ELAN DRC-e (PerkinElmer). Non-contact (tapping) AFM was performed with a n-Tracer SPM (Nanofocus). The cantilever was composed of silicon and had a resonance frequency of approximately 320 kHz and a nominal radius of curvature of less than 8 nm. The images were obtained at room temperature in air. Dynamic light scattering (DLS) studies were performed with a 90 Plus Particle Size Analyzer from Brookhaven Instruments Corporation.

Synthetic procedures

Synthesis of monomer containing phthalonitrile group, 4-((4-vinylbenzyl)oxy)phthalonitrile (VBOP). HPN (11.2 g, 78.1 mmol) and K_2CO_3 (1.47 g, 106 mmol) were added to the round bottom flask with 200 mL of distilled DMF (100 mL). VBC (10 mL, 71.0 mmol) were deoxygenated with N_2 for 30 min followed by injection into the reaction flask. The mixture was reacted at 80 ^{o}C. After 6 h, the reaction mixture was recrystallized in hexane. 15.1 g of the brown solid product was obtained (yield ~ 71%). ^{1}H NMR (TCE-d$_2$): δ = 7.71-7.23 (m, 7H), 6.76-6.70 (dd, 1H), 5.81-5.77 (d, 1H), 5.32-5.30 (d 1H), 5.15 (s, 1H). ^{13}C NMR ($CDCl_3$): δ = 161.9, 138.5, 136.3,

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135.4, 134.1, 128.0, 126.9, 120.2, 119.9, 117.7, 115.8, 115.4, 115.1, 107.8, 71.1. ESI-MS: 283.08 (M + Na^+).

GENERAL PROCEDURE FOR RAFT POLYMERIZATIONS (P1-3). **P1** was synthesized according to the following steps: a dried 10 mL round bottom flask containing AIBN (0.16 mg, 9.6 X 10^{-4} mmol), CPDB (2.13 mg, 9.6 X 10^{-4} mmol) and VBOP (150 mg, 0.58 mmol) was evacuated and refilled with N_2 three times. DMF (0.4 mL) and styrene (2.64 mL, 23.1 mmol) were deoxygenated with N_2 for 30 min and then injected into the reaction flask. The reaction temperature was 65 °C and the reaction was terminated after 20 h. The product was precipitated into excess cold methanol. After filtration and drying under vacuum, a slightly pink powder was collected. The molecular weight of the obtained polymer was determined by SEC (M_n = 4.60 X 10^4, M_p = 5.70 X 10^4, M_w/M_n = 1.15). The composition of the copolymer was derived from SEC and the NMR spectrum (DP_{St} = 409, DP_{VBOP} = 13). ^{1}H NMR ($CDCl_3$): δ = 7.9-6.0 (Ar-H), 5.2-4.8 (Ar-CH_2-O), 2.7-0.8 (-CH-, -CH_2-, -CH_3).

Using the above procedure, **P2** was synthesized from styrene (4.40 mL, 38.4 mmol), VBOP (1 g, 3.84 mmol), AIBN (0.32 mg, 0.002 mmol), and CPDB (4.25 mg, 0.019 mmol). M_n = 4.50 X 10^4, M_p = 5.94 X 10^4, M_w/M_n = 1.18.

P3 was also synthesized following the above procedure from styrene (1.10 mL, 9.6 mmol), VBOP (500 mg, 1.92 mmol), AIBN (0.16 mg, 0.001 mmol), and CPDB (1.06 mg, 0.005 mmol). M_n = 4.11 X 10^4, M_p = 5.33 X 10^4, M_w/M_n = 1.16.

GENERAL PROCEDURE FOR SINGLE-CHAIN POLYMERIC NANOPARTICLES CONTAINING COPPER PHTHALOCYANINES (N1-3). Copolymer **P1** (50 mg, 0.001 mmol), CuCl (1.41 mg, 0.014 mmol) and PN (11.0 mg, 0.086 mmol) was dissolved in benzyl alcohol (50 mL) in the N_2 charged round bottom flask. After the polymer was perfectly dissolved at room temperature, DBU (0.017 mL, 0.11 mmol) was added to the reaction flask. The reaction was started at 140 °C and continued for 29 h at 150 °C. The mixture was completely soluble in the solvent during the entire reaction. The product was precipitated into excess cold methanol. After filtration, the greenish product was dried under vacuum overnight (greenish product weighed 30 mg). After drying, Soxhlet extraction was carried out with THF to extract **N1** from the insoluble impurities. For further purification, the product was precipitated into cold methanol and then dried again. The blue-green **N1** was dried under vacuum overnight (20 mg). UV/Vis measurement sample in each time was analyzed by UV-Vis spectrometer (factor: 2 nm, scan speed: normal). Every sample was prepared as follow: 0.3 mL of the sample was mixed with 2.7 mL of THF. SEC analysis was carried out to confirm the formation of the CuPc in the polymer with decrease in the apparent molecular weight (M_n = 2.3 X 10^4, M_p = 4.5 X 10^4, M_w/M_n = 1.82).

Using the above procedure, **N2** was synthesized from **P2** (50 mg, 0.001 mmol), CuCl (3.77 mg, 0.038 mmol), PN (29.3 mg, 0.23 mmol), and DBU (0.046 mL, 0.30 mmol). M_n = 1.83 X 10^4, M_p = 3.02 X 10^4, M_w/M_n = 2.48.

N3 was also synthesized according to the procedure describe above from **P3** (50 mg, 0.001 mmol), CuCl (6.28 mg, 0.063 mmol), PN (48.8 mg, 0.38 mmol), and DBU (0.08 mL, 0.5 mmol). M_n = 1.69 X 10^4, M_p = 2.31 X 10^4, M_w/M_n = 3.28.

Table 1 Characterization data for precursors and single-chain polystyrene nanoparticle containing copper phthalocyanines

Polymers	Precursor				Nanoparticle						
	% VBOP[a]	$M_{n, SEC}$[b]	$M_{p, SEC}$[b]	PDI[b]	$M_{n, SEC}$[b]	$M_{p, SEC}$[b]	PDI[b]	$R_{h,cal}$[c] (nm)	$R_{h,DLS}$[d] (nm)	Size[e] (nm)	Number of CuPc[f]
P1→N1	3	46000	57200	1.15	23400	45500	1.82	5.70	6.55	4.2	3
P2→N2	9	45000	59400	1.18	18300	30200	2.48	4.52	5.65	4.3	7
P3→N3	17	41100	53300	1.16	16900	23100	3.28	3.88	5.25	4.9	7

[a] Composition of VBOP unit was determined by ^{1}H NMR spectroscopy.

[b] Apparent molecular weight was determined by SEC relative to polystyrene standards.

[c] $R_{h,cal} = (3KM^{a+1}/10\pi N_A)^{1/3}$; M: apparent $M_{p,SEC}$, Mark-Houwink parameter (K = 0.0141 for PS and a = 0.7 in THF), and N_A: Avogadro's number.[44]

[d] $R_{h,DLS}$ was measured in THF by DLS.

[e] Sizes of nanoparticles were measured by AFM height images.

[f] Number of CuPc was calculated using A = εcl where A: absorbance, ε: extinction coefficient (10^5 $Lg^{-1}cm^{-1}$),[45] c: concentration of nanoparticles (M), and l: optical path length (1 cm).

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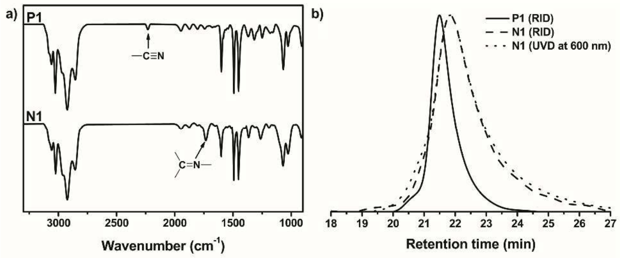

Figure 1 a) FT-IR spectra of **P1** and **N1** and b) SEC traces of **P1** (solid line) and **N1** (dash line: RI detector and dotted line: UV detector at 600 nm).

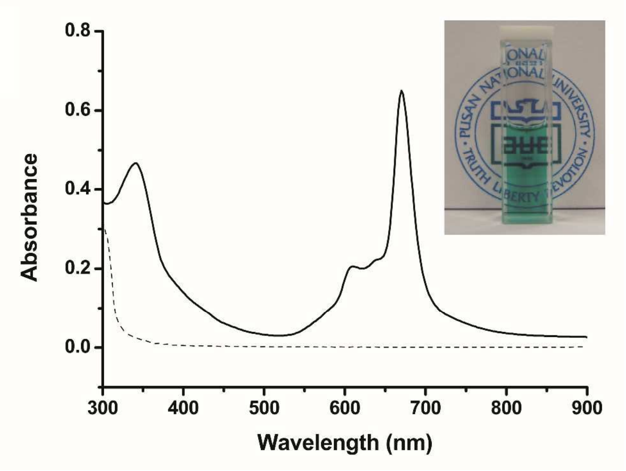

Figure 2 UV/Vis spectra of **P1** (dotted line) and **N1** (solid line, c_{N1} = 2.1 X 10^{-6} M) in THF; (Insert) Digital photograph of **N1** in THF.

Results and discussion

The styrene monomer the containing phthalonitrile group (4-((4-vinylbenzyl)oxy)phthalonitrile, VBOP) was synthesized via a nucleophilic substitution reaction between 4-vinylbenzyl chloride and 4-hydroxyphthalonitrile in good yield (15.1 g; 71%). Copolymers of VBOP and styrene were synthesized by RAFT polymerization using 2-cyano-2-propyl benzodithioate as a chain-transfer agent and 2,2′-azobis(2-methylpropionitrile) as an initiator (Scheme 1). Well-defined copolymers were obtained that contained three different molar feed ratios of VBOP (3 mol%-**P1**, 9 mol%-**P2** and 17 mol%-**P3**) with comparable molar masses (M_n: 41,000-46,000) and low polydispersity (M_w/M_n = 1.15-1.18) (Table 1). The incorporation of the phthalonitrile pendant group in copolymers **P1-3** was confirmed by ^{1}H NMR and FT-IR spectroscopy. The characteristic peaks of the VBOP unit in precursor copolymers were noted for benzylic protons (δ = 5.0) and aromatic proton bearing a nitrile group (δ = 7.6) in the ^{1}H NMR spectrum (Figure S1). The vibronic peaks of the nitrile groups on the VBOP unit were observed at 2200 cm^{-1} in the FT-IR spectrum after copolymerization (Figure 1a). The composition of each monomer was calculated using the area ratio of the aromatic and benzylic protons in the ^{1}H NMR spectrum based on their molecular weight from SEC.

Colored SCPNs (**N1-3**) were prepared by cyclotetramerization of **P1-3** with CuCl and phthalonitrile in benzyl alcohol. In the absence of additional phthalonitrile, CuPcs were formed inefficiently (Figure S4) due to the bulky CuPc reducing the free volume in SCNP. For the efficient formation of CuPc in SCNP, we added phthalonitrile in the reaction vessel. The reaction conditions at high dilution of the SCPN (c = 1.0 mg/mL) was required to minimize intermolecular coupling reactions of CuPCs resulting in insoluble impurities. The color of the reaction mixture changed to bluish green from dark brown after the macrocyclization step. After 29 h, benzyl alcohol and other reagents were removed by precipitation in excess methanol. The product was extracted from insoluble impurities by Soxhlet extraction with THF, which was a good solvent for polystyrene. During the reaction, insoluble impurities resulted from intermolecular reaction between the phthalonitrile groups in the independent polymer chains and cyclotetramerization of free phthalonitriles. Next, the isolated product was redissolved and concentrated prior to precipitation into excess methanol.

The successful formation of SCPNs was confirmed by comparing the SEC elution profiles relative to that of the linear precursor copolymer. SCPNs formed by intramolecular reaction typically exhibit reduced hydrodynamic volumes and longer retention times in the SEC experiments. As expected, **N1** exhibited a longer retention time (21.84 min) compared to its linear precursor copolymer **P1** (21.48 min) in SEC experiments. In addition, copolymers containing a higher ratio of the phthalonitrile group exhibited greater reductions in the hydrodynamic volume and in SEC experiments after macrocyclization reactions. UV detection coupled to the SEC was also used to confirm CuPc linkages in **N1-3** at 600 nm because CuPc exhibits a known spectroscopic absorption in the UV-visible region. In these UV-Vis detection measurements at 600 nm, the elution of the SCPN peaks (**N1-3**) overlaid to those elugrams captured using refractive index detection (RID) eluted more slowly than **P1-3** by the RI detector (Figures 1b and 3). All of these results indicated successful formation of SCPNs based on the presence of CuPc linkages in **N1-3** that were formed by intramolecular cyclotetramerization.

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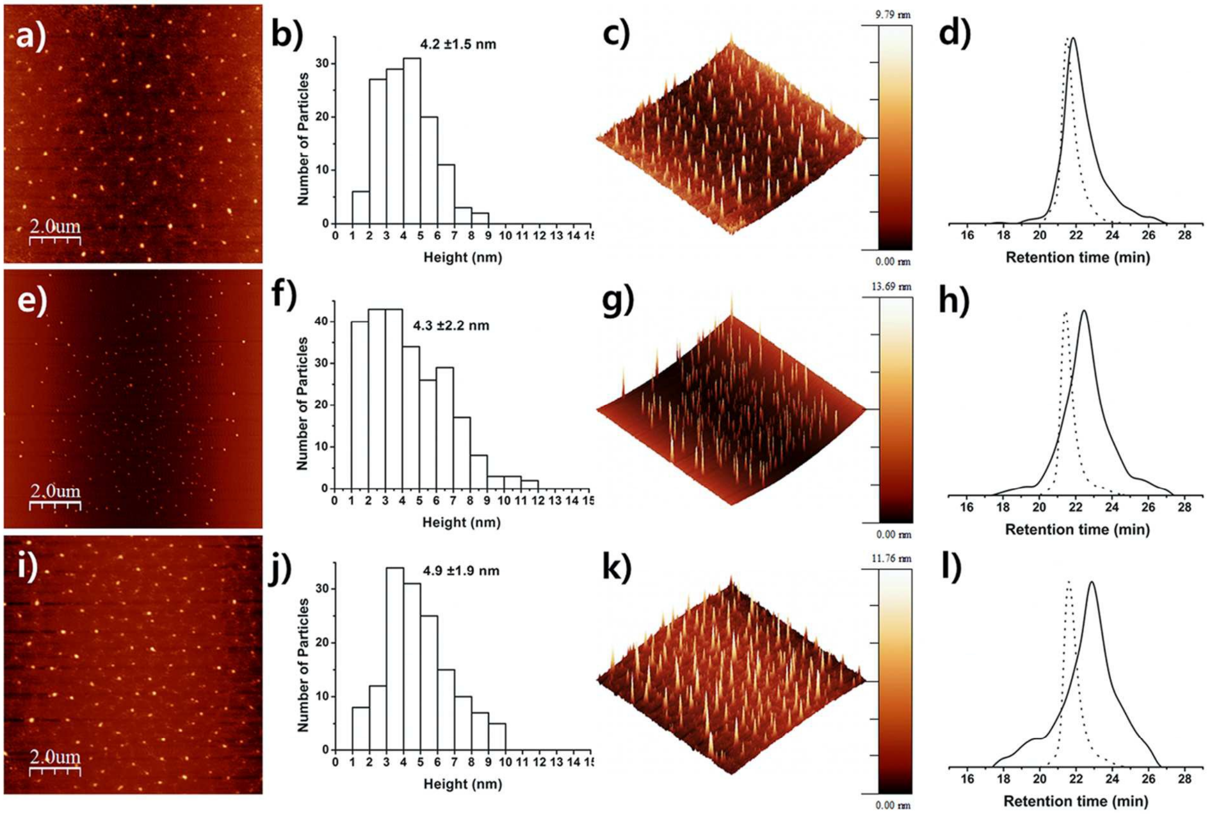

Figure 3 AFM images of single-chain polystyrene nanoparticle containing copper phthalocyanines on a mica surface (a, e, i) and corresponding size distribution histograms (b, f, j); 3-D images corresponding nanoparticles (c, g, k); SEC traces of precursor copolymers (dot) and SCPNs (solid) (d, h, l); top: **N1**, middle: **N2**, bottom: **N3**.

To confirm the formation of CuPcs in SCPNs spectroscopic characterizations were conducted using FT-IR and UV-Vis spectroscopy. FT-IR spectra indicate that the peak corresponding to the cyano group at 2230 cm^{-1} completely disappeared and a new peak corresponding to an imine group appeared at 1720 cm^{-1} after cyclotetramerization (Figure 1a). This result indicates that all of the phthalonitrile groups in the precursor polymer and additional phthalonitriles were consumed in the reaction.

The absorption spectrum of **N1** shows a characteristic strong Q-band, which indicates that **N1** contains CuPc groups resulting from the intramolecular cyclotetramerization of **P1** with CuCl (Figure 2a). The Q-band was slightly broad due to the formation of heterogeneous asymmetric CuPcs between free phthalonitriles and polymer-bound phthalonitriles. The number of CuPc incorporated in **N1** was determined using Lambert-Beer law from the UV absorption spectrum. The concentration of CuPc in a 2.1 X 10^{-6} M **N1** solution was calculated to be 6.5 X 10^{-7} M (A = 0.65 at 670 nm and $\varepsilon = 10^5$ $Lg^{-1}cm^{-1}$) corresponding to 3.4 CuPcs in a **N1**. ICP analysis revealed that **N1** contains 0.678% of copper indicating approximate 4.9 CuPcs in a SCPN. **N2** and **N3** incorporated 7 CuPcs, which were calculated based on UV−Vis analysis. Although **N3** contains a larger number of VBOP units than **N2**, the number of CuPc was saturated due to a lack of sufficient free volume to form CuPcs in the SCPN when the single chain collapsed.

The AFM images indicate that the SCPNs have a uniform size corresponding to the various VBOP/styrene ratios in the polymeric precursors because the nanoparticle solutions were prepared under ultra-dilute conditions (Figure 3). While the SEC traces exhibited an increasing retention time corresponding to the hydrodynamic volume of the nanoparticles, the AFM images of the dried nanoparticles only indicated a weak correlation with the particle size, which was primarily due

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to the comparable molar mass of the linear copolymer precursors. DLS analysis of the SCPNs indicated a decrease in the hydrodynamic radius of the SCPNs as the number of VBOP units increased on the polymer chain (Table 1).

Conclusions

In this paper, we report the first example of preparing CuPc containing SCPNs by the preparation of phthalonitrile containing polystyrene copolymers (made by RAFT polymerization) followed by macrocyclization of the pendant groups to form CuPcs. By controlling the number of VBOP units in the copolymer using RAFT polymerization, the hydrodynamic volume of the resulting nanoparticles decreased, and the number of copper phthalocyanines incorporated in nanoparticles increased. These controllable copper phthalocyanine containing polymeric nanoparticles were soluble in organic solvents, such as THF, benzene, toluene and chloroform. To the best of our knowledge, this is the first example of installing phthalocyanine moieties into SCNP, which offers a new route to prepare solution processable CuPc dyes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: SEC characterization, ^{1}H NMR spectra, and UV/Vis spectra. See DOI: 10.1039/b000000x/

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