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Novel Amphiphilic Multiarm, Starlike Coil−Rod Diblock Copolymers via a Combination of Click Chemistry with Living Polymerization

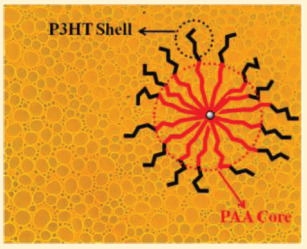
Xinchang Pang,[†,‡] Lei Zhao,[†,‡] Chaowei Feng,[†,‡] and Zhiqun Lin*[,†,‡]

[†]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States

Supporting Information

ABSTRACT: A series of novel amphiphilic 21-arm, starlike diblock copolymers, poly(acrylic acid)-*b*-poly(3-hexylthiophene) (PAA-*b*-P3HT), based on β-cyclodextrin (β-CD) with well-defined molecular architectures and ratio of two chemically distinct blocks were prepared, *for the first time*, via a combination of quasi-living Grignard metathesis method (GRIM), click reaction, and atom transfer radical polymerization (ATRP). The starlike PAA-*b*-P3HT diblock copolymers consist of hydrophilic coil-like PAA cores and hydrophobic rodlike P3HT shells with narrow molecular weight distribution and well-defined molecular weight of each block. Owing to the compact structure, the amphiphilic starlike PAA-*b*-P3HT formed a unimolecular micelle. Emulsion based on these novel amphiphilic starlike, coil−rod diblock copolymers were readily produced by cross-linking hydrophilic coil-like PAA cores with a bifunctional cross-linker, ethylenediamine.



INTRODUCTION

Conjugated polymers have been widely recognized as promising materials for use in electrochromic devices, solar cells, organic filed effect transistors, smart windows, and biosensors.[1] Among the various types of conjugated polymers, regioregular poly(3-hexylthiopene) (P3HT) is one of the most heavily studied organic semiconductors.[2−5] P3HT self-organizes into semicrystalline structures involving lamellar packing of π-stacked thienyl backbones separated by layers of hexyl side chains. P3HT possesses excellent solution processability, environmental stability, high charge carrier mobility, and tailorable electrochemical properties.[6−9] Recent advances in synthesis techniques enable the design of functional rod−coil block copolymers composed of a conjugated, rodlike block and a coil block covalently linked at one end. In comparison to conjugated homopolymers, rod−coil block copolymers are thermodynamically driven to self-assemble into ordered, controllable structures on the tenths of nanometer length scale,[10] comparable to the exciton diffusion length of conjugated polymers, thereby providing optimized morphologies for charge generation and transport. As such, they promise new opportunities for tailoring and optimizing optoelectronic properties for use in photovoltaic cells.

A variety of P3HT-based *linear* rod−coil block copolymers have been synthesized by combining Grignard metathesis polymerization (GRIM)[4,11−16] with controlled radical polymerization (e.g., atom transfer radical polymerization, ATRP),[17,18] anionic polymerization,[13,19,20] cationic polymerization,[21,22] or ring-opening metathesis polymerization (ROMP)[23] to realize intriguing nanostructured assembly and electronic activity. Quite intriguingly, amphiphilic *linear* block copolymers constituted with a rigid P3HT block and a hydrophilic, flexible block have also been reported.[12,24−32] Moreover, ionic or nonionic polymers have been grafted to the conjugated poly(alkylthiophene) backbone to achieve water-soluble *graft* copolymers.[33,34] *To the best of our knowledge, amphiphilic multiarm, starlike, coil−rod block copolymers with well-defined molecular architecture and precisely controlled molecular weight have yet to be rationally designed and synthesized.*

Starlike polymers have received considerable interest over the past decade due to their unique solid state and solution properties.[35−37] They possess most of the properties of high molecular weight materials without the solution viscosity penalty of linear materials of similar molecular weight and offer potential in coatings, additives, and drug and gene delivery applications.[38−42] Notably, most of reported starlike polymers were only multiarm *homopolymers*, and the number of arms was rarely greater than four.[43,33] More importantly, *limited* work was performed on the preparation of starlike *block copolymers* due primarily to the difficulty in purifying starlike macroinitiators and growing the second block at the end of a starlike first block.[44−47]

Amphiphilic molecules self-assemble into a rich family of intriguing structures in solution, including emulsions, multiple emulsions, and micelles[48,49] that are promising for use in encapsulation and delivery technologies. Emulsions are often produced using small amphiphiles, such as lipids and surfactants;[50] they have limited strength and stability. Ideal emulsions for encapsulation and release are those possessing well-characterized and adjustable stability, permeability, and mechanical strength. In this regard, emulsions made from block copolymers embracing a large variety of possible molecular architectures, block chemistry, and molecular weight are much tougher than the lipid counterparts.[14,51] The properties of the resulting emulsions can be

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further tailored by cross-linking.[52] Among all block copolymers, self-assembly of π-conjugated rod−coil block copolymers was demonstrated as a powerful route to supramolecular objects with novel architectures, functions, and physical properties.[5,53−56] The $\pi-\pi$ interaction between conjugated rods provides additional structural control and functionality, significantly differing from those of conventional coil−coil block copolymers.[54−56]

Herein, we report, *for the first time*, a facile route for producing a series of novel amphiphilic 21-arm, starlike, coil−rod diblock copolymers, poly(acrylic acid)-*b*-poly(3-hexylthiopene) (PAA-*b*-P3HT), based on β-cyclodextrin (β-CD) with well-defined molecular architectures, molecular weight, and ratio of two dissimilar blocks via a combination of quasi-living GRIM, click reaction, and ATRP. β-CD is a cyclic oligosaccharide consisting of seven glucose units linked by α-1,4-glucosidic bonds.[57−59] The 21 substitutable hydroxyl groups on the outer surface of β-CD offer the capability of generating a core with 21 initiation sites to form 21-arm, starlike block copolymers. The starlike PAA-*b*-P3HT diblock copolymers consist of hydrophilic coil-like PAA cores and hydrophobic rodlike P3HT shells with narrow molecular weight distribution and controllable molecular weight of each block. This simple yet robust synthetic approach opens up new avenues for creating a wide diversity of amphiphilic multiarm, starlike diblock copolymers with coil−coil, rod−coil, or rod−rod core−shell structures, thereby offering great promise for exploring the fundamental relationship between the starlike nanostructures and their properties in solution and solid state. Furthermore, unimolecular micelles made of single amphiphilic starlike PAA-*b*-P3HT were yielded as a direct consequence of their compact structure. The formation of emulsions based on these novel amphiphilic starlike, coil−rod PAA-*b*-P3HT was explored. The emulsions are composed of hydrophilic coil-like PAA cores cross-linked by adding small amount of ethylenediamine as cross-linker and hydrophobic rodlike P3HT shells. They offer great potential for use in drug encapsulation and release in a controllable manner and as a microreactor to produce hollow functional crystals at the microscopic scale via the reaction between carboxyl acid groups of inner PAA blocks with inorganic precursors.

EXPERIMENTAL SECTION

Materials. 2-Bromoisobutyryl bromide (98%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), anhydrous 1-methyl-2-pyrrolidinone (99.5%), sodium azide (≥99.5%), 2,5-dibromo-3-hexylthiophene (97%), *tert*-butylmagnesium chloride (2.0 M solution in diethyl ether), [1,3-bis(diphenylphosphino)propane]dichloronickel-(II), ethynylmagnesium bromide (0.5 M solution in tetrahydrofuran), and trifluoroacetic acid (TFA, 99.9%) were purchased from Sigma-Aldrich and used as received. CuBr (98%, Sigma-Aldrich) was stirred overnight in acetic acid, filtrated, washed with ethanol and diethyl ether successively, and dried in vacuum. β-Cyclodextrine (β-CD, Sigma-Aldrich) was used as received. *tert*-Butyl acrylate (*t*BA, Sigma-Aldrich 98%), methy ethyl ketone (Fisher Scientific, 99.9%) and *N,N*-dimethylformamide (DMF, Fisher Scientific, 99.9%) were distilled over CaH_2 under reduced pressure prior to use. Tetrahydrofuran (THF, 99%) was refluxed over potassium wire and distilled from potassium naphthalenide solution. All other reagents were purified by common purification procedures.

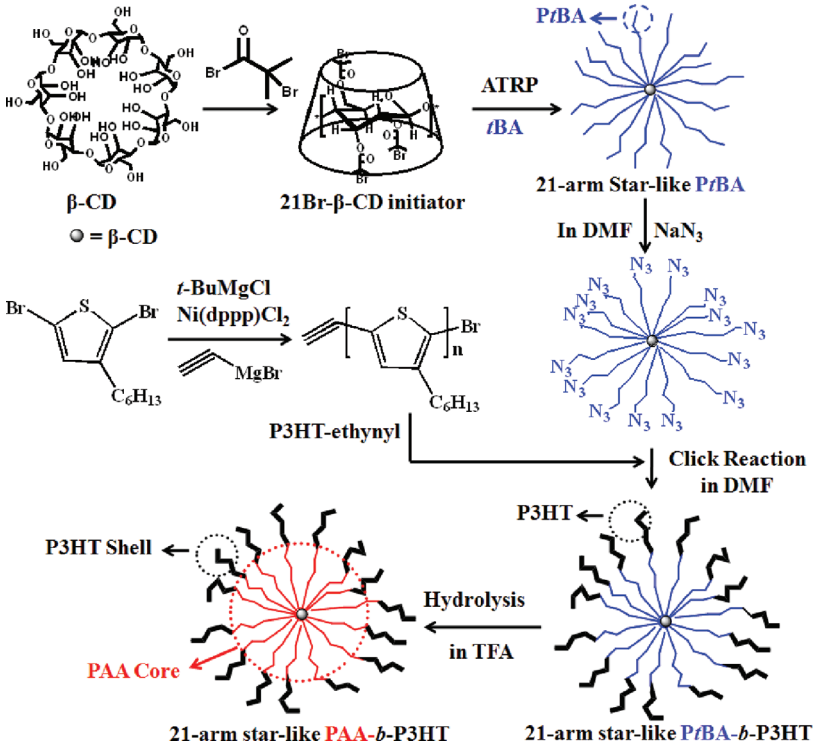
Characterizations. The molecular weight of polymers was measured by GPC, equipped with an Agilent1100 with a G1310A pump, a G1362A refractive detector, and a G1314A variable wavelength detector. THF used as eluent at 35 °C at 1.0 mL/min. One 5 μm LP gel column (500 Å, molecular range: 500−2 × 10^4 g/mol) and two 5 μm LP gel mixed bed columns (molecular range: 200−3 × 10^6 g/mol) were calibrated with PS standard samples. ^{1}H NMR spectra were obtained by a Varian VXR-300 spectroscope. $CDCl_3$ and d_7-DMF were used as solvents. FTIR spectra were recorded by a Magna-550 Fourier transform infrared spectrometer. The morphology of unimolecular micelles composed of amphiphilic starlike PAA-*b*-P3HT diblock copolymer was imaged by TEM (JEOL 1200EX scanning/transmission electron microscope (STEM); operated at 80 kV). TEM samples were prepared by applying a drop of starlike PAA-*b*-P3HT DMF solution (4 μL at c = 1 mg/mL) onto a carbon-coated copper TEM grid (300 mesh) and allowing DMF to evaporate under ambient conditions. Samples were then stained with uranyl acetate. A drop of freshly prepared saturated uranyl acetate aqueous solution (10 μL) was deposited onto dried samples. After 2 min, the excess solution was removed by filter paper, and the sample was allowed to dry. The morphology of emulsions based on starlike, coil−rod PAA-*b*-P3HT was examined by optical microscopy, SEM, and confocal fluorescent microscopy. OM imaging was performed in reflective mode (Olympus BX51). SEM studies were carried out on a Hitachi S-4000 field-emission scanning electron microscope, operating at 10 kV accelerating voltage. Fluorescent images were obtained by confocal fluorescent microscopy (Leica sp5 x). Dynamic light scattering (DLS) data were acquired using a laser light scattering spectrometer (Malvern Autosizer 4700) at 25 °C.

Synthesis of Heptakis[2,3,6-tri-*O*-(2-bromo-2-methylpropionyl]-β-cyclodextrin) (21Br-β-CD). β-CD (6.82 g, 6 mmol, vacuum-dried at 80 °C over calcium oxide overnight immediately prior to use) was dissolved in 60 mL of anhydrous 1-methyl-2-pyrrolidione (NMP) and cooled to 0 °C. 2-Bromoisobutyryl bromide (58.0 mL, 252 mmol) was then added dropwise to the β-CD solution under magnetic stirring. The reaction temperature was maintained at 0 °C for 2 h and then slowly increased to ambient temperature, after which the reaction was allowed to continue for 22 h. The brown solution obtained was concentrated in a vacuum oven for 12 h. The resulting syruplike product was diluted with 100 mL of dichloromethane and then washed sequentially with saturated $NaHCO_3$ aqueous solution (3 × 200 mL) and DI water (3 × 200 mL). The organic layer obtained was concentrated in a vacuum oven and subsequently crystallized in cold *n*-hexane to produce a white precipitate (18.21 g, yield = 71.2%). The chemical compositions of 21Br-β-CD were confirmed by FTIR: 2931 cm^{-1} (ν_{C-H}), 1737 cm^{-1} ($\nu_{C=O}$), 1158 cm^{-1} (ν_{C-O-C}), 1039 and 1105 cm^{-1} (coupled ν_{C-C} and ν_{C-O}). ^{1}H NMR in $CDCl_3$: δ = 1.8 (broad s, 126H, C**H**$_3$), 3.5−5.4 (49 H, sugar protons).

Preparation of 21-Arm, Starlike PtBA with Azide End Group (PtBA-N$_3$). 21-Arm, starlike P*t*BA with bromine end groups (P*t*BA-Br) was prepared by ATRP of *t*BA in methyl ethyl ketone, using 21Br-β-CD with 21 ATRP initiation sites as a macroinitiator and CuBr/PMDETA as a cocatalyst. Briefly, an ampule charged with CuBr (0.0707 g), PMDETA (0.1707 g), 21Br-β-CD (0.1 g), *t*BA (42.9 mL), and 43 mL of methyl ethyl ketone was vacuumed by three freeze−thaw cycles in liquid N_2, then sealed, and placed in an oil bath at 60 °C. The ampule was taken out from the oil bath and dipped in liquid N_2 at different desired times to terminate the polymerization. The solution was then diluted with acetone, passed through a neutral alumina column to remove the catalyst, and precipitated in the mixed solvents of methanol/water (v/v = 1/1). After filtration, the product was purified by dissolution−precipitation twice with acetone and methanol/water and dried at 40 °C in vacuum for 2 days. ^{1}H NMR in $CDCl_3$: δ = 2.05−1.30 (C**H**$_2$CH and −(CO)−OCH(C**H**$_3$)$_3$, repeat unit of P*t*BA), δ = 2.56−2.06 (CH_2C**H**, repeat units of P*t*BA), and 1.21 (−(CO)−C(C**H**$_3$)$_2$−).

The precipitate of starlike P*t*BA-Br (3.60 g) was dissolved in DMF (15 mL), and sodium azide (Br in starlike PtBA:sodium azide = 1:10; molar ratio) was added to the solution. The reaction mixture was stirred

Scheme 1. Synthetic Route to Novel Amphiphilic 21-Arm, Starlike Coil−Rod Diblock Copolymer, PAA-*b*-P3HT



for 24 h at room temperature. Dichloromethane (25.0 mL) was added to the mixture. The mixture was then washed with distilled water for three times. The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed by vacuum. The final product, 21-arm, starlike PtBA with azide end group (i.e., PtBA−N_3), was collected and dried at 40 °C in vacuum oven for 4 h (yield = 95.4%).

Preparation of Ethynyl-Terminated P3HT (P3HT-Ethynyl). Ethynyl-terminated P3HT was synthesized by a quasi-living Grignard metathesis (GRIM) method. Briefly, 2,5-dibromo-3-hexylthiophene (0.815 g, 2.5 mmol) was dissolved in THF (5 mL) in a three-neck flask and stirred under Ar. *tert*-Butylmagnesium chloride (1.25 mL, 2.5 mmol) was added with a syringe. The mixture was stirred for 2 h at room temperature. Subsequently, it was diluted to 25 mL with THF, and Ni(dppp)Cl_2 (22.5 mg, 0.041 mmol) was added. The resulting mixture was first stirred for 10 min at room temperature, producing intermediate P3HT, which was then reacted with ethynylmagnesium bromide (2 mL, 1 mmol) in THF for 30 min. After precipitating the reaction mixture in methanol, filtering in an extraction thimble, and washing by Soxhlet extraction with methanol, hexanes, and chloroform sequentially, ethynyl-terminated P3HT (i.e., P3HT−≡) was obtained. The final pure P3HT−≡ was recovered after complete chloroform evaporation. The regioregularity of P3HT was greater than 98% as determined by ^{1}H NMR. The number-average molecular weight and PDI of ethynyl-terminated P3HT were 5100 g/mol (based on ^{1}H NMR), 4100 g/mol (based on GPC), and 1.18 (GPC), respectively. Yield = 40.8%. ^{1}H NMR ($CDCl_3$, δ (ppm)): δ = 6.98 (s, 1H), δ = 3.05 (s, 1H), δ = 2.8 (t, 2H), δ = 1.7 (m, 2H), δ = 1.43 (m, 2H), δ = 1.36 (m, 4H), and δ = 0.92 (t, 3H).

Synthesis of 21-Arm, Starlike Diblock Copolymers, PtBA-*b*-P3HT, by Click Reaction. 21-Arm, starlike P*t*BA-N_3, and P3HT−≡ were dissolved in DMF (10 mL) in a dry ampule. CuBr and PMDETA were added, and the reaction mixture (P3HT−≡:starlike P*t*BA-N_3:copper bromide:PMDETA = 1.2:1:10:10; molar ratio) was degassed by three freeze−pump−thaw cycles in liquid N_2. The ampule was first immersed in an oil bath at 90 °C for 24 h, and then taken out of the oil bath, and placed in liquid N_2 to terminate the reaction. The mixture was diluted with THF and passed through an alumina column to remove the copper salt. The product was precipitated in cold methanol and dried in vacuum oven at 40 °C for 4 h, yielding 21-arm, starlike diblock copolymer, P*t*BA-*b*-P3HT.

Formation of Amphiphilic 21-Arm, Starlike Diblock Copolymer PAA-*b*-P3HT by Hydrolysis of *tert*-Butyl Ester Groups of PtBA Block. In a typical process, starlike diblock copolymer, P*t*BA-*b*-P3HT (0.3 g), was dissolved in 30 mL of CH_2Cl_2, and then 10 mL of trifluoroacetic acid was added. The reaction mixture was stirred at room temperature for 24 h. After the hydrolysis, the resulting starlike diblock copolymer, PAA-*b*-P3HT, was gradually precipitated in CH_2Cl_2. The final product was purified, washed with CH_2Cl_2, and thoroughly dried under vacuum at 40 °C overnight.

Preparation of Unimolecular Micelles from Amphiphilic 21-Arm, Starlike, Coil−Rod PAA-*b*-P3HT Diblock Copolymer. A small amount (∼10 mg) of amphiphilic 21-arm, starlike PAA-*b*-P3HT (i.e., sample A in Table 2) was dissolved in anhydrous DMF (∼10 mL) at a concentration of 1 mg/mL at room temperature. The solution was stirred for 2 days.

Formation of Emulsions from Amphiphilic 21-Arm, Starlike, Coil−Rod PAA-*b*-P3HT Diblock Copolymer. Amphiphilic starlike PAA-*b*-P3HT (i.e., sample A in Table 2) was dissolved in chloroform under sonication at 30 °C to yield a saturated solution. Subsequently, 1 mL of ethylenediamine−water solution at the volume ratio of ethylenediamine:water = 1:5 was added to the 4 mL PAA-*b*-P3HT chloroform solution. The resulting mixture was mechanically mixed using a pulsing vortex mixer for 30 min. After that, the chloroform phase was extracted and deposited on a glass cover slide for characterization.

RESULTS AND DISCUSSION

Synthesis of Heptakis[2,3,6-tri-*O*-(2-bromo-2-methylpropionyl]-β-cyclodextrin) (21Br-β-CD). In light of recent reports

on multifunctional initiators produced by using 2-bromoisobutyl bromide to directly modify the compounds containing hydroxyl groups,[58,59] in this work, a simple route was utilized to synthesize the heptakis[2,3,6-tri-*O*-(2-bromo-2-methylpropionyl]-β-cyclodextrin) (i.e., 21Br-β-CD) initiator by directly reacting 2-bromoisobutyric bromide with β-CD as the latter possesses 21 substitutable hydroxyl groups on its outer surface[57−59] (Scheme 1). However, a challenge remained in that anhydrous pyridine, which is a commonly used good solvent for β-CD, was immiscible with 2-bromoisobutyl bromide, leading to precipitation. As a result, the yield was greatly reduced. It is noteworthy that a similar precipitation was reported when 2-bromopropionyl bromide was used and the precipitate was a pyridine salt.[58] To overcome this problem, an appropriate solvent for β-CD was needed, which was compatible with both 2-bromoisobutyl bromide and small amounts of HBr. To this end, 1-methyl-2-pyrrolidione (NMP) was employed as solvent for the reaction of 2-bromoisobutyl bromide with β-CD, producing 21Br-β-CD with a high yield of 71.2% (Scheme 1). The resulting 21Br-β-CD is a white powder that is moderately soluble in aqueous solution and highly soluble in most organic solvents.

As noted above, the hydroxyl groups on β-CD were esterified by 2-bromoisobutyryl bromide to yield the ATRP macroinitiator, 21Br-β-CD. The complete esterification of 21 hydroxyl groups was confirmed by ^{1}H NMR (Figure S1), in which δ = 1.8−2.2 (126H) was attributed to the methyl protons of 21Br-β-CD and δ = 3.5−5.5 (49H) was assigned to residues of β-CD. The hydroxyl group conversion can be calculated based on the following equation

$$E_{T\_OH} = \frac{A_b}{18A_a} \times 100\% \quad (1)$$

where E_{T_OH} is the conversion efficiency of hydroxyl groups and A_b and A_a are the integral area of methyl protons of 21Br-β-CD and the integral area of protons (H_a; the peaks at δ = 5.2−5.3), respectively. An E_{T_OH} of 100% was obtained, suggesting that hydroxyl groups were completely converted into bromoisobutyryl units.

Preparation of 21-Arm, Starlike PtBA with Azide End Group (PtBA-N_3). ATRP of *t*BA was performed in methyl ethyl ketone at 60 °C using 21Br-β-CD as a macroinitiator and PMDETA/CuBr as a cocatalyst (Scheme 1). The obtained 21-arm, starlike P*t*BA-Br was transformed into azide-functionalized P*t*BA (i.e., P*t*BA-N_3) by reacting with sodium azide in DMF at room temperature. Four starlike P*t*BA-N_3 with different molecular weights were synthesized as summarized in Table S1. They showed monomodal GPC traces (Figure S2). The molecular weight of P*t*BA increased with polymerization time, and the molecular weight distributions of all polymers were low (PDI < 1.1). Notably, the molecular weight of starlike P*t*BA-N_3 derived from the ^{1}H NMR analysis was close to the theoretical values but remarkably different from those obtained from GPC; this was due to the different hydrodynamic volume of starlike polymers compared to the linear PS standard used in GPC columns.

The initiation efficiency in synthesis of copolymers by ATRP has been widely studied. It was demonstrated that not every initiating site generated a polymer chain and incomplete initiation was attributed to steric hindrance as a result of the high density of initiating centers.[60−62] In this work, however, the density of initiating centers in 21Br-β-CD was much lower than that reported in literature[63−65] (i.e., 21 sites in 21Br-β-CD as compared to 60−70 reported); thus, higher initiation efficiency is expected. The initiation efficiency of bromoisobutyryl for ATRP of monomer *t*BA can be estimated from the ^{1}H NMR spectrum shown in Figure S3:

$$E_{T\_bromoisobutryl} = \frac{M_{n,\,theory}}{21M_{n,\,PtBA}} \times 100\% \quad (2)$$

where $E_{T\_bromoisobutyryl}$ is the reaction efficiency of bromoisobutyryl for ATRP of monomer *t*BA, $M_{n,\,theory}$ is the theoretical value of M_n of starlike P*t*BA calculated from the monomer conversion and the concentration of the 21Br-β-CD macroinitiator, and $M_{n,\,PtBA}$ is the M_n of each P*t*BA arm calculated based on the ^{1}H NMR spectrum. Thus, an $E_{T\_bromoisobutyryl}$ = 99.21% was obtained, suggesting that nearly all bromoisobutyryl groups with 21 initiation sites were involved in the polymerization of *t*BA, and 21-arm, starlike P*t*BA homopolymers were successfully produced.

Figure S3 shows the ^{1}H NMR spectrum of sample 1 of starlike P*t*BA-N_3 obtained after the reaction for 3 h (Table S1). An intense characteristic peak at δ = 1.45 ppm (peak b) corresponded to the methyl protons in *tert*-butyl group (−C(**C**H_3)$_3$). The chemical shift at δ = 1.21 ppm represented the methyl protons at the α-end of P*t*BA-N_3 chain. The conversion of −Br to $-N_3$ was confirmed by the emergence of signals at δ = 3.08−3.20 ppm (CH_2**C**H−N_3; the end group of P*t*BA) (Figure S3); it was further evidenced by the FTIR measurement, in which a characteristic stretching of $-N_3$ at 2112 cm^{-1} was observed (Figure S4).

Synthesis of 21-Arm, Starlike Diblock Copolymers, PtBA-*b*-P3HT, by Click Reaction. Click reaction has been widely used in polymer chemistry over the past several years due to its high specificity, quantitative yield, and nearly perfect fidelity in the presence of most functional groups.[66,67] In this work, we utilized a click reaction to synthesize 21-arm, starlike diblock copolymer, P*t*BA-*b*-P3HT, by reacting P*t*BA-N_3 with P3HT having a complementary terminal alkyne group (i.e., a "graft-onto" approach; Scheme 1). To this end, ethynyl-terminated P3HT (i.e., P3HT−≡) was first prepared by end-capping P3HT synthesized by the Grignard metathesis (GRIM) method with ethynylmagnesium bromide.[11] The click reaction between the azide end group of P*t*BA-N_3 and terminal alkyne functional group of P3HT−≡ was performed in the presence of CuBr/PMDETA in DMF at 90 °C. The resulting starlike P*t*BA-*b*-P3HT block copolymers are summarized in Table 1. Compared to the ^{1}H NMR spectrum of starlike P*t*BA-N_3 (Figure S3), the characteristic peak

Table 1. Summary of 21-Arm, Starlike Diblock Copolymers, P*t*BA-*b*-P3HT

entry[a]	$M_{n,GPC}$[b]	M_w/M_n[c]	$M_{n,NMR}$[d]	yield (%)	efficiency (%)[e]
sample a	139 500	1.15	279 300	82.2	98.1
sample b	177 800	1.11	425 040	80.9	98.6
sample c	238 300	1.18	738 780	84.6	98.3
sample d	296 900	1.16	1160 880	85.2	98.9

[a] Four samples (a, b, c, d) were prepared by click reaction between P3HT−≡ and four P*t*BA-N_3, i.e., sample 1, sample 2, sample 3, and sample 4 in Table S1, respectively. [b] Number-average molecular weight, $M_{n,\,GPC}$, determined by GPC, calibrated by PS standard. [c] The polydispersity index determined by GPC. [d] $M_{n,NMR}$ calculated from ^{1}H NMR data: $M_{n,NMR}$ of starlike P*t*BA-*b*-P3HT = $M_{n,NMR}$ of starlike P*t*BA-N_3 (see Table S1) + 21$M_{n,P3HT}$ × E_{T_Click}. [e] Efficiency of click reaction (E_{T_Click}), calculated from ^{1}H NMR spectra of the starlike P*t*BA-*b*-P3HT.

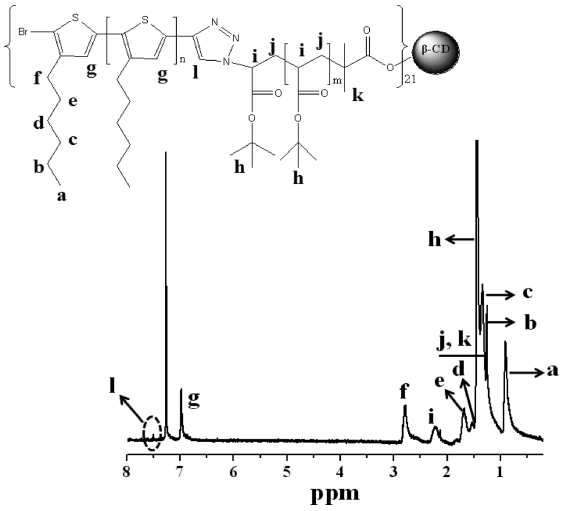


Figure 1. ^{1}H NMR spectrum of 21-arm, starlike diblock copolymer, P*t*BA-*b*-P3HT (i.e., sample a in Table 1; solvent: $CDCl_3$).

of CH_2CH-N_3 (i.e., the end group of P*t*BA) at δ = 3.08−3.20 ppm disappeared in starlike P*t*BA-*b*-P3HT diblock copolymer (Figure 1), while a signal associated with the triazole ring at δ = 7.60−7.41 ppm emerged (i.e., peak l), signifying the success of the click reaction between P*t*BA-N_3 and P3HT−≡. The characteristic peaks of thiophene at δ = 6.98 ppm, hexyl group from P3HT at δ = 0.92−2.80 ppm, methyl protons in *t*-butyl group (−C(CH_3)$_3$ in P*t*BA) at δ = 1.45 ppm, and methyl protons (i.e., peak k) at the α-end of the copolymer chain at δ = 1.21 ppm were also clearly evident, confirming that the coupling of P*t*BA-N_3 with P3HT−≡ was markedly successful. On the basis of the ^{1}H NMR spectrum of starlike P*t*BA-*b*-P3HT, the efficiency of the click reaction can be estimated by the following equation:

$$E_{T\_Click} = \frac{9 \times 166.3 \times A_g \times M_{n,PtBA}}{128.17 \times A_h \times M_{n,P3HT}} \times 100\% \quad (3)$$

where E_{T_Click} is the reaction efficiency of click reaction, A_g and A_h are the integral area of thiophene group protons at δ = 6.98 ppm on the P3HT block and the integral area of methyl protons in *tert*-butyl group (−C(CH_3)$_3$) at δ = 1.45 ppm on the P*t*BA block, respectively, and 128.17 and 166.3 are the molecular weights of *t*BA monomer and 3HT monomer, respectively. $M_{n,PtBA}$ and $M_{n,P3HT}$ are M_n of P*t*BA-N_3 (Table S1) and of P3HT−≡, respectively, calculated based on their ^{1}H NMR spectra. All E_{T_Click} are nearly 100%, reflecting that all coupling sites (i.e., -N_3) of 21-arm, star-like P*t*BA-N_3 were consumed in the click reaction.

The success of the click reaction was further demonstrated by an FTIR measurement (Figure S5). In comparison to the FTIR spectrum of starlike P*t*BA-N_3, the disappearance of characteristic stretching of $-N_3$ at δ = 2112 cm^{-1} accompanied by the appearance of a signal at δ = 1684 cm^{-1}, corresponding to the triazole ring, indicated that the $-N_3$ group was transformed into the triazole group. The FTIR spectra (Figure 3 and Figure S5) also show the presence of the C=C stretching vibrations (δ(asym) ~1510 cm^{-1} and δ(sym) ~ 1460 cm^{-1}) corresponding to poly(3-hexylthiophene). This also constitutes a proof for the formation of the block copolymer by click reaction.

It is worth noting that in order to couple each P*t*BA-N_3 arm with P3HT−≡, a slight excess amount of P3HT−≡ was used (i.e., P3HT−≡:P*t*BA-N_3 = 1.2:1; molar ratio). Because of large

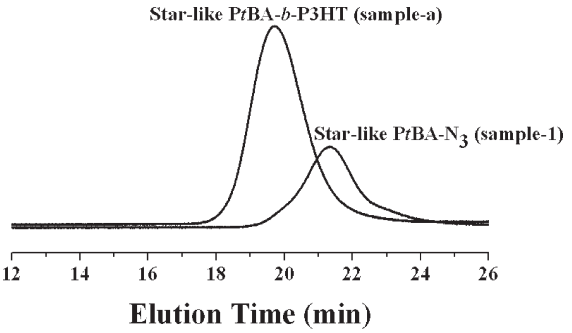


Figure 2. GPC traces of 21-arm, starlike P*t*BA-N_3 (i.e., sample 1 in Table S1) and the resulting P*t*BA-*b*-P3HT obtained by click reaction of azide-functionalized P*t*BA (i.e., P*t*BA-N_3) with ethynyl-terminated poly(3-hexylthiophene) (i.e., P3HT−≡) (i.e., sample a in Table 1).

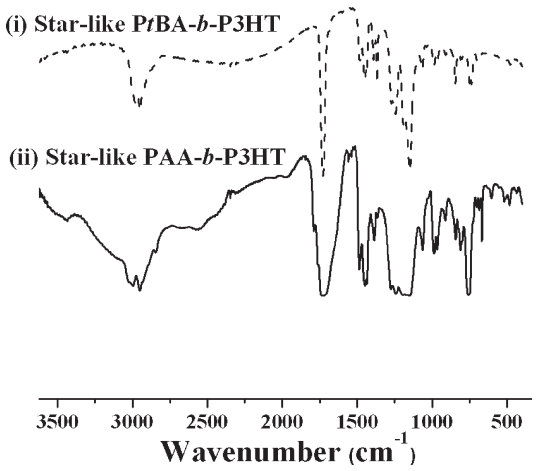


Figure 3. FTIR spectra of 21-arm, starlike diblock copolymers: (i) starlike diblock copolymer, P*t*BA-*b*-P3HT (i.e., sample a in Table 1), and (ii) the resulting amphiphilic starlike diblock copolymer, PAA-*b*-P3HT (i.e., sample A in Table 2).

difference in the molecular weight between P3HT−≡ and the resulting P*t*BA-*b*-P3HT, after click reaction, the excess P3HT−≡ was easily removed from the reaction mixture by fractional precipitation using THF as solvent and methanol as precipitator. The GPC traces of P*t*BA-*b*-P3HT are monomodal and have low PDI (<1.2) (Figure 2). Similar to the values shown in Table S1, the molecular weights of starlike P*t*BA-*b*-P3HT measured by GPC were different from those derived from ^{1}H NMR as a result of the different hydrodynamic volume of starlike polymers in comparison to the linear PS standard in GPC columns (Table 1).

Formation of Amphiphilic 21-Arm, Starlike Diblock Copolymers, PAA-*b*-P3HT by Hydrolysis of *tert*-Butyl Ester Groups of PtBA Block. Hydrophilic poly(acrylic acid) (PAA) is a weak polyelectrolyte, in which the degree of ionization is governed by the pH and ionic strength of the aqueous solution.[68] PAA possesses many unique properties, including the transformation of polarity as a function of pH and the interaction with metal ions, colloidal particles, and biomolecules.[69−72] These properties make block copolymers containing PAA very attractive for applications in reverse assembly,[70,73] stabilization of inorganic particles,[74] crystal growth modifiers,[71] drug carriers,[69] and gene therapy.[72,75] In this work, *tert*-butyl substituent in

Table 2. Summary of Amphiphilic 21-Arm, Starlike Diblock Copolymers, PAA-*b*-P3HT

entry[a]	$M_{n,PAA}$[b]	$M_{n,P3HT}$[c]
sample A	4500	5100
sample B	8400	5100
sample C	16800	5100
sample D	28100	5100

[a] Four samples (A, B, C, D) were prepared by hydrolysis of P*t*BA block in sample a, sample b, sample c, and sample d (Table 1), respectively. [b] Number-average molecular weight, $M_{n,PAA}$, of each PAA block calculated based on the molecular weight difference between P*t*BA (before hydrolysis) and PAA (after hydrolysis): $M_{n,PAA} = (M_{n,PtBA})/(128.17) \times 72.06$, where 128.17 and 72.06 are the molecular weight of *t*BA and AA monomers, respectively. [c] Number-average molecular weight, $M_{n,P3HT}$, of each P3HT shell calculated from ^{1}H NMR data.

starlike P*t*BA-*b*-P3HT diblock copolymer can be readily hydrolyzed by trifluoroacetic acid, a process which is highly selective and efficient,[76,77] yielding amphiphilic 21-arm, starlike PAA-*b*-P3HT composed of hydrophilic coil-like PAA cores and hydrophobic rodlike P3HT shells. The ^{1}H NMR spectra of a representative starlike P*t*BA-*b*-P3HT before and after hydrolysis are shown in Figure S6. Four amphiphilic starlike core−shell PAA-*b*-P3HT diblock copolymers were prepared, and the molecular weights of PAA cores are summarized in Table 2.

The disappearance of the intense characteristic peak at δ = 1.45 ppm, corresponding to methyl protons of *tert*-butyl group, reflected that P*t*BA blocks were completely hydrolyzed to PAA. Additional evidence was provided by FTIR measurement, in which a broad absorbance was observed in the range of 2500−3600 cm^{-1}, indicating the formation of carboxylic acid group of PAA (Figure 3). Furthermore, the carbonyl stretching shifted from 1726 cm^{-1} in P*t*BA to 1700 cm^{-1} in PAA.

Emulsions Formation from Amphiphilic Starlike, Coil−Rod PAA-*b*-P3HT Diblock Copolymers. Because of its compact structure (i.e., smaller hydrodynamic volume and radius of gyration), the starlike PAA-*b*-P3HT has much less interchain entanglement, thereby facilitating the formation of unimolecular micelles composed of single starlike PAA-*b*-P3HT, as measured by dynamic light scattering (DLS) and TEM. The amphiphilic starlike PAA-*b*-P3HT (i.e., sample A in Table 2) completely dissolved in DMF (c = 1 mg/mL) and was readily dispersed as unimolecular micelle. The unimolecular micelle possessed a monodisperse size distribution with a *z*-average hydrodynamic diameter, D_h, of 20 nm as evidenced by DLS measurement (Figure S7), in which a narrow single peak was observed. To further examine the unimolecular micellar structure of amphiphilic starlike PAA-*b*-P3HT, TEM imaging after staining with uranyl acetate was performed (Figure S8).[78] The dark dots in the TEM micrograph were PAA cores as uranyl acetate selectively stained PAA blocks of unimolecular micelles.[79] The average diameter of the PAA core was 9 ± 1.8 nm (Figure S8), half of the size of unimolecular micelles measured by DLS.

Subsequently, amphiphilic starlike, coil−rod PAA-*b*-P3HT was exploited to produce emulsions (using sample A in Table 2). The sample was dissolved in chloroform with sonication at 30 °C to form a saturated solution. Then the ethylenediamine water solution at the volume ratio of 1:5 was added into the starlike PAA-*b*-P3HT solution. Ethylenediamine is a bifunctional molecule and readily reacted with the carboxylic acid groups of PAA, thereby cross-linking PAA blocks together. After evaporation of chloroform and

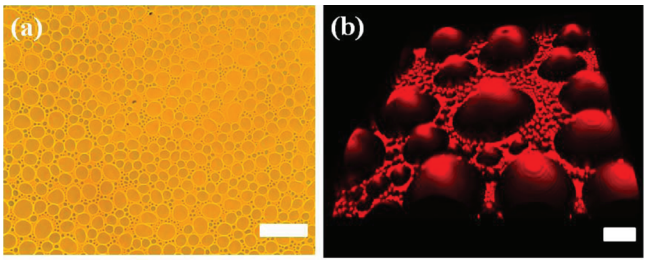


Figure 4. (a) Optical micrograph of emulsions composed of amphiphilic starlike, coil−rod PAA-*b*-P3HT. Scale bar = 100 μm. (b) Confocal fluorescent micrograph of emulsions. Scale bar = 20 μm.

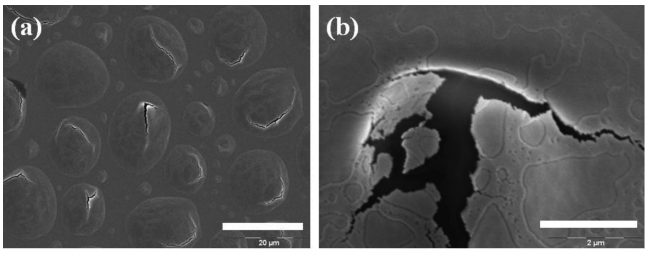


Figure 5. SEM images of emulsions. (a) Scale bar = 20 μm. (b) Scale bar = 2 μm.

water, highly packed, nearly circular emulsions with an average diameter of 20 μm surrounded by tiny emulsions were observed (Figure 4a). Confocal fluorescent microscopy measurement showed that the emulsions were hollow (Figure 4b), emitting red fluorescence originating from the P3HT shell. The formation of emulsions was also confirmed by SEM (Figure 5 and Figure S9), where cracks occurred when a layer of Au was coated on the surface under vacuum for imaging. The shell of emulsions was clearly evident at the crack region (Figure 5b).

It is noteworthy that ethylenediamine used as cross-linker played an important role in the formation of emulsions by locking in the PAA blocks of starlike diblock copolymers. No emulsions were observed without the addition of ethylenediamine. To the best of our knowledge, although *micelles* of conjugated block copolymers have been demonstrated,[5,53−56] this is the *first* report of the formation of *emulsions* based on P3HT-based block copolymers.

CONCLUSIONS

In summary, functionalized β-CD was exploited as a useful macroinitiator for preparing a series of amphiphilic 21-arm, starlike, coil−rod PAA-*b*-P3HT diblock copolymers with precisely tailorable molecular architectures and ratio of two chemically distinct blocks (i.e., hydrophilic PAA core and hydrophobic, luminescent, semiconductor P3HT shell) via a combination of GRIM, click reaction, and ATRP. These amphiphilic starlike diblock copolymers possessed narrow molecular weight distribution with the molecular weight of both the core and shell blocks being well controlled by changing the reaction time during ATRP and quasi-living GRIM, respectively. They formed unimolecular micelles as a result of the compact structure and reduced interchain entanglement. Emulsions can be readily produced using these novel amphiphilic starlike, coil−rod PAA-*b*-P3HT diblock copolymers by cross-linking the PAA cores with ethylenediamine. We envision that by rational selection of inorganic precursors a wide

spectrum of functional or multifunctional nanocrystals capped with polymer shells can be readily produced by the reaction of carboxyl acid groups of inner PAA blocks with the precursors. Furthermore, the present synthetic approach is simple yet robust and may be extended to create a myriad of multiarm, starlike diblock copolymers (or multiblock copolymers) with different conformations (e.g., coil−coil, coil−rod, or rod−rod for diblock copolymers), hydrophilicity (i.e., hydrophilic, hydrophobic, or amphiphilic), and functions (luminescent, semiconducting, stimuli-responsive (thermal, pH, and light), etc.) for fundamental study of the relationship between the starlike nanostructures (as well as complex nanoscale assemblies yielded upon them) and their properties in solution and the solid state. Such intriguing starlike copolymers would find potential applications in adaptive coatings, additives, and biomimetic materials. Emulsions formed based on them may hold promise for use in drug delivery and as microreactors to create hollow functional crystals.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra, GPC traces, FTIR spectra, DLS data, TEM image, and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: zhiqun.lin@mse.gatech.edu.

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