Synthesis of Star Polymer Architectures with Site-Isolated Chromophore Cores

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Received January 29, 2008; Revised Manuscript Received February 27, 2008

ABSTRACT: We report the synthesis of star polymers with site-isolated chromophores obtained by nitroxide-mediated polymerization and reversible addition−fragmentation chain transfer techniques through the "arm first" method. Linear polymer precursors such as α-alkoxyamine-terminated polystyrene (PS) and thioester-terminated poly(acrylic acid) (PAA) were prepared followed by the addition of fluorescent divinyl cross-linkers derived from the fluorene and thiophene families. We first synthesized organic soluble star polymers containing hexyl-functionalized fluorene and thiophene cross-linkers with PS. Second, ethylene oxide (EO)-functionalized fluorene cross-linkers were incorporated into PAA linear precursors to give water-soluble star polymers with site-isolated chromophore core units. The photoluminescence increased significantly while the emitting wavelength corresponded with highly dilute, nonconjugated chromophores in solution. This effect is indicative for a highly localized concentration of chomophores in the star polymer cores that are covalently connected but do not show the typical effects of concentrated monomers in solution such as aggregation, fluorescence quenching, and a red shift of emission wavelength. The site isolation of chomophores in star polymers leads to nanostructures with highly photoluminescent core units while the emanating linear polymers are available for further functionalizations.

Introduction

In recent years there has been a significant increase in the development of procedures that combine architectural control with flexibility in the incorporation of functional groups due to the increasing demand for functionalized soft materials. Well-defined three-dimensional structures such as microgels,[1–6] star polymers,[2–9] micelles,[10,11] and dendrimers[8,12,13] have been explored because they are considered to be building blocks for a variety of nanotechnology applications that take advantage of the high number of functional groups. In particular, star polymers, which are composed of multiple polymer chains emanating from a central core, have advantages due to their compact structure and synthetic ease of preparation. Among synthetic methods based on living free radical polymerizations,[14] the bulk of research in this area has focused on the use of atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP). Nevertheless, the utilization of reversible addition−fragmentation chain transfer polymerization (RAFT) in the synthesis of star polymers has increased considerably within recent years and has led to versatile star polymer architectures.[10,15] Regardless of the method of polymerization, preparation of star polymers can be categorized into three classes: namely, the "arm-first",[4,5,16,17] "coupling-onto",[18] and the "core-first"[19] techniques. The constantly increasing sophistication of these techniques has given means to further explore the utilization of monomers and macroinitiators with the goal to systematically functionalize submacromolecular locations such as the core units[9,20] or the peripheral linear polymer "arms".[21] For example, the group of Sawamoto synthesized core-functionalized star polymers by cross-linking preformed macroinitiators with divinyl derivatives containing functions such as amides, esters, and hydroxyl groups.[2,4,17,22] In another approach introduced by the group of Matyjaszewski, linear macromonomers are cross-linked with divinyl cross-linker which was proven as a valid method to incorporate an average number of 2.4 pyrene groups into core units that originated from functionalized ATRP initiators.[23] The limitation of star polymers containing one end functional group per arm can be overcome by the replacement of starting linear polymers with hybrid dendron−block−linear copolymers to gain access to site-specific polymer drug delivery vehicles as reported by Qiao, Hawker, and co-workers.[24]

We are interested in creating star polymers that contain a high degree of chromophores as core functionalities to investigate site-isolation effects that have been facilitated in a number of macromolecular architectures and are powerful attributes in the development of devices, biosensors, imaging reagents, and photosensitizers. Examples of this concept have been linear and globular dendritic architectures containing site-isolated central porphyrin cores[25] and luminescent ruthenium tris(bipyridine)-centered star polymers.[26,27] Other investigators reported the encapsulation of conjugated polymers and confinement of electroactive units in silica particles, resulting in materials with improved photostability and extinction coefficients comparable to those of quantum dots.[28] These properties demonstrate that the control of structural and physicochemical parameters have an extremely high impact on the electrooptical characteristics when site-isolated within scaffolds at the nanoscale and has fueled the investigation of polymeric materials as biomedical imaging reagents. Site-isolation strategies involve linear conjugated backbones such as poly(*p*-phenylene ethynylene) substituted with branched poly(ethylene oxide) side chains have led to nonionic, nonprotic amphiphilic derivatives that display both respectable solubility and exceptionally high fluorescence quantum yields.[29]

In order to further refine entirely organic structures with the possibility of engaging multiple functionalities and implementing other versatile building blocks, our goal was to confine fluorescent monomers as core units into the core of star polymer architectures soluble in organic and aqueous solvent systems. In this design, the linear polymeric arms emanating from the cross-linked chromophore core provide star polymer architectures soluble in organic and aqueous solvent systems. As core units, we focused first on fluorene and thiophene families. Fluorene derivatives contain a rigid, planar biphenyl unit which allows facile substitution at the remote C_9 site, thus improving the solubility of the resulting material without significantly increasing steric interactions in the synthesis of polymer linear

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10.1021/ma800216v CCC: $40.75
Published on Web 04/30/2008

backbones.[30] In this vein, we proposed the synthesis of fluorene cross-linkers with hexyl units and ethylene oxide (EO) units at the C_9 site. Additionally, we investigated hexyl-modified thiophene monomers as cross-linking entities to provide a variety of different optoelectronic cores. It was our goal to develop novel methodologies to implement the synthesized building blocks such as the core monomers together with tailored linear polymers to prepare star polymers with novel electro-optical features. Thereby, we facilitate the NMP polymerization technique to form linear polystyrene macroinitiators to investigate the feasibility of hexyl-modified fluorescent core entities to form star polymer architectures soluble in organic solvent systems. Furthermore, the RAFT polymerization technique was evaluated in the direct synthesis of poly(acrylic acid) macroinitiators rather than employing indirect methods that require deprotection of acrylate derivatives after star polymer synthesis.[27,31] In order to implement polyacrylate linear precursors into nano-objects, a careful adjustment of the parameters described for the arm-first approach of star polymer synthesis had to be re-evaluated.

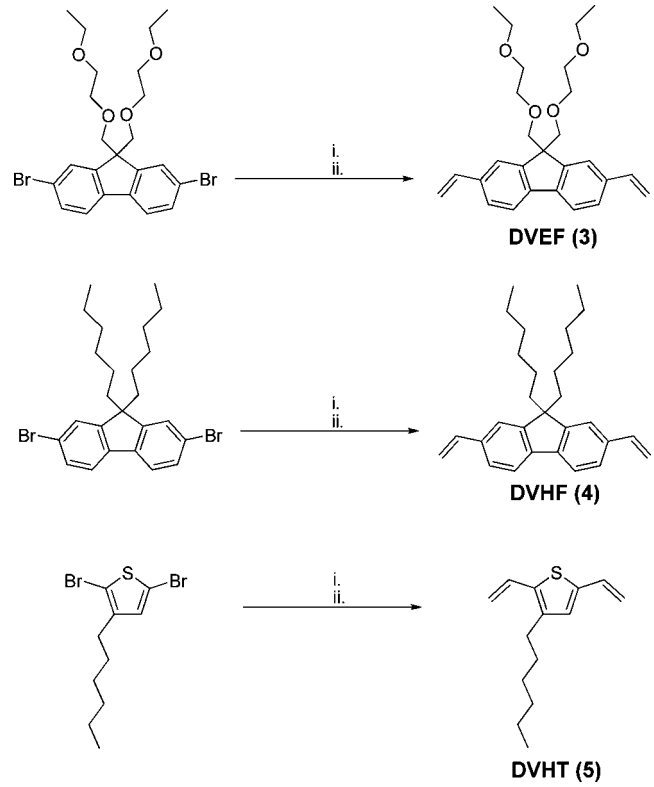
In this report, we describe the synthesis of well-defined star polymer architectures featuring novel fluorene and thiophene cross-linking moieties that are tailored to form hydrophilic and hydrophobic nanoobjects from polystyrene and polyacrylate macroinitiators. These architectures represent a class of organic nanostructures that can be further explored toward a higher degree of specificity to integrate functional groups and bioactive organic and inorganic entities.

Experimental Section

Materials. 2,7-Dibromofluorene (Aldrich, 97%), tetrabutylammonium bromide (Aldrich, 99%), 1-bromo-2,2-methoxyethoxyethane (Acros, 90%), vinyltrimethylsilane (Acros, 97%), triphenylphosphine (PPh_3, Aldrich, 99%), palladium acetate ($Pd(OAc)_2$, Aldrich, 98%), triethylamine (NEt_3, Aldrich, 99.5%), 9,9′-dihexyl-2,7-dibromofluorene (Aldrich, 97%), styrene (Acros, stabilized), acrylic acid (Acros, 99.5%), and azobis(isobutyronitrile) (AIBN, Aldrich, 98%) were used as received. SnakeSkin pleated dialysis tubing was obtained from Pierce Biotechnology, Inc. (Rockford, IL). 2,2,5-Trimethyl-2-(1-phenylethoxy)-4-phenyl-3-azahexane (α-alkoxyamine),[32] 4-cyanopentanoic acid dithiobenzoate,[33] and 2,5-dibromo-3-hexylthiophene[34] were prepared as described previously. All solvents were commercially available and used as received.

Techniques. Analytical thin layer chromatography (TLC) was carried out on commercial Merck plates coated with silica gel GF254 (0.24 mm). Column chromatography was carried out with Merck silica gel, 230−400 mesh. ^{1}H NMR and ^{13}C spectra (δ, ppm) were recorded on a 400 MHz FT-NMR spectrometer at ambient temperature. All spectra were recorded in $CDCl_3$ or MeOD, and the resonances were measured relative to residual solvent. Weight-average (M_w) molecular weights relative to linear polystyrene and polydispersity indexes (PDI = M_w/M_n) were determined by gel permeation chromatography (GPC) at ambient temperature using tetrahydrofuran (THF) as solvent (1.0 mL/min), a set of 10^2, 10^3, 10^5, and 10^6 Å Styragel 5 μm columns, a Waters 410 differential refractometer, and Millenium Empower 2 software. Particle size and absolute molecular weights were determined by dynamic light scattering (DLS) and static light scattering (SLS), respectively, on a Zetasizer Nano Series instrument at 25 °C with a CGS-3 compact goniometer system by Malvern Instruments equipped with a vertically polarized 35 mW He−Ne 633 laser with polystyrene-based samples dissolved in dichloromethane and polyacrylate-based samples dissolved in methanol. All samples were dissolved overnight, filtered through a 0.45 μm filter, and run at a fixed 90° angle with the light wavelength at 690 nm. The values of refractive index increment (dn/dc) for star polymers were measured in THF at 25 °C by using a refractometer. UV−vis absorption spectra were obtained with a Varian Cary 50 spectrophotometer, and polystyrene-based architectures were analyzed in cyclohexane whereas polyacrylate-based samples were analyzed in methanol. Photoluminescence spectra were taken on an ISS PCI photon counting spectrofluorometer in their respective solvents. Fluorescence quantum yields (Φ_f) were determined relative to 9,10-diphenylanthracene in cyclohexane ($\Phi = 0.9$[35]) as the standard. A Thermo Finnigan LCQ Deca XP quadrapole ion trap mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with an atmospheric pressure chemical infusion (APCI) ionization source operating in electrospray mode was used in positive ion mode to acquire mass spectrum data.

Scheme 1. Synthesis of Fluorescent Divinyl Cross-Linker Monomers, 9,9-Bis(2-(2-methoxyethoxy)ethyl)ethyl)-2,7-divinylfluorene (DVEF), 9,9-Dihexyl-2,7-divinylfluorene (DVEF), and 3-Hexyl-2,5-divinylthiophene (DVHT)[a]



[a] (i) vinyltrimethylsilane, $Pd(OAc)_2$, PPh_3, Et_3N, dimethylformamide, 100 °C; (ii) n-Bu_4NF/tetrahydrofuran, 90 °C.

Synthesis of 2,7-Dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)fluorene, 2. 2,7-Dibromofluorene (10.0 g, 30.9 mmol) was added to a mixture of aqueous potassium hydroxide (175 mL, 50%), tetrabutylammonium bromide (2.1 g, 6.5 mmol), and 1-bromo-2-(2-methoxyethoxy)ethane (28.4 g, 155 mmol) at 75 °C. After 30 min, the mixture was cooled to room temperature and extracted with dichloromethane. The organic layers were washed successively with water, aqueous HCl (1 M), water, and brine, dried over magnesium sulfate, and concentrated. The product was purified by flash column chromatography (5:1 hexanes/ethyl acetate) to give a yellow oil (8.3 g, 83%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.45−7.6 (m, 6H, ArH), 3.3 (s, 6H, OCH_3), 3.2 (s, 4H, OCH_2), 2.75 (t, 4H, OCH_2, J = 7.1 Hz), 2.35 (t, 4H, OCH_2, J = 7.1 Hz), 1.55 (s, 4H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 149.4, 139.88, 136.93, 125.77, 120.68, 119.77, 113.49, 69.83, 66.96, 68.99, 58.91, 50.86, 39.72, 17.23. ESI-MS (CH_3CN, positive): m/z = 546 ($M^+ + H_3O$, 100%), 544 ($M^+ + O$, 49%), 529 ($M^+ + H$, 48%).

Synthesis of 9,9-Bis(2-(2-methoxyethoxy)ethyl)-2,7-divinylfluorene, DVEF, 3. Vinyltrimethylsilane (11.4 g, 114 mmol), NEt_3 (12.5 g, 126 mmol), PPh_3 (0.97 g, 3.7 mmol), and $Pd(OAc)_2$ (0.42 g, 1.9 mmol) were dissolved in 20 mL of anhydrous dimethylformamide (DMF) and added to a solution of **2** in 5 mL of DMF (6.0 g, 11 mmol). The mixture was purged with N_2 and heated at 100 °C in a sealed flask. After 1 h, additional vinyltrimethylsilane (2.85 g, 28.4 mmol), Et_3N (6.25 g, 61.7 mmol), PPh_3 (0.485 g, 1.85

Scheme 2. Synthesis of Star Polymers (DVHT PS) (a) and (DVHF PS) (b) Utilizing Divinylhexylthiophene Derivative (DVHT), 5, and Divinylhexylfluorene Derivative (DVHF), 4, as Cross-Linking Units and α-Alkoxyamine-Terminated Macroinitiator (PS)

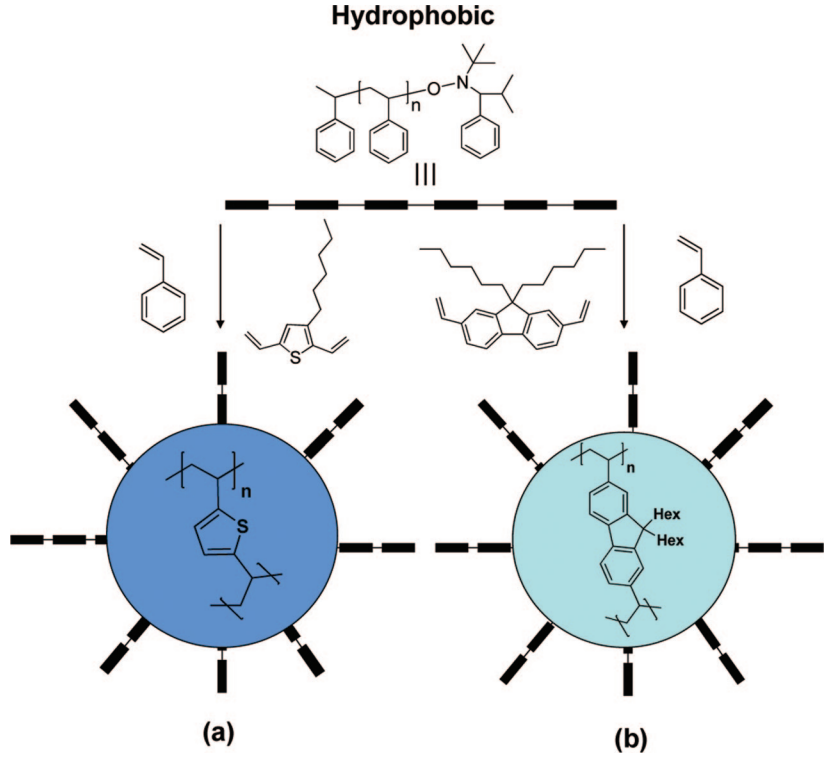


Table 1. Representative Experiments for DVHF PS Polymer Stars

entry	$M_{w,RI}$ (kg/mol)[a]	reactant ratio (PS/DVHF/styrene)[b]	$M_{w,RI}$ (kg/mol)[c]	PDI[d]
9	1.2	1/3.5/10		
10	1.2	1/3.2/10	115	1.61
11	9	1/3.2/8	190 (254)[e]	1.28

[a] α-Alkoxy-terminated polystyrene PS, weight-average molecular weight (M_w) after purification. [b] Star polymer (DVHF PS) from [PS]/[DVHF]/[styrene], [PS] = α-alkoxy-terminated polystyrene, [DVHF] divinylhexyl fluorene derivative, **4**, and styrene as comonomer. [c] Weight-average molecular weight (M_w) after precipitation; gel permeation chromatography (GPC) data relative to PS standards. [d] Polydispersity (PDI = M_w/M_n), measured by GPC with tetrahydrofuran as eluent and integrated RI detector; calibration with linear PS as standard. [e] Weight-average molecular weight, measured by static light scattering (SLS).

mmol), and $Pd(OAc)_2$ (0.21 g, 0.94 mmol) were dissolved in 5 mL of DMF and added via syringe to the solution. The reaction flask was then purged with N_2 three times. After 2 h, another equivalent of vinyltrimethylsilane (2.85 g, 28.4 mmol), Et_3N (6.25 g, 61.7 mmol), PPh_3 (0.485 g, 1.85 mmol), and $Pd(OAc)_2$ (0.21 g, 0.94 mmol) in 5 mL of DMF were added via syringe to the solution. The reaction flask was again purged with N_2 three times. After 24 h, the solution was allowed to cool to room temperature, diluted in dichloromethane, and filtered. The solution was then washed with water (3 × 200 mL). The organic layers were collected, dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (5:1 hexanes/ethyl acetate) to yield a yellow oil which crystallized at room temperature. The purified product was dissolved in 10 mL of 1.0 M tetrabutylammonium fluoride (TBAF) in THF and heated to 80 °C for 24 h. The reaction mixture was diluted in CH_2Cl_2 and washed with water (3 × 100 mL), and the organic layers were collected and concentrated in vacuo. The product was purified by column chromatography (2:1 hexanes/ethyl acetate) to give a yellow oil (3.81 g, 90.7%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.4−7.7 (m, 6H, Ar*H*), 6.80 (dd, 1H, CH_2CH, J = 17.6, J = 10.5 Hz), 5.82 (d, 1H, C*H*, J = 16.7 Hz), 5.25 (d, 1H, C*H*, J = 10.9 Hz), 3.3 (m, 6H, OCH_3), 3.2 (m, 4H, OCH_2), 2.75 (t, 4H, OCH_2, J = 6.1 Hz), 2.45 (t, 4H, OCH_2, J = 6.1 Hz), 1.6 (s, 6H, CH_3CH_2). ^{13}C NMR ($CDCl_3$): δ 149.40, 139.88, 136.93, 125.77, 120.68, 119.77, 113.49, 69.83, 71.95, 66.96, 58.91, 50.86, 39.72, 17.23. ESI-MS (CH_3CN, positive): m/z = 423 (M^+ + H, 100%), 440 (M^+ + H_2O, 96%).

Synthesis of 9,9-Dihexyl-2,7-divinylfluorene, DVHF, 4. Vinyltrimethylsilane (14.3 g, 142 mmol), Et_3N (15.7 g, 155 mmol), PPh_3 (1.22 g, 4.6 mmol), and $Pd(OAc)_2$ (0.52 g, 2.3 mmol) were dissolved in 30 mL of anhydrous DMF and added to a solution of 9,9-dihexyl-2,7-dibromofluorene in 5 mL of DMF (7.0 g, 14 mmol). The mixture was purged with N_2 and heated at 100 °C in a sealed flask. After 1 h, additional vinyltrimethylsilane (3.56 g, 35.5 mmol), Et_3N (7.82 g, 77.3 mmol), PPh_3 (0.61 g, 2.3 mmol), and $Pd(OAc)_2$ (0.26 g, 1.2 mmol) were dissolved in 5 mL of DMF and added via syringe to the solution. The reaction flask was then purged with N_2 three times. After 2 h, another equivalent of vinyltrimethylsilane (3.56 g, 35.5 mmol), Et_3N (7.82 g, 77.3 mmol), PPh_3 (1.22 g, 4.6 mmol), and $Pd(OAc)_2$ (0.52 g, 2.3 mmol) were dissolved in 5 mL of DMF and added via syringe to the solution. The reaction flask was again purged with N_2 three times. After 24 h, the solution was allowed to cool to room temperature, diluted in dichloromethane, and filtered. The solution was then washed with water (3 × 200 mL). The organic layers were collected, dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (5:1 hexanes/ethyl acetate). The purified product was dissolved in 10 mL of 1.0 M TBAF in THF and heated to 80 °C for 24 h. The reaction mixture was diluted in CH_2Cl_2 and washed with water (3 × 100 mL), and the organic layers were collected and concentrated in vacuo. The product was purified by column chromatography (2:1 hexanes/ethyl acetate) to give a colorless oil (4.95 g, 70.7%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.32 (m, 6H Ar*H*), 6.81 (dd, 1H, CH_2CH, J = 17.6, J = 10.9 Hz), 5.85 (d, 1H, C*H*, J = 17.6 Hz), 5.28 (d, 1H, C*H*, J = 10.7 Hz), 1.9 (m, 4H, CH_2), 0.95 (m, 16H, CH_2), 0.70 (t, 6H, CH_2CH_3, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 150.1, 142.1, 139.5, 138.5, 129.3, 127.2, 123.2, 115.2, 54.0, 44.2, 30.1, 28.7, 23.2, 22.1, 14.8. ESI-MS (CH_3CN, positive): m/z = 403 (M^+ + OH, 100%).

Synthesis of 3-Hexyl-2,5-divinylthiophene, DVHT, 5. Vinyltrimethylsilane (22.0 g, 222 mmol), Et_3N (48.8 g, 482 mmol), PPh_3

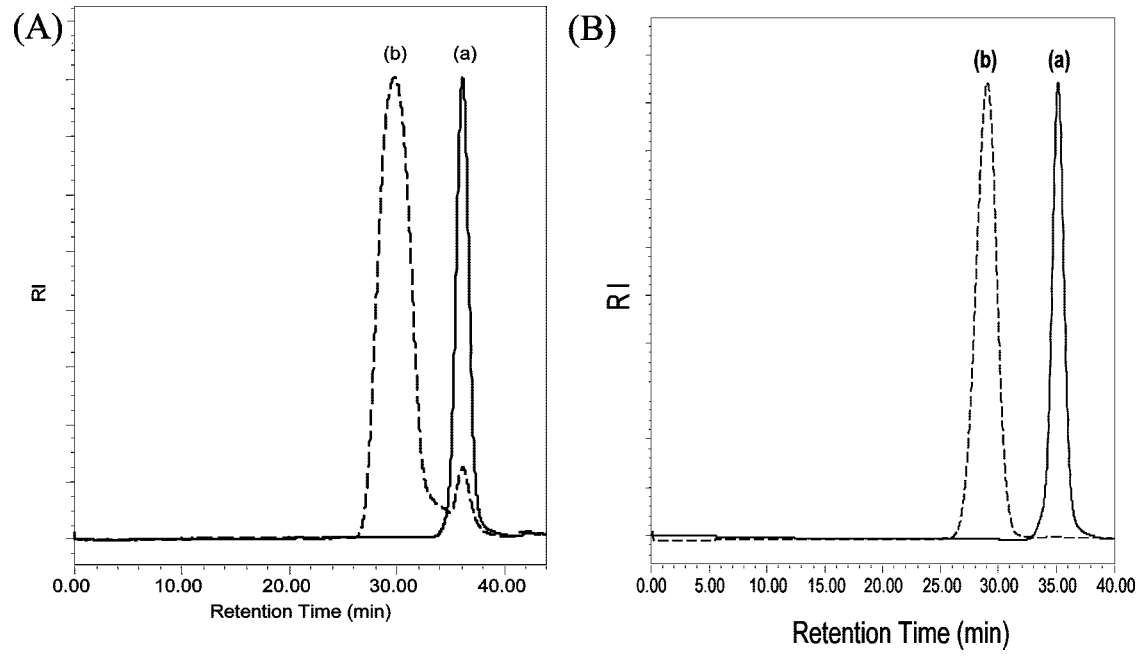


Figure 1. (A) Comparison of gel permeation chromatography (GPC) traces for (a) the α-alkoxyamine-terminated polystyrene macroinitiator, PS, **11** (M_w = 9.4 kg/mol, PDI (M_w/M_n) = 1.13) and (b) DVHF PS star polymer from [PS]/[DVHF]/[styrene], [PS] = α-alkoxy-terminated polystyrene, [DVHF] divinylhexylfluorene derivative, **4**, and styrene as comonomer (M_w = 190 kg/mol, PDI (M_w/M_n) = 1.28) after precipitation. (B) Comparison of GPC traces of (a) α-alkoxyamine-terminated polystyrene macroinitiator PS, **11**, and (b) (DVHF PS) star polymer from [PS]/[DVHF]/[styrene], [PS] = α-alkoxy-terminated polystyrene, [DVHF] divinylhexylfluorene derivative, **4**, and styrene as comonomer (M_w = 201 kg/mol, PDI (M_w/M_n) = 1.21) after fractional precipitation in acetone/ether.

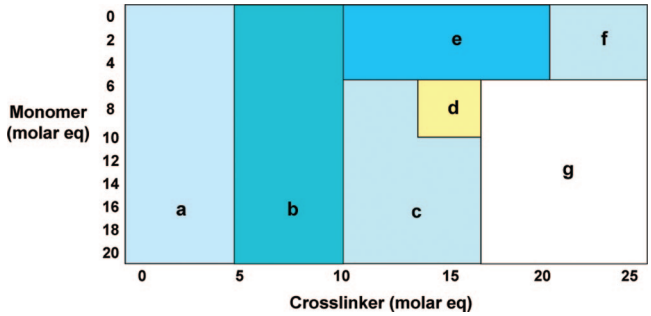


Figure 2. DVHT PS star polymer formation. Regions **a** and **b**: primarily oligomerized linear polymer chains; region **c**: high molecular weight products, high polydispersity stars; region **d**: high molecular weight, low polydispersity stars; region **e**: low molecular weight, high polydispersity stars; region **f**: high molecular weight, high polydispersity stars; region **g**: gel formation.

(3.79 g, 14.5 mmol), and $Pd(OAc)_2$ (1.63 g, 7.27 mmol) were dissolved in 40 mL of DMF and added to a solution of 2,5-dibromo-3-hexylthiophene in DMF (14.5 g, 44.3 mmol). The mixture was purged with N_2 and heated at 100 °C in a sealed flask. After 1 h, additional vinyltrimethylsilane (11.0 g, 111 mmol), Et_3N (24.4 g, 241 mmol), PPh_3 (1.9 g, 7.3 mmol), and $Pd(OAc)_2$ (0.82 g, 3.6 mmol) were dissolved in 20 mL of DMF and added via syringe to the solution. The reaction flask was then purged with N_2 three times. After 2 h, another equivalent of vinyltrimethylsilane (11.0 g, 111 mmol), Et_3N (24.4 g, 241 mmol), PPh_3 (1.9 g, 7.3 mmol), and $Pd(OAc)_2$ (0.82 g, 3.6 mmol) in 20 mL of DMF were added via syringe to the solution. The reaction flask was again purged with N_2 three times. After 24 h, the solution was allowed to cool to room temperature, diluted in dichloromethane, and filtered. The solution was then washed with water (3 × 200 mL). The organic layers were collected, dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (20:1 hexanes/ethyl acetate) to yield a dark brown oil. The purified product was dissolved in 10 mL of 1.0 M TBAF in THF and heated to 80 °C for 24 h. The reaction mixture was diluted in CH_2Cl_2 and washed with water (3 × 100 mL), and the organic layers were collected and concentrated in vacuo. The product was purified by column chromatography (2:1 hexanes/ethyl acetate) to give a yellow oil (12.1 g, 83.4%). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.86 (m, 1H, Ar*H*), 6.56 (q, 2H, CH_2CH), 5.48 (d, 1H, C*H*, J = 17.1 Hz), 5.08 (d, 1H, C*H*, J = 10.9 Hz), 2.64 (m, 2H, CH_2), 1.57 (m, 8H, CH_2), 0.98 (m, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 131.05, 129.89, 127.96, 127.12, 124.95, 114.71, 113.21, 32.18, 31.29, 29.17, 28.97, 22.37, 20.56, 13.94. ESI-MS (CH_3CN, positive): m/z = 237 (M^+ + OH, 100%).

Table 2. Representative Experiments for DVHT PS Polymer Stars

entry	$M_{w,RI}$ (kg/mol)[a]	reactant ratio[b] (PS/DVHT)	$M_{w,RI}$ (kg/mol)[c]	PDI[d]
12(a)	9.3	1/3.2	21	1.34
13(a)	9.2	1/3.6	22	1.09
14(a)	9.2	1/3.9	22	1.07
15(b)	7.2	1/6.5	23	1.28
16(d)	7.2	1/11.6	49 (98)[e]	1.58
17(d)	7.2	1/14.9	70 (140)[e]	1.83

[a] α-Alkoxy-terminated polystyrene PS, weight-average molecular weight (M_w) after purification. [b] Star polymer (DVHT PS) from [PS]/[DVHT], [PS] = α-alkoxy-terminated polystyrene, [DVHF] divinylhexyl thiophene derivative, **5**. [c] Weight-average molecular weight (M_w) after precipitation; gel permeation chromatography (GPC) data relative to polystyrene standards. [d] Polydispersity (PDI = M_w/M_n), measured by GPC with tetrahydrofuran as eluent and integrated RI detector; calibration with linear PS as standard. [e] Weight-average molecular weight, measured by static light scattering (SLS).

Macroinitiators. General Procedure for Styrene Polymerization, 6. A mixture of styrene (5.2 g, 50 mmol) and 2,2,5-trimethyl-2-(1-phenylethoxy)-4-phenyl-3-azahexane (0.16 g, 0.5 mmol) was degassed by three freeze/pump/thaw cycles, sealed under argon, and heated at 124 °C for 8 h. The viscous reaction mixture was then allowed to cool, dissolved in dichloromethane (10 mL), and precipitated into methanol (500 mL). The white powder was filtered and then dried in vacuo to yield the α-hydridoalkoxyamine-terminated polystyrene (4.36 g, 83.8%, M_w = 9000, PDI = 1.17).[32] ^{1}H NMR ($CDCl_3$): δ (ppm) 6.32−7.4 (br m), 1.28−2.12 (br m).

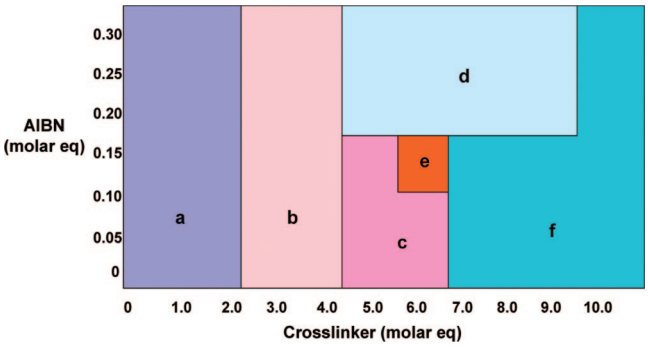


Figure 3. DVEF PAA star polymer formation. Regions **a** and **b**: oligomerized linear polymer chains; region **c**: oligomerized stars, low molecular weight products, low polydispersity; region **d**: low molecular weight, high polydispersity stars; region **e**: high molecular weight, low polydisperisty stars; region **f**: high molecular weight, high polydispersity stars.

General Procedure for Acrylate Polymerization, 7. A mixture of acrylic acid (3.6 g, 50 mmol), 4-cyanopentanoic acid dithiobenzoate (0.14 g, 0.59 mmol), and azobis(isobutyronitrile) (AIBN) (0.016 g, 0.100 mmol) was degassed by three freeze/pump/thaw cycles, sealed under argon, and heated at 70 °C for 16 h. The viscous reaction mixture was then allowed to cool, dissolved in methanol (10 mL), and precipitated once into ethyl acetate (500 mL). The polymer was filtered and then dried in vacuo to give the desired polymer (3.10 g, 86.1%, M_w = 7700, PDI = 1.11). ^{1}H NMR ($CDCl_3$): δ (ppm) 5.03 (br s, COOH), 4.35 (br s, C*H*), 2.68 (br s, CH_2), 2.42 (br s, CH_2), 1.95 (br s, CH_2), 1.50−1.85 (br m, CH_2).

General Procedure for Formation of Hexylfluorene Star Polymers, 10 and 11. A mixture of the polymeric macroinitiator, **6** (2.0 g, 0.29 mmol, M_w = 7300, PDI = 1.17), styrene (0.2791 g, 2.20 mmol), and **4** (0.346 g, 0.88 mmol) was dissolved in chlorobenzene (1.86 mL), degassed by four freeze/pump/thaw cycles, and sealed under argon. The polymerization mixture was then stirred at 124 °C for 16 h and allowed to cool, and the star polymer, **11**, was obtained after precipitation into methanol (2.3 g, 84%, M_w = 190 400, PDI = 1.28). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.32−7.2 (br m), 1.28−2.12 (br m).

General Procedure for Formation of Hexylthiophene Star Polymers, 16 and 17. A mixture of the polymeric macroinitiator, **6** (2.0 g, 0.30 mmol, M_w = 7200, PDI = 1.09), styrene (0.258 g, 2.48 mmol), and **5** (0.916 g, 4.15 mmol) was dissolved in chlorobenzene (2.9 mL), degassed by four freeze/pump/thaw cycles, and sealed under argon. The polymerization mixture was then stirred at 124 °C for 16 h and allowed to cool, and the star polymer, **16**, was obtained after precipitation into methanol (3.1 g, 90%, M_w = 49 400, PDI = 1.58). ^{1}H NMR ($CDCl_3$): δ (ppm) 6.32−7.2 (br m), 0.81−2.12 (br m).

General Procedure for Formation of EO Fluorene Star Polymers, 20−23. A mixture of the polymeric macroinitiator, **7** (2.0 g, 0.22 mmol, M_w = 7700, PDI = 1.11), **3** (0.668 g, 1.55 mmol), and AIBN (0.43 mg, 0.03 mmol) was dissolved in 2% H_2O in THF (6.0 mL), degassed by four freeze/pump/thaw cycles, and sealed under argon. The polymerization mixture was then stirred at 85 °C for 48 h and allowed to cool, and the star polymer, **23**, was obtained after precipitation using ethyl acetate followed by dialysis against methanol (1.9 g, 71%, M_w = 68 500, PDI = 1.32). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.10−7.28 (br m, Ar*H*), 5.03 (br s, C*H*), 4.35 (br s, CH_2), 2.68 (br s, CH_2), 2.42 (br s, CH_2), 1.95 (br s, CH_2), 1.50−1.85 (br m, CH_2).

Results and Discussion

For the synthesis of star polymer architectures featuring isolated chromophores, we employed the arm-first technique, which has demonstrated a high versatility toward a broad range of core monomers and linear macroinitiators. In our approach, we introduced entities such as fluorene and thiophene as cross-linkers to form fluorescent cores in star polymer architectures. The implementation of fluorene and thiophene units as core entities required the modification to divinyl derivatives, which will react with the linear polymer macroinitiators with living dormant chain ends. The cross-linked core should have the luminescence of the monomer rather than of linear poly(thiophenes) and poly(fluorenes) because of the resulting connectivity of the individual cross-linking entities over alkyl chains. Furthermore, the selected monomers were substituted with hexyl (**4**) and ethylene oxide (EO) units (**3**) to foster the hydrophobic and hydrophilic character of the star polymers, respectively. The EO derivative was synthesized from 2,7-dibromofluorene and 1-bromo-2-(2-methoxyethoxy)ethane to yield the EO-substituted dibromofluorene monomer for further modification. The conversion of the dibromo units to the reactive divinyl cross-linking derivative was maintained via a Heck reaction previously reported for the synthesis of novel *o*-quinodimethane precursors.[36] Here, the vinyl functionality is achieved in a one-step procedure that encloses an intermediate of a trimethylsilyl-protected vinyl derivative to form the desired divinyl product in good yields after deprotection with TBAF. In this fashion, we converted the dibromo derivatives into their corresponding divinyl (**3**−**5**) compounds to be investigated as cross-linking units in star polymer formation (Scheme 1).

As previously reported,[6,37] star polymer formation is affected by numerous parameters, i.e., molecular weight of the linear arms of the star, amount and nature of difunctional cross-linking reagent, use of a comonomer, and the nature and concentration of solvent. We prepared the linear polystyrene (PS) macroinitiators through NMP polymerization methods with α-hydridoalkoxyamine as initiator with molecular weights below 10 000 and polydispersities between 1.05 and 1.15.

Since the amount of cross-linking agent has a significant affect on star formation, several trials were employed to determine the appropriate feed ratio of cross-linking agent to macroinitiator with the diverse cross-linkers prepared. In the preparation of star polymer architectures we first employed DVHF PS cross-linked star polymers (Scheme 2). Initial trials involved a feed ratio of [PS]/[DVHF]/[styrene] = 1/3.5/10 (**9**) (Table 1); however, gel formation was observed. When smaller amounts of cross-linker, such as a feed ratio of [PS]/[DVHF]/[styrene] = 1/3.2/10, were introduced, we observed star polymer formation (**10**). However, these stars possessed rather large polydispersities (1.5−1.9), and further optimization experiments were necessary. A feed ratio of [PS]/[DVHF]/[styrene] = 1/3.2/8 gave well-defined DVHF PS star polymers in relatively high percent yield (84%) (**11**) (Figure 1).

Initially, the synthesis of thiophene star polymers (DVHT PS, Scheme 2) was employed with equivalent conditions that had been successful for the formation of well-defined DVHF PS stars (Table 1) since comparable conditions applied in relation to type, amount of solvent, and temperature. However, a significantly larger amount of cross-linker was necessary to form DVHT PS star polymers. Preliminary experiments involved the use of relatively small amounts of cross-linking agent. Feed ratios of [PS]/[DVHT]/[styrene] = 1/3.2/8 lead to oligomer formation (**12(a)**), corresponding to region **a** of Figure 2. Upon introduction of considerably larger amounts of cross-linker, with a feed ratio of [PS]/[DVHT]/[styrene] = 1/15/8, star polymer (**17(d)**) formation was observed (Table 2, region **d** in Figure 2).

In order to conduct a complete evaluation of the star polymer formation with the DVHT monomer (Figure 2) in average 20−30 experiments are necessary, but it is important to note that only five initial trials are necessary to determine the region and starting point for star polymer formation. Representative experiments of these trials are summarized in Table 2. Once

Scheme 3. Synthesis of Star Polymers (DVEF PAA) Utilizing Divinylethoxyfluorene Derivative (DVEF), 3, as Cross-Linking Units and Dithioester End-Capped Polyacrylate Macroinitiator (PAA)

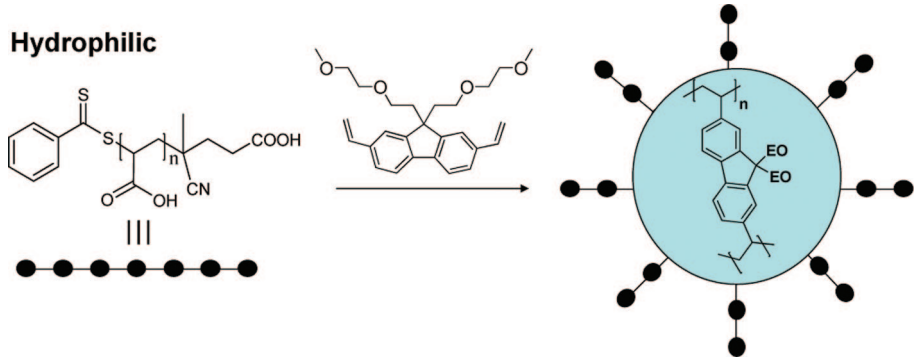


Table 3. Representative Experiments for DVEF PAA Polymer Stars

entry	$M_{w,RI}$ (kg/mol)[a]	reactant ratio[b] (PAA/DVEF)	$M_{w,RI}$ (kg/mol)[c]	PDI[d]
18(a)	6.2	1/1.8	25	1.12
19(b)	6.2	1/2.5	30	1.23
20(b)	7.3	1/3.0	33	1.24
21(b)	7.3	1/3.5	33	1.24
22(e)	9.0	1/5.2	36 (70)[d]	1.29
23(e)	7.7	1/6.0	69 (185)[e]	1.32

[a] Dithioester end-capped polyacrylate macroinitiator (PAA), weight-average molecular weight (M_w) after purification. [b] Star polymer (DVEF PAA) from [PAA]/[DVEF], [PAA] = dithioester end-capped polyacrylate, [DVEF] divinylethoxy fluorene derivative, **3**. [c] Weight-average molecular weight (M_w) after dialysis; gel permeation chromatography (GPC) data relative to polystyrene standards. [d] Polydispersity (PDI = M_w/M_n), measured by GPC with tetrahydrofuran as eluent and integrated RI detector; calibration with linear PS as standard. [e] Weight-average molecular weight, measured by static light scattering (SLS).

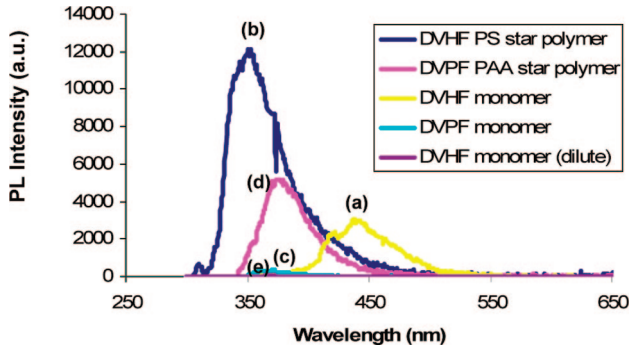


Figure 4. Photoluminescence (PL) spectra of (a) DVHF monomer, **4**, in solution (2×10^{-3} mM in cyclohexane), (b) DVHF PS star polymer **11** in solution (2×10^{-3} mM in cyclohexane), (c) DVEF, **3**, monomer in solution (2×10^{-3} mM in cyclohexane), (d) DVEF PAA star polymer **23** in solution (2×10^{-3} mM in methanol), and (e) DVHF monomer, **4**, in dilute solution (1×10^{-3} mM).

appropriate parameters for star polymer formation were verified, it was necessary to further adjust the parameters to define the entire region of well-defined star polymer formation. In order to evaluate the time point for the optimum star polymer yield that results in low polydispersity stars with high conversion and high molecular weight, we took samples at time points from 8 to 72 h. The conversion below 16 h was too low and above 24 h gave high molecular weight stars with high polydispersities. The most well-defined star polymers from polystyrene macroinitiators were formed at 16 h.

In order to synthesize water-soluble star polymers, we chose to synthesize linear polyacrylates (PAA) via the RAFT polymerization procedures. The RAFT approach was selected because of its facile application to a wide range of functional groups, such as OH, NH_2, and COOH. In the synthesis of star polymers derived from RAFT polymerization techniques, we focused on the use of PAA macroinitiators from highly efficient dithioester chain transfer agents (CTA), such as 4-cyanopentanoic acid dithiobenzoate[33] and also 2,2′-dimethylpropionate dithiobenzoate. We observed that the quality of the linear polyacrylates did not significantly vary by the use of the two initiators mentioned above, but we chose to continue the synthesis of the polyacrylates with the reported 4-cyanopentanoic dithiobenzoate that gave well-defined polyacrylate macroinitiators with low polydispersities of 1.12.

Several aspects of the RAFT star polymer synthesis differed from the NMP method. Initial experiments followed the same procedure as the NMP star synthesis, which included the reaction of macroinitiator with cross-linker and comonomer. However, it was determined that comonomer was not required in RAFT star polymer synthesis. Moreover, RAFT star formation required a radical starter, such as AIBN, to reinitiate polymerization of the macroinitiator. The temperature proved also to be a key factor in the star polymer formation. Although some RAFT polymerization techniques are conducted at 70 °C, star polymer formation did not take place at such a low temperature and had to be elevated to 85 °C to initiate star polymer synthesis. We began the RAFT star polymer synthesis with cross-linker amounts comparable to DVHF PS stars. With a feed ratio of [PAA]/[DVEF]/[AIBN] = 1/3.2/0.20, star polymer formation was not observed, and larger amounts of cross-linker were introduced to achieve high quality star polymers.

With the addition of nearly twice as much cross-linker as required in DVHF PS star synthesis, we were able to form well-defined nanostructures displaying a low polydispersity (Figure 3). The optimum feed ratio for successful star formation

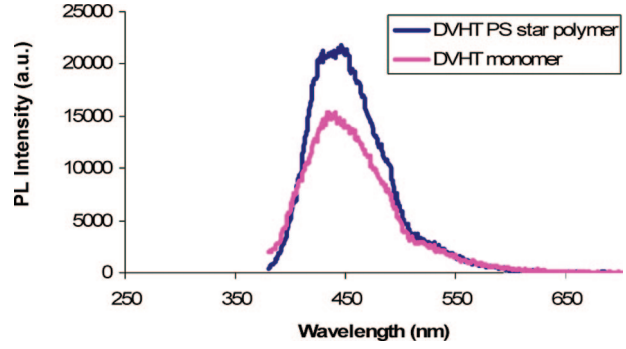


Figure 5. Photoluminescence (PL) spectra of DVHT monomer, **5**, and star polymer DVHT PS, **23**, in solution (3×10^{-3} M in cyclohexane).

displaying a low polydispersity and high molecular weight was determined to be [PAA]/[DVEF]/[AIBN] = 1/6.0/0.10 (**23(e)**) after a series of trials. As shown for the polystyrene star synthesis (Scheme 3), we also evaluated the optimum star polymer yield by verifying the conversion at different time points during synthesis. Samples were taken during a time frame of 8−96 h. We found that less than 24 h led to oligomers, while at duration times above 24 h star polymer formation was observed. At 48 h conditions for low polydispersity and high molecular weight star polymer were found to be at optimum values together with high conversion rates. Longer reaction times decreased the quality of the stars, and high polydispersity star polymers were formed. Representative experiments are summarized in Table 3 and give the feed ratios for the characteristic regions identifying ideal conditions for star polymer synthesis which are shown in Figure 3.

In order to complete the characterization of the synthesized star polymer architectures, we employed dynamic light scattering techniques to determine the diameter and employed static light scattering methods for the absolute molecular weight measurements. DVHF PS stars displayed an average size of 11 nm, owing to the smaller amount of cross-linker incorporated, in contrast to DVEF PAA stars that exhibited an average size of 20 nm and DVHT PS stars with an average size of 90 nm due to the even higher amount of cross-linking unit necessary to form well-defined star polymers. In respect to molecular weight measurements, DVHF PS star polymers maintained an absolute molecular weight of 250 kDa, while DVEF PAA star polymers had an average absolute molecular weight of 185 kDa, corresponding to 30−40 arms per nanostructure while DVHT stars displayed an average absolute molecular weight of 330 kDa.

After we found the ideal conditions to synthesize well-defined star polymers, we probed the resulting conformation and environment of the chromophores as core entities in the star polymeric architectures by UV−vis absorption and photoluminescence measurements in solution. We first investigated the photoluminescence properties (PL) of the star polymers containing fluorene-derived core entities which were recorded by excitation at the absorption maximum. Figure 4 shows that the star polymer from linear α-alkoxyamine-terminated polystyrene (DVHF PS, **11**) with incorporated DVHF (**4**) displayed an absorption and emission wavelength of 313 and 353 nm, respectively. The emission maximum of the DVHF monomer **4** displayed two maxima depending on the concentration in solution at 423 and 434 nm and at 367 nm for the lowest concentration. Analogous results were obtained for the DVEF PAA polymeric stars with an absorption wavelength of 340 nm and emission wavelength of 376 nm, with the DVEF monomer emitting at 367 nm. We also observed an almost doubled PL intensity of the emission spectra of the star polymer architectures in contrast to the monomer as a result of the cross-linking event during star polymer formation. We concluded that cross-linked core structures prevent π-stacking of the chromophores maintained by the sterical hindrance of the hexyl and EO-functionalized divinyl derivatives as well as a reduction of the extinction among molecules and increase in $\pi-\pi^*$ transition energies in contrast to the monomers in solution. Additionally, the cross-linking event enhances the structural disorder of monomers in close proximity to each other that increases the binding energy of the excitons and leads to increase in photoluminescence. We further observed that strongly diluted divinyl monomers **3** and **4** emitted at nearly the same wavelength as the star polymers **11** and **23** but with a much lower photoluminescence. Together with this observation we can suggest that the site-isolated cross-linking units show electronic features of individual chromophores while avoiding fluorescence quenching and a red shift by aggregation effects seen in concentrated monomer solutions such as demonstrated for the DVHF monomer. At the same time, the conformation of the core chromophores displayed a highly localized concentration of connected but disordered chomophores that lead to a much higher PL intensity.

The star polymer architectures that are comprised with thiophene cross-linking units displayed similar electro-optical characteristics. The thiophene star polymers from α-alkoxyamine-terminated polystyrene displayed absorption and emission wavelengths of 370 and 434 nm, respectively, while thiophene monomer (**5**) had an emission wavelength of 434 nm (Figure 5). The PL intensity increased by 10%, also caused by a sterically induced reduction of extinction and increased isotropy through the cross-linking during star polymer synthesis in addition to an increased quantum yield of 3.2%. Also here, the conformation of the chromophores in the star polymer systems suggested connectivity over individual chromophore entities, as the optical properties from photoluminescence spectroscopy indicated. In comparison to the fluorene star polymers, these results demonstrated that conformational changes of the cross-linked monomer are specifically pronounced in monomer units that extend one aromatic system and are more prone to π-stacking and aggregation in solution. It will be our future goal to extend the series and prepare star polymers that maintain the conformation of the connected chromophores in the core as demonstrated before but yield lower energy emission wavelength.

Conclusions

A series of fluorescent star polymers that represent a new class of organic nanostructures were synthesized through the "arm first" method, implementing α-alkoxyamine-terminated polystyrene and dithioester end-capped polyacrylate as linear precursors. We investigated novel fluorescent core units from fluorene and thiophene families that were solubilized with hexyl and ethylene oxide units in order to enhance the solubility in organic and aqueous environment accompanying the physicochemical character of the emanating linear polymer chains in the PS and PAA stars, respectively. The cross-linking units were first functionalized, integrating solubilizing units followed by the transformation of the dibromine derivatives into divinyl entities facilitated in a one-step procedure utilizing a Heck reaction. While divinylbenzyl groups as core units are well documented, we developed new protocols for the successful integration of core forming fluorescent cross-linking units. The stars composed with ethylene oxide-modified fluorene derivative and thiophene cross-linker required larger amounts of the cross-linker in order to give high quality star polymers compared to the stars formed with hexyl-functionalized fluorene. The dimensions of the star polymers correlated with the relative amount of cross-linker and appeared to be larger (70−100 nm) for the thiophene-derived star polymers than for the fluorene-derived systems (10−20 nm), and absolute molecular weights between 185 and 330 kDa were determined. The photoluminescence intensity increased significantly at wavelengths corresponding to the dilute, nonconjugated monomers. These results mirror the conformational environment of the first cross-linked, site-isolated chromophores in star polymer architectures and showed that the cross-linked core chomophores are conjugated to result in isotropically disordered systems that yield highly localized concentrations of emitting entities. This principle will be extended to gain access to highly fluorescent star polymer architectures containing a broader range of emitting chromophores.

Acknowledgment. E.H. gratefully acknowledges Vanderbilt University for a junior faculty start-up fund and financial support from the CAREER program of the National Science Foundation

under Award CHE-0645737. C.T.A. was supported by a Chemistry-Biology Interface Program Fellowship under an NIH Training Grant No. T32 GMO65086-5.

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