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Highly Luminescent Nanoparticles: Self-Assembly of Well-Defined Block Copolymers by $\pi-\pi$ Stacked BODIPY Dyes as Only a Driving Force

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ABSTRACT: Well-defined polymers incorporated BODIPY dyes into the PMMA side chain, and the block copolymers were synthesized by the RAFT process. The controlled/living character of the polymerization of MMA monomers with pendant BODIPY dyes was confirmed by the formation of the narrow molecular weight distribution products, the linear first-order kinetic plot, linear increase of molecular weight with the conversion, and block extension with styrene. The SEM images of the obtained homopolymers showed micrometer-sized blubber particle- or chain-like structures, which come from the aggregated particles by strong intermolecular $\pi-\pi$ stacking of BODIPY dyes. In contrast, the designed block copolymers formed nanoparticles with enhanced luminescence ($\Phi_F > 0.70$) by preventing higher molecular weight polystyrene segment from aggregation by the strong $\pi-\pi$ stacking.

Introduction

Herein we provide evidence that BODIPYs (4,4′-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes) supply a facile self-assembling of block copolymers exhibiting highly luminescence by $\pi-\pi$ stacking interaction as only a driving force, i.e., the construction of luminescent nanoparticles. Recently, there has been increased interest in using BODIPY dyes as optical sensitivity materials for biochemical labeling, photonic molecular system, organogelators, and light-emitting devices[1] because of its advantageous characteristics, such as high extinction coefficients, high quantum yields, and the fact that its excitation wavelength lies in the visible-wavelength range.[2−4] The incorporation of organoboron dyes containing BODIPYs into a polymer main chain,[5] side chain,[6] or initial end[7] have drawn attention as electroluminescent devices, organic field-effect transistors, photovoltaics, etc.[8] Previously, we have demonstrated that BODIPY-based π-conjugated polymers exhibited supramolecular self-assembled particle, fiber, and network structures by strong $\pi-\pi$ stacking interaction originated from the highly planar structure of BODIPY.[9] Further, the incorporation of BODIPYs into polymer side chain has also been some of the intriguing research topics. For example, García-Moreno and Amat-Guerri et al. have demonstrated that novel BODIPY-based polymers were prepared by free-radical copolymerization of methyl methacrylate with BODIPY monomers having the 8-position substituted by long alkyl chains[10] or phenyl groups,[11] tethered with methacryloyloxy group, and exhibited efficient and highly photostability toward laser in liquid solution as well as in solid polymeric matrices. However, their morphologies have not yet been investigated in spite of BODIPY structures triggering strong $\pi-\pi$ stacking interaction. Therefore, well-defined poly(methyl methacrylate)s (PMMA) having pendant BODIPY dyes or the block copolymers will provide a new sophisticated supramolecular self-assembly system, for constructing two- and three-dimensional arrangements of the BODIPY units in polymer materials.

This article reports the synthesis and characterization of the self-organization of well-defined polymers having pendant BODIPY units and the block copolymers by reversible addition−fragmentation chain transfer (RAFT) process. To manipulate unique luminescent functions and morphologies of these BODIPY-containing polymers and the block copolymers, it is desirable to control various factors, including chemical structures of main chain, chain length, location, and stacking of the BODIPY units.

Experimental Section

Instrumentation. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H NMR and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard in CD_2Cl_2, and ^{11}B NMR spectra were referenced externally to $BF_3 \cdot OEt_2$ (sealed capillary). Number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by size exclusion chromatography (SEC) with a TOSOH 8020 series [a dual pump system (DP-8020), a column oven (CO-8020), and a degasser (SD-8020)] equipped with three consecutive polystyrene gel columns [TOSOH gels: α-4000, α-3000, and α-2500] and a refractive index (RI-8020) and an ultraviolet detector (UV-8020) at 40 °C. The system was operated at a flow rate of 1.0 mL/min with tetrahydrofuran as an eluent. Polystyrene standards were employed for calibration. UV−vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, fluorescence emission spectra were measured on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and fluorescence micrograph on fluorescence microscope OLYMPUS IX71. Scanning electron microscopy (SEM) images were performed using a JEOL JSM-5600 operated at an accelerating voltage of 15 kV. SEM samples were prepared by putting desired precipitates on the conducting tape attached by SEM grid. Elemental analysis was conducted by an ELEMENTAR vario MICRO Cube. Dynamic light scattering (DLS) measurements were performed at 25 °C with Otsuka FPAR-1000 at a 90° detection angle.

Materials. Cumyl dithiobenzoate (CDB),[13d] F-BODIPY-Br,[11] and monomer **1**[11] were prepared according to the literature. 2,2-Azobis(isobutyronitrile) (AIBN) was obtained from

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Wako Chemical, Co., and recrystallized from methanol prior to use. Styrene (St) was obtained from Wako Chemical, Co., and was distilled under vacuo. Other reagents were commercially available and used as received.

PA-BODIPY-Br. This compound was synthesized by a modification of a literature procedure.[9] To a solution of phenylacetylene (12 mL, 69.5 mmol) in anhydrous THF (200 mL) was added dropwise EtMgBr (64 mL, 64.0 mmol, 1.0 M in THF) at room temperature under nitrogen. The solution was stirred at 50 °C for 3 h. The mixture was then added at room temperature via a cannula to a solution of F-BODIPY-Br (15.0 g, 28.7 mmol) in anhydrous THF (100 mL). After the mixture was stirred at 70 °C for 6 h, the solvent was removed by rotary evaporation. The residue was treated with water and extracted with $CHCl_3$. The organic extracts were washed with water and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography eluted with $CHCl_3$/hexane to give a bright red solid in 40% yield (7.90 g, 11.5 mmol). ^{1}H NMR (CD_2Cl_2): δ = 7.26 (m, 4H, $-C_6H_2$), 7.13 (m, 6H, $-C_6H_3$), 3.32 (t, 2H, J = 6.8 Hz, $-CH_2-$Br), 2.96 (t, 2H, J = 8.4 Hz, $\rangle C-CH_2-$), 2.73 (s, 6H, BODIPY$-CH_3 \times 2$), 2.41 (q, 4H, J = 7.5 Hz, BODIPY$-CH_2- \times 2$), 2.32 (s, 6H, BODIPY$-CH_3 \times 2$), 1.75 (t, 2H, J = 7.2 Hz, $\rangle CCH_2-CH_2-$), 1.61−1.58 (m, 2H, $\rangle CC_2H_4-CH_2-$), 1.45−1.43 (m, 2H, $\rangle CC_3H_6-CH_2-$), 1.30−1.25 (m, 10H, $-(CH_2)_5-$), 1.02 ppm (t, 6H, J = 7.5 Hz, BODIPY$-CH_2-CH_3 \times 2$). ^{13}C NMR (CD_2Cl_2): δ = 152.4, 145.6, 134.6, 133.3, 131.6, 129.5, 128.4, 127.4, 125.5, 95.5, 95.4, 34.6, 33.3, 32.2, 30.6, 29.8, 29.8, 29.8, 29.1, 29.0, 28.5, 17.8, 15.1, 14.2, 13.8 ppm. ^{11}B NMR (CD_2Cl_2): δ = −13.9 ppm. Anal. Calcd for $C_{43}H_{52}N_2BBr$: C, 75.11; H, 7.62; N, 4.05. Found: C, 75.08; H, 7.54; N, 3.99.

Monomer 2. This compound was synthesized by a modification of a literature procedure.[10,11] A solution of potassium methacrylate (4.48 g, 34.9 mmol), PA-BODIPY-Br (6.0 g, 8.73 mmol), tetrabutylammonium bromide (0.14 g, 0.44 mmol), and a small amount of hydroquinone in *N*,*N*-dimethylformamide (500 mL) was stirred at 40 °C under nitrogen and the dark. After 24 h, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate, and then the solvent was evaporated in vacuo. The residual product was purified by silica gel column chromatography eluted with hexane/chloroform to give **2** as a viscous red oil in 81% yield (4.92 g, 7.10 mmol). ^{1}H NMR (CD_2Cl_2): δ = 7.36−7.20 (m, 4H, $-C_6H_2 \times 2$), 7.18−7.09 (m, 6H, $-C_6H_3 \times 2$), 5.96 (s, 1H), 5.44 (s, 1H), 4.02 (t, 2H, J = 6.6 Hz, $-O-CH_2-$), 2.97 (t, 2H, J = 8.6 Hz, $\rangle C-CH_2-$), 2.73 (s, 6H, BODIPY$-CH_3 \times 2$), 2.41 (q, 4H, J = 7.5 Hz, BODIPY$-CH_2- \times 2$), 2.32 (s, 6H, BODIPY$-CH_3 \times 2$), 1.83 (s, 3H, $C{=}C-CH_3$), 1.60−1.54 (m, 4H, $\rangle CCH_2-CH_2- \times 2$), 1.49−1.39 (m, 2H, $-OCHH_2-CH_2-$), 1.28−1.24 (m, 10H, $-(CH_2)_5-$), 1.02 ppm (t, 6H, J = 7.5 Hz, BODIPY$-CH_2-CH_3 \times 2$). ^{13}C NMR (CD_2Cl_2): δ = 167.6, 152.5, 145.7, 137.2, 134.6, 133.3, 131.7, 129.6, 128.4, 127.5, 125.6, 125.0, 95.6, 95.3, 65.1, 32.2, 30.7, 29.8, 29.8, 29.8, 29.6, 29.1, 29.0, 26.3, 17.8, 15.1, 14.2, 13.8 ppm. ^{11}B NMR (CD_2Cl_2): δ = −13.9 ppm. Anal. Calcd for $C_{47}H_{52}N_2BO_2$: C, 81.48; H, 8.29; N, 4.04. Found: C, 81.29; H, 8.58; N, 4.15.

Synthesis of Poly1. 1 (105.7 mg, 0.20 mmol), CDB (2.2 mg, 0.008 mmol), AIBN (0.66 mg, 0.004 mmol), and anisole (0.1 mL) were placed in a dry glass ampule equipped with a magnetic stir bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. After the ampule was flame-sealed under vacuum, it was held at 60 °C for 4 h. The reaction was stopped by rapid cooling with liquid nitrogen. The reaction mixture was precipitated in a large excess of methanol and isolated by filtration. The resulting product was dried under vacuum at room temperature to yield the corresponding polymer as an orange solid. The polymer had M_n = 10 600 and M_w/M_n = 1.17 according to SEC using polystyrene calibration. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in CD_2Cl_2, and the decreased integration of the monomer C═C−H peak at around 5.5 ppm was determined on the basis of almost same methylene peaks ($-CH_2-O-CO-$) in the polymer and the monomer at around 3.7−4.0 ppm. Conversion determined by this method was 72%. ^{1}H NMR (CD_2Cl_2): δ = 7.83 (m, initiator end), 7.35−7.22 (m, initiator end), 4.09−3.76 (m, 2H, $-O-CH_2-$), 3.07−2.89 (m, 2H, $\rangle C-CH_2-$), 2.61−2.42 (m, 6H, BODIPY$-CH_3 \times 2$), 2.41−2.37 (m, 4H, BODIPY$-CH_2- \times 2$), 2.36−2.22 (m, 6H, BODIPY$-CH_3 \times 2$), 1.72−1.53 (m, 2H, $-(CH_2)-$ (main chain)), 1.50−1.43 (m, 2H, $-OCHH_2-CH_2-$), 1.42−1.18 (m, 10H, $-(CH_2)_5-$ (side chain)), 1.13−0.73 ppm (m, 6H, $-CH_3 \times 2$ (BODIPY and MMA)). ^{13}C NMR (CD_2Cl_2): δ = 165.4, 151.9, 145.2, 135.9, 132.7, 130.8, 123.3, 67.5, 45.1, 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 28.6, 28.2, 26.3, 17.1, 14.7, 13.2, 12.2 ppm. ^{11}B NMR (CD_2Cl_2): δ = 0.20 ppm.

Synthesis of Poly2. ^{1}H NMR (CD_2Cl_2): δ = 7.82 (m, initiator end), 7.52−7.36 (m, 4H, $-C_6H_2 \times 2$), 7.29−7.15 (m, 6H, $-C_6H_3 \times 2$), 4.07−3.78 (m, 2H, $-O-CH_2-$), 3.18−2.97 (m, 2H, $\rangle C-CH_2-$), 2.95−2.76 (m, 6H, BODIPY$-CH_3 \times 2$), 2.59−2.43 (m, 4H, BODIPY$-CH_2- \times 2$), 2.43−2.31 (m, 6H, BODIPY$-CH_3 \times 2$), 1.75−1.58 (m, 2H, $-(CH_2)-$ (main chain)), 1.57−1.46 (m, 2H, $-OCHH_2-CH_2-$), 1.44−1.21 (m, 10H, $-(CH_2)_5-$ (side chain)), 1.17−0.76 ppm (m, 6H, $-CH_3 \times 2$ (BODIPY and MMA)). ^{13}C NMR (CD_2Cl_2): δ = 165.0, 151.9, 145.2, 135.9, 132.7, 130.8, 123.3, 67.5, 45.1, 31.9, 30.5, 29.8, 29.6, 29.5, 28.8, 28.3, 25.2, 17.5, 14.9, 13.9, 13.5 ppm. ^{11}B NMR (CD_2Cl_2): δ = −13.3 ppm.

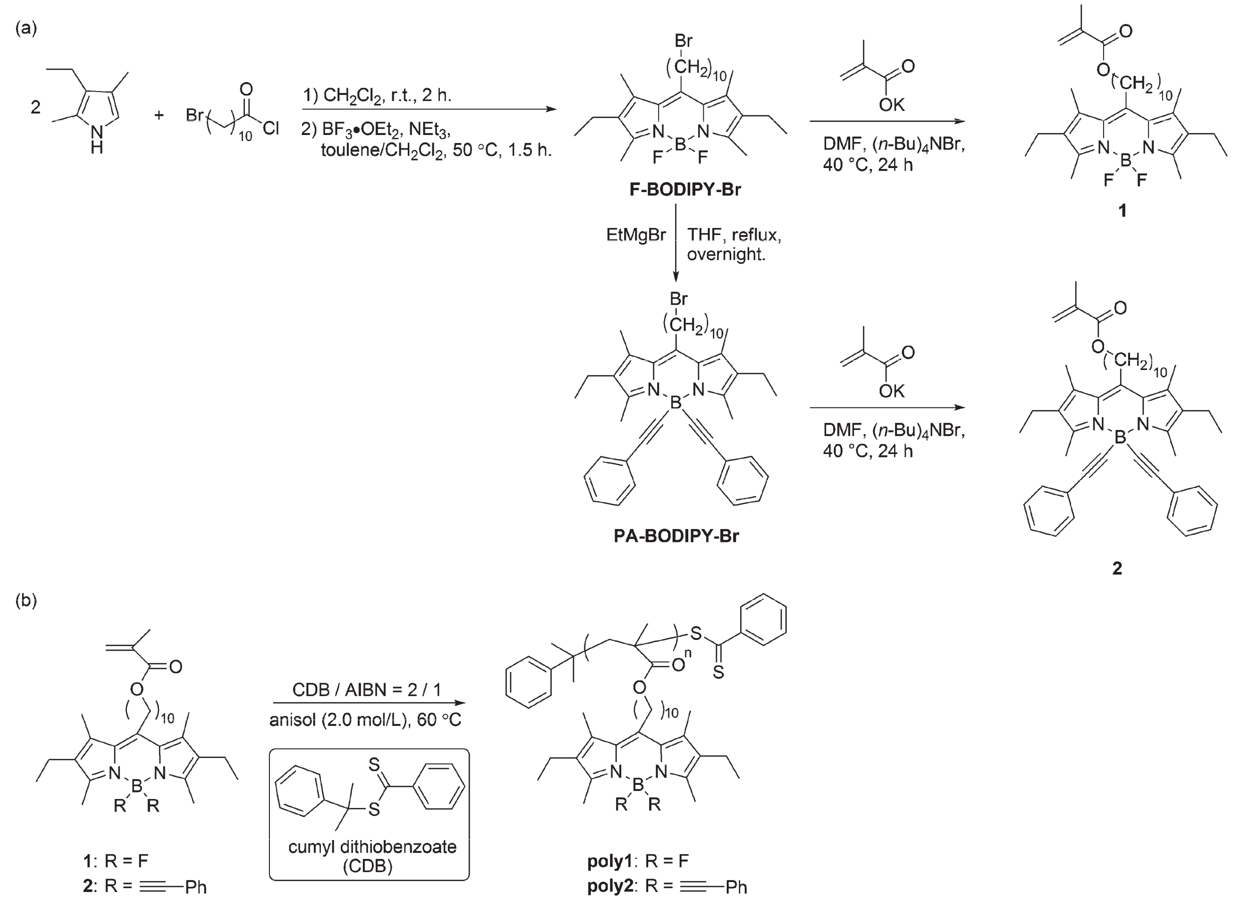
Synthesis of Poly(1-*block*-St). Macro-CTA1 (13.8 mg, 0.0013 mmol; poly**1**, M_n = 10 600, M_w/M_n = 1.17), styrene (0.15 mL, 1.30 mmol), and AIBN (0.11 mg, 0.000 65 mmol) were placed in a dry glass ampule equipped with a magnetic stir bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. The ampule was subsequently immersed in an oil bath preheated to 60 °C, and it was held for 15 h before being quenched by rapid cooling with liquid nitrogen. The reaction mixture was precipitated in a large excess of methanol and isolated by filtration. The resulting product was dried under vacuum at room temperature to yield the corresponding polymer as an orange powder in 35% yield (M_n = 82 500, M_w/M_n = 1.44). ^{1}H NMR (CD_2Cl_2): δ = 7.18−6.80 (C_6H_3, polystyrene), 6.68−6.23 (C_6H_2, polystyrene), 3.87−3.78 ($-O-CH_2-$, macro-CTA), 3.00−2.86 (BODIPY$-CH_3$, macro CTA), 2.76−2.67 (BODIPY$-CH_3$, macro-CTA), 2.42−2.33 (BODIPY$-CH_2-$, macro-CTA), 2.32−2.22 (BODIPY$-CH_3$, macro-CTA), 1.95−1.62 ($-CH_2-$, polystyrene), 1.91−1.09 ($C_6H_5-CH\langle$, polystyrene), 1.04−0.90 ppm ($-CH_3$, macro CTA). ^{11}B NMR (CD_2Cl_2): δ = −0.43 ppm.

Synthesis of Poly(2-*block*-St). This block copolymer was obtained by using macro-CTA2 (15.4 mg, 0.0013 mmol; poly**2**, M_n = 11 800, M_w/M_n = 1.12) as an orange powder in 41% yield. M_n = 59 300. M_w/M_n = 1.41. ^{1}H NMR (CD_2Cl_2): δ = 7.18−6.81 (C_6H_3, polystyrene), 6.66−6.25 (C_6H_2, polystyrene), 3.86−3.75 ($-O-CH_2-$, macro-CTA), 2.41−2.33 (BODIPY$-CH_3$, macro-CTA), 2.32−2.29 (BODIPY$-CH_3$, macro-CTA), 2.25−2.19 (BODIPY$-CH_3$, macro-CTA), 1.97−1.61($-CH_2-$, polystyrene), 1.60−1.09 ($C_6H_5-CH\langle$, polystyrene), 1.00−0.85 ppm ($-CH_3$, macro-CTA). ^{11}B NMR (CD_2Cl_2): δ = −13.8 ppm.

Results and Discussion

The synthetic approach to prepare two BODIPY-based monomers, 4,4′-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacenes (**1**)[11] and 4,4-bis(phenylethynyl)-4-bora-3*a*,4*a*-diaza-*s*-indacenes (**2**), having the 8-position substituted by a decyl group, tethered with a methacryloyloxy group, is outlined in Scheme 1a. Meso-1-bromodecyl-substituted BODIPY dye F-BODIPY-Br was prepared through the condensation of 11-undecanoyl chloride with 2,4-dimethylpyrrole and chelation with BF_3OEt_2 in the presence of triethylamine. PA-BODIPY-Br having a bis(phenylacetyl)borane group was also synthesized by the reaction of F-BODIPY-Br and

Scheme 1. Synthesis of BODIPY-Based Monomers, 1 and 2 (a), and Reversible Addition−Fragmentation Chain Transfer Homopolymerization of 1 and 2 (b)



Grignard derivative. Further reaction of F-BODIPY-Br or PA-BODIPY-Br with potassium methacrylate afforded methacryl-substituted BODIPY-based monomers **1** and **2**. The obtained monomers were polymerized using cumyl dithiobenzoate (CDB), which is a suitable RAFT agent for methacrylates,[12,13] by the sealed tube technique (Scheme 1b). When the polymerizations of **1** and **2** were carried out using CDB with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator at $[\mathrm{M}]_0/[\mathrm{CDB}]_0/[\mathrm{AIBN}]_0 = 50/2/1$ in anisole (2.0 mol/L) at 60 °C, high conversions (**1**: 81%; **2**: 62%), determined by ^{1}H NMR spectroscopy, were achieved after 8 h, and all polymers, poly**1** and poly**2**, were obtained as orange solids. The resulting polymers showed a sharp symmetrical size-exclusion chromatography (SEC) peaks (poly**1**: $M_\mathrm{w}/M_\mathrm{n}$ = 1.17; poly**2**: $M_\mathrm{w}/M_\mathrm{n}$ = 1.12) without shoulder and tailing. The number-average molecular weights, measured by a SEC in THF at 40 °C, were M_n = 10 600 and 11 800, respectively, which are in good agreement with theoretical values (M_n = 10 900 and 11 000) calculated from the monomer/CTA molar ratio and the polymer conversion [M_n(theoretical) = ([monomer]/[CDB] = 25) × conversion × molecular weight (MW) of monomer + MW of CDB]. The characteristic structures of the obtained polymers were supported by ^{1}H and ^{13}C NMR spectroscopies, and the tetracoordination states of the boron atoms were confirmed by ^{11}B NMR spectroscopy (poly**1**: $\delta_\mathrm{B} = 0.20$; poly**2**: $\delta_\mathrm{B} = -13.3$ ppm), indicating that the RAFT polymerization of **1** and **2** proceeded efficiently without any damage on the boron atoms.

The expected M_n and the narrow $M_\mathrm{w}/M_\mathrm{n}$ values of the polymerization imply the controlled nature of this RAFT process. Figure 1a shows time vs conversion and first-order kinetic plots for the polymerizations of **1** and **2** at the ratio $[\mathrm{M}]_0/[\mathrm{CDB}]_0/[\mathrm{AIBN}]_0 = 50/2/1$. The polymerization of **1** was fast, in which more than 72% conversion was reached within 4 h, whereas less than 45% conversion could be reached in the same period when the polymerization of **2** was conducted. The linear first-order kinetic plots are seen for **2**. In contrast, the approximately linear kinetic plots of **1** are observed until 8 h. At the last stage of the polymerization, the polymerization rate decreases apparently, which may be due to an inactivation of radical species during the polymerization. Nevertheless, as shown in Figure 1b, a linear increase of the M_n with conversion on each monomer reveals a constant number of propagating chain throughout the polymerization and the absence of nondegenerative chain transfer reaction. Notably, the M_n values, determined by SEC, of the obtained polymers were in good agreement with the theoretical dotted lines. The SEC traces (refractive index) of poly**1** and poly**2** obtained at different reaction times are shown in Figure 1c,d. A progressive increase of molar mass with conversion with narrow unimodal peaks (poly**1**: $M_\mathrm{w}/M_\mathrm{n}$ = 1.15−1.17; poly**2**: $M_\mathrm{w}/M_\mathrm{n}$ = 1.11−1.12) is clearly seen, as normally evidenced for a controlled/living polymerization.

Scanning electron microscopy (SEM) was used to visualize the assemblies of the obtained polymers after drying the THF solution (c = 0.01 g/L) on a glass plate. The SEM image of poly **1** (M_n = 10 600, $M_\mathrm{w}/M_\mathrm{n}$ = 1.17) revealed a wide range of blubber particles from micrometers to nanometers (Figure 2a), and the image of poly**2** (M_n = 11 800, $M_\mathrm{w}/M_\mathrm{n}$ = 1.12) showed the presence of micrometer-sized chian-like structures formed by aggregation of each particle, which was roughly 1.18 μm in diameter (Figure 2b). These differences in the morphology of each polymer might depend on the planar nature of BODIPY structures; i.e., the virtue of $\pi-\pi$ stacking on the BODIPY unit having B−F bonds is larger than that having phenylethynyl groups; on the

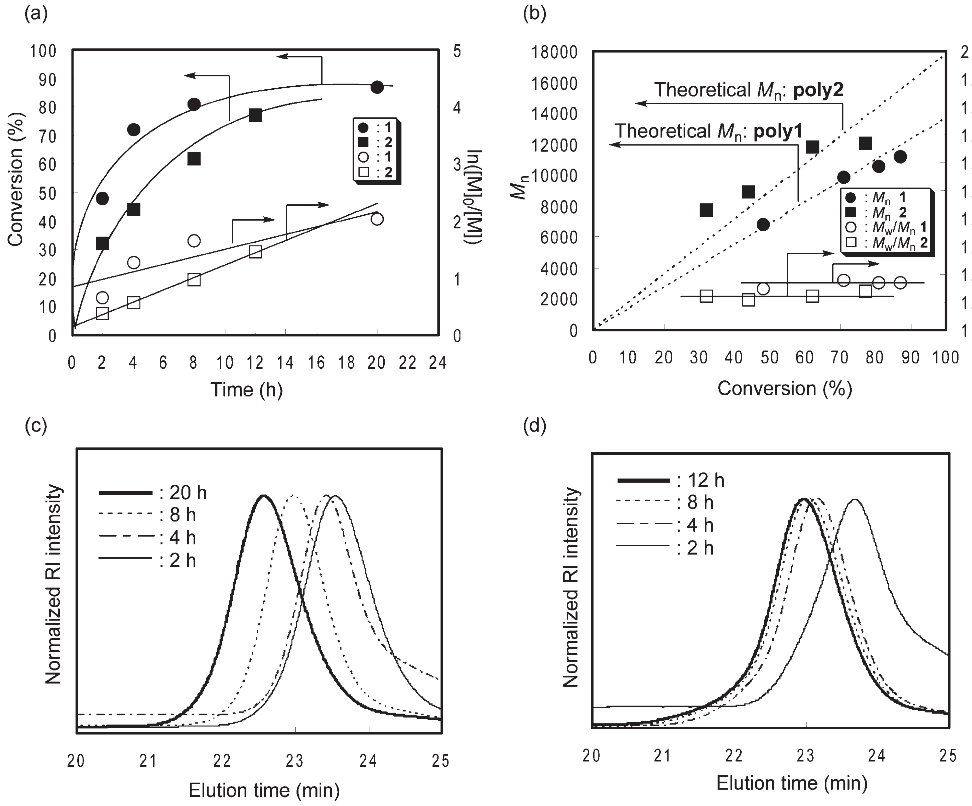


Figure 1. (a) Conversion as a function of polymerization time and first-order kinetic plots and (b) dependence of M_n and M_w/M_n on the monomer conversion for the polymerization of **1** and **2**, and evolution of SEC traces with polymerization time for the polymerizations of **1** (c) and **2** (d) with AIBN in the presence of CDB at $[M]_0/[CDB]_0/[AIBN]_0 = 50/2/1$ in anisole (2.0 mol/L) at 60 °C, where CDB = cumyl dithiobenzoate and AIBN = 2,2′-azobis(isobutyronitrile). Monomer concentration = 0.1 g/0.2 mL.

contrary, the steric hindrance between the BODIPY units in the poly**2** is higher. Accordingly, it was difficult to afford nanoparticle as a target self-assemble structure due to aggregation growing continuously by strong intermolecular $\pi-\pi$ staking. Herein, we anticipate that it is possible to prepare nanoparticles by synthetic technique of AB diblock copolymer; i.e., the aggregation from intermolecular self-organization of BODIPY units in the side chains is inhibited by higher molecular weight polystyrene segments. According to this hypothesis, poly**1** and poly**2** were employed as macro-chain-transfer agent (macro-CTA1 and macro-CTA2, respectively) for block copolymerization with styrene (St). The polymerizations were carried out at 60 °C at the ratio $[St]_0/[macro\text{-}CTA]_0/[AIBN]_0 = 1000/1/0.5$, and the obtained block copolymers, poly(**1**-*block*-St) and poly(**2**-*block*-St), were 35% and 41% yields after 24 h, respectively (Figure 3a). The SEC chromatograms of the starting macro-CTAs and the second-growth polymers showed that the molecular weights shifted clearly to the higher range (Figure 3b,c). However, the molecular weight distributions of the resulting block copolymers were relatively high ($M_w/M_n > 1.40$), and some tailing was detected, suggesting insufficient blocking efficiency and/or the existence of a small number of dead chains. The molecular weights of the obtained poly(**1**-*block*-St) and poly(**2**-*block*-St) were $M_n = 82\,500$ and 59 300, respectively. The degree of polymerization (DP) using macro-CTA1 (DP = 20) and macro-CTA2 (DP = 17), estimated by M_n from SEC, were 685 and 463, respectively. The structures of the obtained block copolymers were supported by ^{1}H NMR spectroscopy. Under similar condition to homopolymers, the morphologies of the obtained block copolymers were observed by SEM measurement. As we expected, poly(**1**-*block*-St) and poly(**2**-*block*-St) represented purposeful nanosized particles, which were approximately 143 and 571 nm, respectively. Further, the size distributions of these aggregates in THF solution (c = 0.1 g/L) were very large as measured from dynamic light scattering (DLS) measurement (poly**1**: 1332.8 ± 248.9 nm; poly**2**: 1634.1±332.6 nm). However, the distributions of the obtained block copolymers were so small (poly(**1**-*block*-St): 11.1 ± 1.8 nm; poly(**2**-*block*-St): 12.6±1.0 nm), supporting that the obtained block copolymers can not construct the particle- or chain-like structures in the solution states. Different particle sizes from SEM and DLS analysis would be responsible for the concentration of self-assembly due to only $\pi-\pi$ stacking interaction as noncovalent bond between BODIPY units in each polymer. Further, X-ray diffraction (XRD) of poly**1** and poly**2** showed the d-spacings of around 4.32 and 4.38 Å, respectively, which are characteristic of π-stacked packing. However, characteristic spacings assignable to π-stacked packing of poly(**1**-*block*-St) and poly(**2**-*block*-St) were not observed (Figure 4). These results indicate that the block copolymers prevented BODIPY units in the side chains from aggregation of strong intermolecular $\pi-\pi$ stacking by the introduction of higher molecular weight polystyrene segments.

The optical properties of monomers and the obtained polymers were investigated with UV−vis absorbance and fluorescence spectroscopies (Figure 5). Commonly, all compounds showed almost similar absorption maxima at around 520 nm attributable to BODIPY ligand and also exhibited almost the same emission maxima at around 539−542 nm, which excited at each absorption maxima corresponding to BODIPY ligand moiety. The absolute fluorescence quantum yields (Φ_F), measured by integrating sphere method, of the homopolymers (poly**1**: $\Phi_F = 0.37$; poly**2**: $\Phi_F = 0.49$) were lower than those of monomers (**1**: $\Phi_F = 0.90$; **2**: $\Phi_F = 0.86$), originating from collisional quenching of the excited state by $\pi-\pi$ stacking.[14] In contrast, higher Φ_F of the block copolymers (poly(**1**-*block*-St): $\Phi_F = 0.70$; poly(2-*block*-St): $\Phi_F = 0.72$) were observed as compared to those

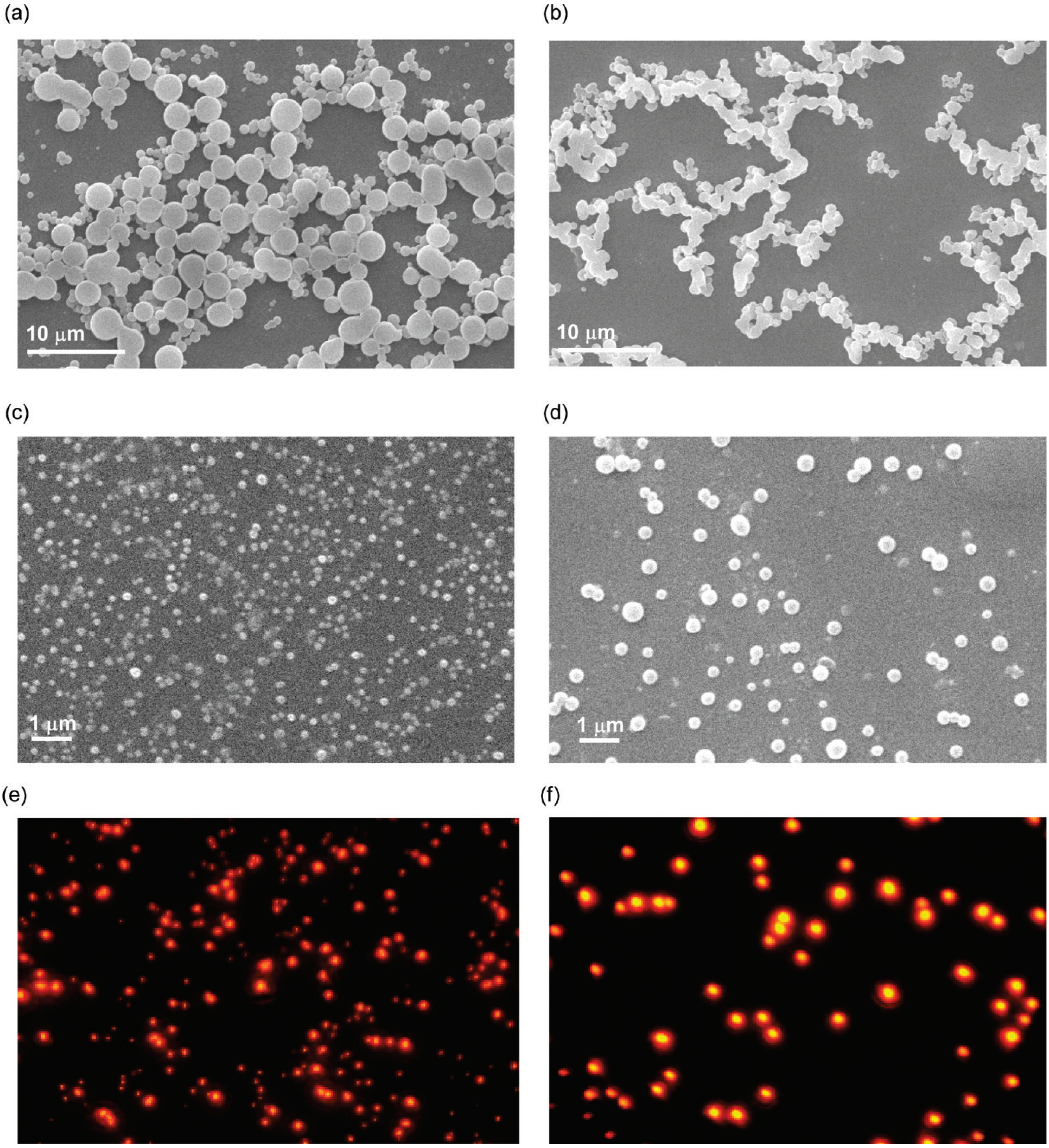


Figure 2. SEM micrographs of poly**1** (($M_n = 10\,600$, $M_w/M_n = 1.17$) (a), poly**2** ($M_n = 11\,800$, $M_w/M_n = 1.12$) (b), poly(**1**-*block*-St) ($M_n = 82\,500$, $M_w/M_n = 1.44$) (c), and poly(**2**-*block*-St) ($M_n = 59\,300$, $M_w/M_n = 1.41$) (d) dried at room temperature for 12 h from THF solution (0.01 g/L) on a glass plate, and fluorescence micrograph of poly(**1**-*block*-St) (e) and poly(**2**-*block*-St) (f) dried at room temperature for 12 h from THF solution (0.01 g/L) on a glass plate.

of the corresponding homopolymers, indicating that the inhibition of the π-stacked self-assembly by polystyrene with high molecular weight. Further, the aggregates of each block copolymer after drying the THF solution ($c = 0.01$ g/L) on a glass plate were directly observed by fluorescence microscopy (Figure 2e,f). Unquestionably, their observations illustrated strongly orange fluorescent nanoparticle architectures without blubber particle- and chain-like formations geminated from the aggregated particles.

In summary, we have shown the synthesis and self-assemble behavior of well-defined polymers by incorporated BODIPY dyes into the PMMA side chain and the block copolymers by RAFT process. The controlled/living character of the polymerization of MMA monomers with pendant BODIPY dyes was confirmed by the formation of the narrow molecular weight distribution products, the linear first-order kinetic plot, linear increase molecular weight with the conversion, and block extension with styrene. The optical properties of the obtained polymers were studied by UV−vis absorption and fluorescence spectroscopies. The SEM image of the obtained poly**1** and poly**2** showed blubber particle- and chain-like structures, respectively, which come from the aggregated particles by strong intermolecular $\pi-\pi$ stacking of BODIPY dyes. In contrast, the obtained block copolymers formed nanometer-sized particles with enhanced luminescent properties by preventing higher molecular weight

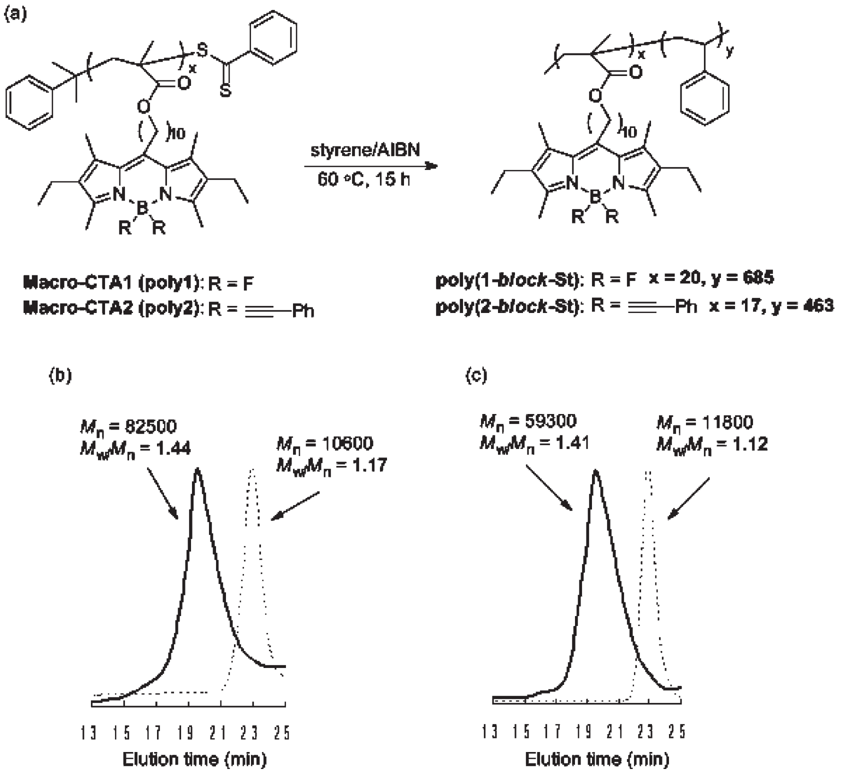


Figure 3. (a) Block polymerization of styrene (St) with macro-chain-transfer agents, macro-CTA1 and macro-CTA2, SEC traces of (b) the parent macro-CTA1 (dotted trace) and block extension with styrene (solid trace), and (c) the parent macro-CTA2 (dotted trace) and block extension with styrene (solid trace).

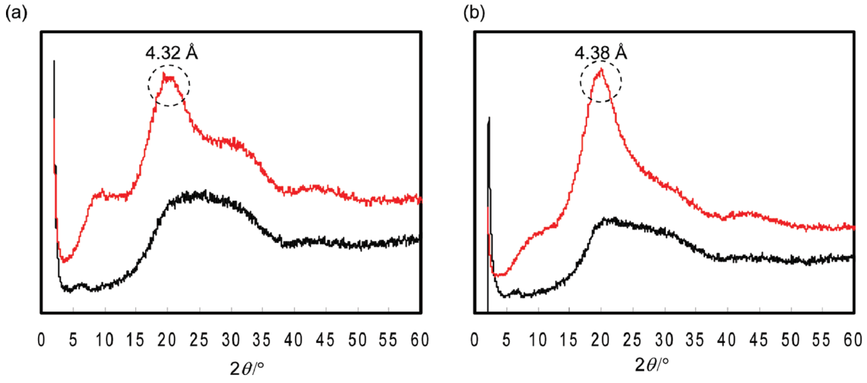


Figure 4. XRD profiles of (a) poly**1** (red line) and poly(**1**-*block*-St) (black line) and (b) poly**2** (red line) and poly(**2**-*block*-St) (black line).

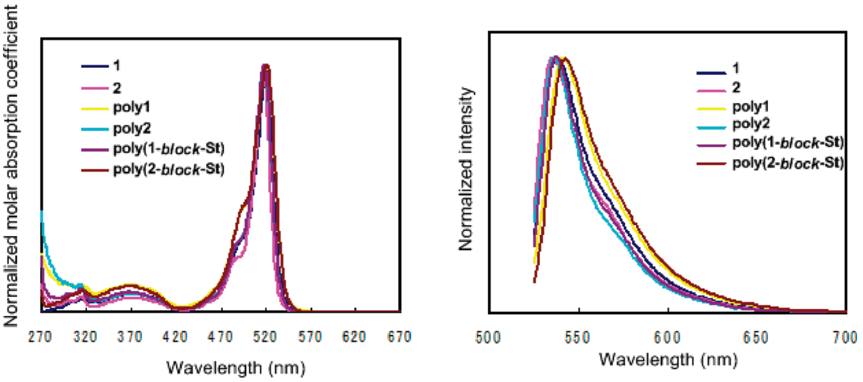


Figure 5. (a) Normalized UV–vis spectra and (b) normalized fluorescence spectra of **1**, **2**, poly**1**, poly**2**, poly(**1**-*block*-St), and poly(**2**-*block*-St) in THF solution.

polystyrene segment from aggregation by the strong π–π stacking. We think that these nanoparticles consisting of polystyrene as the main segments in the block copolymers [poly($\mathbf{1}_{20}$-*block*-St_{685}) and poly($\mathbf{2}_{17}$-*block*-St_{463})] can be regarded as "luminescent polystyrene nanoparticles" and believe that this paper represents the first report on the controlled synthesis of pseudo-polystyrene sharing both high luminescence and nanoparticle formation.

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