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Light and temperature responsive block copolymer assemblies with tunable fluorescence emissions

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ABSTRACT

A dual-responsive amphiphilic diblock copolymer, poly(styrene-*co*-1-(2-methacryloxyethoxy)-2-(2-pyridyl)benzimidazole)-*block*-Poly(*N*-isopropylacrylamide-*co*-3-biphenyl-3-phenyl-8-methacryloxy-3*H*-naphtho[2,1-*b*]pyran-*co*-4-methamino-9-allyl-1,8-naphthalimide), also denoted as P(St-*co*-PBI)-*b*-P(NIPAM-*co*-NP-*co*-MANI), was synthesized by reversible addition fragmentation chain transfer polymerization followed by assembling into micelles with hydrophobic P(St-*co*-PBI) block as core and thermoresponsive P(NIPAM-*co*-NP-*co*-MANI) block as the shell in aqueous solution. Dynamic light scattering, transmission electron microscopy and optical transmittance were used to characterize the particle morphology and thermosensitivity of the micelles solution. In addition, the fluorescence emission of the micelles could be reversibly modulated "on" and "off" by the photochromic naphthopyran upon UV and thermal back reaction, which promoted naphthopyran transformation between merocyanine forms and original closed form. Moreover, the spatial distance between the two fluorescence dyes could be regulated by temperature, resulting from the collapse or extension of PNIPAM in aqueous solution. This property enabled the polymeric assemblies to serve as sensitive ratiometric fluorescent thermometers.

1. Introduction

Fluorescent materials have drawn increasing attention owing to their potential applications in biological imaging [1,2] and labeling [3,4]. Fluorescent polymers and polymeric assemblies with stimuli-responsive moieties to display apparent responses to external stimuli (such as temperature, light, pH, redox, mechanical forces, and magnetism) [5–7] are especially attractive. These unique properties enable them to serve in various applications.

Poly(*N*-isopropylacrylamide) (PNIPAM) is a thermoresponsive polymer that can undergo phase transition at lower critical solution temperature (LCST) around 32 °C [8–10]. The polymer chains are hydrophilic and stretched in solution below the critical temperature, but the chains collapse and shrink from hydrated coils to hydrophobic globules above 32 °C in aqueous solution. Therefore, the modulation of fluorescence signals upon external temperature stimuli can be achieved by incorporating thermoresponsive PNIPAM moieties into a certain polymer and labeling with fluorophores [11–13]. On the other hand, light is known to be another advantageous external stimuli for its high spatiotemporal resolution and non-invasive nature [14]. Combining the light and temperature responsive groups with fluorophores should be tempting to fabricate fluorescent photo-switchable materials with higher temporal and spatial detection resolution. For example, Liu et al. reported photoswitchable and thermotunable multicolor fluorescent silica nanoparticles based on PNIPAM and spiropyran responsive moieties and found that the fluorescence emission could be tunable via temperature and UV light [15]. They further prepared thermoresponsive polymeric micelles, which exhibited three-state switching of luminescence upon light, temperature and pH stimuli [16]. However, the use of naphthopyrans (NP) as light responsive moieties in polymer to modulate the fluorescence switching is less well-known. Naphthopyrans, a type of important photochromic compounds [17], present two major colored merocyanine forms (transoid-cis, TC, and transoid-trans, TT) upon continuous UV light irradiation, whereas they convert to the closed form in the dark or under visible light. Moreover, naphthopyrans possess some advantages for their applications in optical switches, optical memories and ophthalmic lenses because of their special properties, such as fine control over fading kinetics and good thermal reversibility [18].

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Herein, we prepared an amphiphilic diblock copolymer containing blue fluorescence 1-(2-methacryloxyethoxy)-2-(2-pyridyl) benzimidazole (PBI) in the hydrophobic polystyrene (PSt) block and green fluorescent 4-methamino-9-allyl-1,8-naphthalimide (MANI) with photochromic naphthopyran moieties in the thermoresponsive PNIPAM block. The fluorescence emission of the diblock copolymer micelles could be reversibly modulated by the photochromic naphthopyran upon UV and visible light/thermal bleaching reaction. Moreover, fluorescence resonance energy transfer (FRET) efficiency between PBI and MANI dyes was increased at an elevated temperature, since the shrinkage of PNIPAM led to the closer spatial distance between the two fluorescence dyes. This special property enabled the polymeric assemblies to act as sensitive ratiometric fluorescent thermometers.

2. Experimental section

2.1. Materials

N-isopropylacrylamide was recrystallized from a mixture of benzene and n-hexane (1/3, v/v) for three times. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from 95% ethanol and dried under vacuum. Styrene (St) was washed with aqueous NaOH (5.0 wt %) for three times and then distilled at reduced pressure. Toluene and 1,4-dioxane were distilled prior to use and ultrapure water (resistivity > 18 M cm^{-1}) was used for all experiments. 4-Bromo-1,8-naphthalic anhydride (Energy Chemical), allylamine (Aladdin) and methylamine (Aladdin) and other organic reagents were used as received. S-1-Dodecyl-S′-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (DDMAT) was prepared according to previous literature procedures [19].

2.2. Synthesis of 3-biphenyl-3-phenyl-8-methacryloxy-3H-naphtho [2,1-b]pyran monomer (NP)

3-Biphenyl-3-phenyl-8-methacryloxy-3*H*-naphtho[2,1-*b*]pyran was synthesized according to the literature procedures [20–22]. Typical procedures were as follows: 6-hydroxynaphthalen-2-yl methacrylate was prepared by the reaction between 2,6-naphthalenediol (1.6 g, 10 mmol) and methacryloyl chloride (0.97 mL, 10 mmol) in CH_2Cl_2 (15 mL) at room temperature for 12 h. The crude product was purified by silica gel column chromatography using ethylacetate/petroleum ether (1/10) as eluant. (White powder, yield 42%) ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.64–7.60 (m, 2H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.19–7.17 (m, 1H), 7.06–7.04 (m, 2H), 6.40 (s, 1H), 5.79 (m, 1H), 5.32 (s, 1H), 2.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 18.4, 109.4, 118.4, 118.5, 121.5, 127.4, 127.6, 128.8, 129.2, 132.4, 135.8, 146.6, 153.2, 166.5. MS (ESI-TOF): *m/z* calcd for $C_{14}H_{12}NaO_3$: 251.0682; found: 251.0679 $[M + Na]^+$. M.p. 186–188 °C. IR (KBr, cm^{-1}): 445, 478, 623, 654, 707, 816, 859, 900, 944, 1015, 1041, 1157, 1178, 1211, 1227, 1266, 1303, 1327, 1351, 1388, 1438, 1522, 1606, 1634, 1678, 1718, 2928, 2960, 3043, 3426.

A mixture of 6-hydroxynaphthalen-2-yl methacrylate (1 g, 4.67 mmol), 1-([1,1′-diphenyl]-4-yl)-1-phenylprop-2-yn-1-ol (1.2 equiv) and para-toluenesulfonate (10 mol %) in dry CH_2Cl_2 solution (8 mL) were stirred at room temperature for 24 h. The reaction mixture was evaporated to dry under reduced pressure, and the residues were purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (4/1) as eluant. (White powder, yield 49.3%) ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.97 (d, *J* = 9 Hz, 1H), 7.61 (d, *J* = 9 Hz, 1H), 7.53–7.51 (m, 8H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.41–7.38 (m, 2H), 7.34–7.30 (m, 3H), 7.29–7.27 (m, 1H), 7.26–7.22 (m, 3H), 6.37 (s, 1H), 6.31 (d, *J* = 10 Hz, 1H), 5.75 (m, 1H), 2.07 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 18.3, 76.7, 77.0, 77.2, 82.4, 114.1, 119.0, 119.1, 119.2, 119.4, 121.7, 122.7, 126.8, 126.9, 127.0, 127.1, 127.2, 127.3, 127.5, 127.7, 128.0, 128.1, 128.6, 129.3, 129.5, 135.8, 140.3, 143.6, 144.5, 146.9, 150.3, 165.9. MS (ESI-TOF): *m/z* calcd for $C_{35}H_{26}O_3$: 495.1944; found: 495.1955 $[M]^+$. M.p. 202–204 °C. IR (KBr, cm^{-1}): 415, 545, 690, 762, 809, 899, 947, 1001, 1084, 1152, 1229, 1322, 1372, 1446, 1478, 1521, 1549, 1632, 1688, 1729, 2802, 3061, 3385, 3738, 3852.

2.3. Synthesis of 1-(2-methacryloxyethoxy)-2-(2-pyridyl) benzimidazole monomer (PBI)

1-(2-Methacryloxyethoxy)-2-(2-pyridyl)benzimidazole was synthesized according to previous reports [23,24]. Firstly, 1-(2-hydroxyethyl)-2-(2-pyridyl)benzimidazole was prepared according to literature procedures. Secondly, triethylamine (2.02 g, 20 mmol) was added dropwise to a cold (ice/water) stirred solution of 1-(2-hydroxyethyl)-2-(2-pyridyl)benzimidazole (2.39 g, 10 mmol) and methacryloyl chloride (1.56 g, 15 mmol) in dry CH_2Cl_2 (15 mL). The reaction solution was stirred for 24 h at rt. The mixture was evaporated to dryness under reduced pressure and the crude product was purified by silica gel column chromatography using ethylacetate/petroleum ether (2/10) as eluant. (White powder, yield: 87%) ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.52–8.51 (m, 1H), 8.35 (d, *J* = 7.5 Hz, 1H), 7.76 (m, 1H), 7.71–7.68 (m, 1H), 7.38–7.36 (m, 1H), 7.20–7.17 (m, 3H), 5.69 (s, 1H), 5.28–5.27 (m, 1H), 5.03 (t, *J* = 5.5 Hz, 2H), 4.53 (t, *J* = 5 Hz, 2H), 1.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 17.9, 44.0, 63.8, 110.1, 119.6, 122.7, 123.4, 123.7, 124.4, 125.8, 135.3, 136.5, 136.7, 141.7, 148.3, 149.3, 149.7, 166.9. MS (ESI-TOF): *m/z* calcd for $C_{35}H_{26}O_3$: 308.1399; found: 308.1394 $[M]^+$. M.p. 63–65 °C. IR (KBr, cm^{-1}): 430, 462, 505, 576, 647, 693, 740, 797, 843, 874, 942, 999, 1037, 1092, 1161, 1241, 1322, 1368, 1439, 1514, 1586, 1629, 1713, 1772, 2987, 3047, 3740.

2.4. Synthesis of 4-methamino-9-allyl-1,8-naphthalimide (MANI)

MANI was synthesized according to previous reported procedures [25]: 4-bromo-1,8-naphthalic anhydride (2.76 g, 10 mmol) and allylamine (0.855 g, 15 mmol) were refluxed in ethanol for 4 h to form 4-bromo-n-substituted-1,8-naphthali-mides. 4-Bromo-n-substituted-l,8-naphthalimides (0.315 g, 1 mmol), methylamine (0.1 g, 1.5 mmol), triethylamine (0.152 g, 1.5 mmol), and $CuSO_4 \cdot 5H_2O$ (0.01 g) were dissolved in 2-methoxyethanol (10 mL) under stirring. The solution was heated at 90 °C for 5 h. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using ethylacetate/petroleum ether (1/3). (Orange powder, yield: 63%) ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.60–8.59 (m, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.08–8.07 (m, 1H), 7.64–7.60 (m, 1H), 6.73 (d, *J* = 9 Hz, 1H), 6.04–5.97 (m, 1H), 5.40 (s, 1H), 5.32–5.27 (m, 1H), 5.19–5.17 (m, 1H), 4.80–4.79 (m, 2H), 3.15 (d, *J* = 5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 30.6, 42.1, 104.4, 110.6, 117.1, 120.3, 123.1, 124.8, 125.9, 129.7, 131.2, 132.6, 134.5, 150.1, 163.8, 164.3. MS (ESI-TOF): *m/z* calcd for $C_{16}H_{14}N_2O_2$: 267.1123, found: 267.1128 $[M]^+$. M.p. 247–249 °C. IR (KBr, cm^{-1}): 420, 520, 581, 655, 690, 768, 817, 943, 973, 1088, 1152, 1242, 1297, 1353, 1379, 1417, 1446, 1547, 1576, 1636, 1681, 2939, 2987, 3388, 3740.

2.5. Synthesis of P(St-co-PBI) polymer

The procedures employed for the preparation of P(St-*co*-PBI) were as follows. St (2.1 g, 20 mmol), PBI (0.018 g, 0.06 mmol), DDMAT (72.8 mg, 0.2 mmol), AIBN (6.6 mg, 0.04 mmol) and toluene (4 mL) were added to a 25 mL dried flask with a magnetic bar. The flask content was degassed by three freeze–pump–thaw cycles and then was filled with nitrogen. The polymerization was carried out at 65 °C for 24 h and the solvent was evaporated to dryness under reduced pressure. The polymer was dissolved in THF (1 mL) and