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Synthesis, characterization and fluorescence adjustment of well-defined polymethacrylates with pendant π-conjugated benzothiazole via atom transfer radical polymerization (ATRP)

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ABSTRACT

Two compounds containing the benzothiazole moiety, 4-(2-benzothiazole-2-yl-vinyl)-phenyl methacrylate (BVMA) and 2-bromo-2-methyl-propionic acid 4-(2-benzothiazole-2-yl-vinyl)-phenyl ester (BPBVE) were synthesized. Atom transfer radical polymerization (ATRP) of BVMA was conducted at 60 °C using BPBVE and CuBr/2,2′-bipyridine (BPY) as initiator and catalyst, respectively. Chain extension with 4-methacryloxy-hexyloxy-4′-nitrostilbene (MHNS) was conducted using PBVMA as the macroinitiator. The homopolymer PBVMA in DMF solution emitted blue fluorescence, and the copolymer PBVMA-b-PMHNS emitted orange fluorescence at about 610 nm due to the intramolecular energy transfer. ATRP of BVMA was also conducted using 2-bromo-2-methyl-propionic acid 4-nitrostilbene-hexyloxy ester (BPNHE) as an initiator. The obtained polymer was characterized via ^{1}H NMR and the fluorescence intensity was found to change with increasing number average molecular weight (M_n). The polymer with $M_n = 15900$ emitted white fluorescence in DMF solution.

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1. Introduction

The development of white-light-emitting polymers has been the subject of intense academic research because of their potential application in full-color flat-panel displays and solid-state lighting [1–10]. Polymer blending and doping methods are the simplest ways of realizing white-light emissions via spin coating; however, they always suffer from phase separation over time, which results in device instability [11,12]. The problem can be circumvented by developing single-polymer systems with different emission components.

Atom transfer radical polymerization (ATRP) is one of the most efficient controlled/living-radical polymerization (CLRP) methods [13–15]. Many well-defined polymers carrying pendant-functional groups have been prepared through ATRP of functionalized monomers [16–30]. We are interested in using ATRP to adjust the fluorescent property through the macroinitiator concept [14,31] and molecular weight control due to the “living”/controlled characteristic. We recently synthesized an AB-type copolymer, poly(4-(2-benzoxazole)-benzyl ester-block-4-2-(9-anthryl)-vinyl-styrene) [PMABE-b-PAVS] by using PMABE as a macro-initiator and AVS as the second monomer via ATRP. The fluorescent emission could be controlled in the range from 375 to 490 nm due to component adjustment of two fluorophores in the block copolymer [32]. We also prepared a series of well-defined polymers with di-color emission by introducing a blue-fluorescent monomer and a green-fluorescent initiator into the same chain. The emission spectra could be easily tuned in the range from 420 to 500 nm by changing the polymer chain length [33]. However, the emission spectra of these polymers could only be tuned over a limited region. To realize white-light emission from a single polymer, the emission should cover the whole visible range from 400 to 700 nm. However, as known, the perception of white light in the human vision system can be created through a combination of blue and orange emissions.

To aim at adjusting the fluorescent property in the whole visible range through such a combination of blue and orange emissions, we synthesized a blue emission monomer BVMA and the selected monomer MHNS as the orange emission candidate. We also synthesized BPNHE which was used as an orange emission initiator for ATRP of BVMA.

2. Experimental section

2.1. Materials

2-Methylbenzothiazole (98%; Fluka) was used as received. 4-Hydroxybenzaldehyde (Sinopharm Chemical Reagent Co., Ltd) was

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recrystallized from water and dried under vacuum. 2-Bromo-2-methylpropionyl bromide (97%; Alfa Aesar) was used as received. Methacryloyl chloride (≥98%, Haimen Best Fine Chemical Co. Ltd) was distilled under vacuum before using. CuBr (98.5%; Sinopharm Chemical Reagent Co., Ltd) was purified in acetic acid, washed with methanol and dried under vacuum to obtain a white powder. 4-Methacryloxy-hexyloxy-4′-nitrostilbene (MHNS) was synthesized as described in the literature [34]. Other agents were used as received.

2.2. Instruments and methods

Conversions of monomer were determined by gravimetry. ^{1}H NMR spectra were measured on an INOVA 400 MHz NMR spectrometer, using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. Molecular weights and the polydispersity relative to PMMA were determined on a Waters1515 GPC with THF as solvent at a flow rate of 1 mL/min with a column temperature of 30 °C. UV–Vis absorption spectra of the initiator, monomer and polymer in DMF solutions were recorded on a Shimadzu RF540 spectrophotometer. Room temperature emission and excitation spectra were recorded using an Edinburgh-920 fluorescence spectra photometer. Elemental analyses of C, H and N were measured with an EA1110 CHNO-S instrument.

2.3. Synthesis of initiator and monomer

2.3.1. Synthesis of 4-(2-benzothiazole-2-yl-vinyl)-phenol

A mixture of 2-methylbenzothiazole (6.0 g, 0.04 mol), 4-hydroxybenzaldehyde (4.9 g, 0.04 mol) and acetic anhydride (8.2 g, 0.08 mol) was refluxed for 24 hours under a nitrogen atmosphere. The crystal was obtained after cooling to the room temperature, and was dissolved by adding sodium hydroxide solution (100 mL, 10%) to the mixture and heated at 80 °C for 1 h. Then the solution was filtered and the product was precipitated when the pH of the solution was adjusted to 6–7 by adding HCl solution (20%). The product was obtained by recrystallizing from ethanol, as a yellow powder.

Yield: 62%. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.06 (d, $J = 7.8$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.7$ Hz, 2H), 7.54–7.35 (m, 4H), 6.85 (d, $J = 8.4$ Hz, 2H), H of –OH is D exchangeable and was not found. ELEM. ANAL. Calcd. (%): C, 71.15; H, 4.35; N, 5.53. Found (%): C, 71.24; H, 4.30; N, 5.39.

2.3.2. Synthesis of 2-bromo-2-methyl-propionic acid 4-(2-benzothiazole-2-yl-vinyl)-phenyl ester (BPBVE)

4-(2-benzothiazole-2-yl-vinyl)-phenol (2.5 g, 0.01 mol) was dissolved in a mixture of Et_3N (2.0 g, 0.02 mol) and THF (80 mL), and cooled in an ice-water bath. Then a solution of 2-bromo-2-methylpropionyl bromide (2.3 g, 0.01 mol) in THF (20 mL) was added drop-wise under a nitrogen atmosphere. The mixture was stirred for 1 h and the ice-water bath was removed. The reaction was continued with stirring for 24 h at room temperature and the solution was filtered and poured into water. The precipitated product was washed in ethanol and purified by a column of silica gel using a mixed solvent of petroleum ether and ethyl acetate (V:V = 2:1) as eluent.

White powder. Yield: 64%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.01 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 2H), 7.55–7.36 (m, 4H), 7.20 (d, $J = 8.2$ Hz, 2H), 2.10 (s, 6H). ELEM. ANAL. Calcd. (%): C, 56.72; H, 3.98; N, 3.48. Found (%): C, 56.77; H, 4.06; N, 3.26.

2.3.3. Synthesis of 4-(2-benzothiazole-2-yl-vinyl)-phenyl methacrylate (BVMA)

BVMA was synthesized follow the synthetic procedure for BPBVE except that methacryloyl chloride was used instead of 2-bromo-2-methylpropionyl bromide.

White powder. Yield: 73%. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.99 (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 7.54–7.33 (m, 4H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.36 (s, 1H), 5.78 (s, 1H), 2.06 (s, 3H). ELEM. ANAL. Calcd. (%): C, 71.03; H, 4.67; N, 4.35. Found (%): C, 71.07; H, 4.77; N, 4.04.

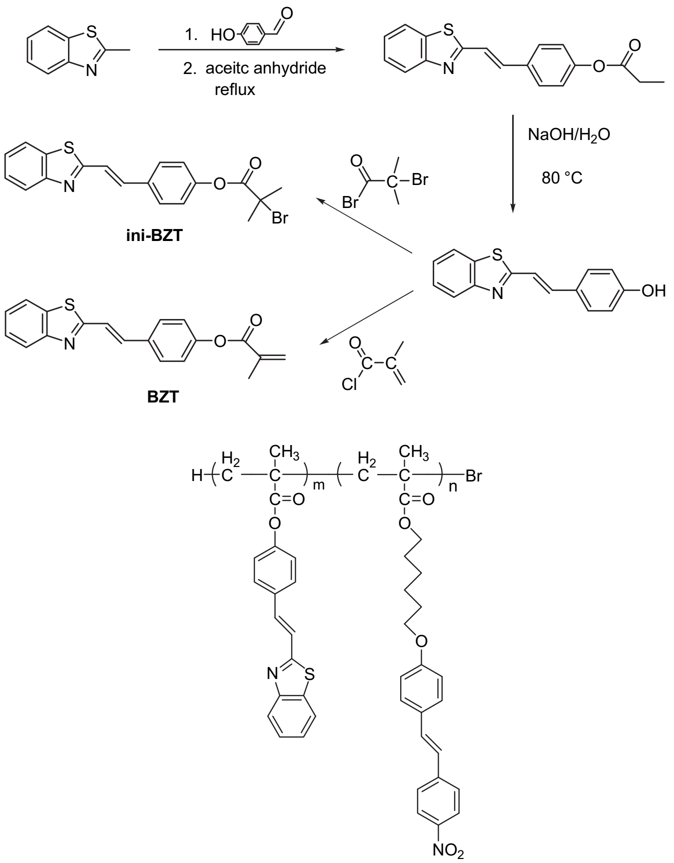
2.3.4. Synthesis of 2-bromo-2-methyl-propionic acid 4-nitrostilbene-hexyloxy ester (BPNHE)

BPNHE was synthesized following the synthetic procedure for MHNS except that 2-bromo-2-methylpropionyl bromide was used instead of methacryloyl chloride.

Yellow powder. Yield: 65%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.21 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 7.6$ Hz, 2H), 7.23 (d, $J = 16.4$ Hz, 1H), 7.01 (d, $J = 16.4$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 2H), 4.20 (m, $J = 6.4$ Hz, 2H), 4.01 (t, $J = 6.0$ Hz, 2H), 1.94 (s, 6H), 1.85–1.69 (m, 4H), 1.60–1.40 (m, 4H). ELEM. ANAL. Calcd. (%): C, 58.44; H, 5.37; N, 2.61. Found (%): C, 58.78; H, 5.74; N, 2.38.

2.4. Polymerization of BVMA

In a general ATRP procedure, CuBr, BPY, cyclohexanone (monomer/cyclohexanone = 1:5 g mL^{-1}), initiator and BVMA were mixed in a three-neck round-bottom flask. The polymerization was maintained at 60 °C under N_2 atmosphere. Samples were taken out by a syringe at different time intervals and diluted with tetrahydrofuran (THF). The diluted solution was passed through an alumina column to remove the copper catalyst, and the filtrate was precipitated by addition of ethyl acetate ($V_{\text{ethyl acetate}}/V_{\text{THF}} = 10/1$). The reprecipitation process was repeated three times, followed by drying under vacuum at room temperature.



Scheme 1. General procedures for the synthesis of ini-BZT and BZT. Structure of polyBZT-b-NTS.

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