Polymer 50 (2009) 4807–4812

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

Liang Zhang, Qing-Feng Xu, Jian-Mei Lu*, Na-Jun Li, Feng Yan, Li-Hua Wang

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Renai Road, Suzhou 215123, China

ARTICLE INFO

Article history:
Received 18 January 2009
Received in revised form
29 July 2009
Accepted 12 August 2009
Available online 14 August 2009

Keywords:
Atom transfer radical polymerization (ATRP)
Block copolymers
Fluoropolymers

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.

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

* Corresponding author. Fax: +86 51265880367.
E-mail address: lujm@suda.edu.cn (J.-M. Lu).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.08.015

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.

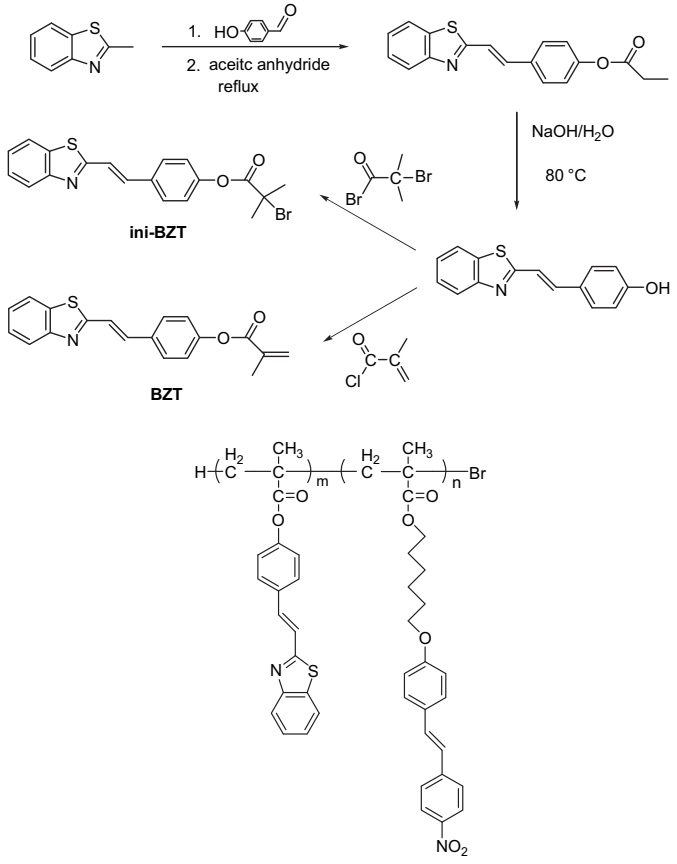
2.3.4. Synthesis of 2-bromo-2-methyl-propionic acid 4-nitrostilbene-hexyloxy ester (BPNHE)

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 ($V_{ethyl\ acetate}/V_{THF} = 10/1$). 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.

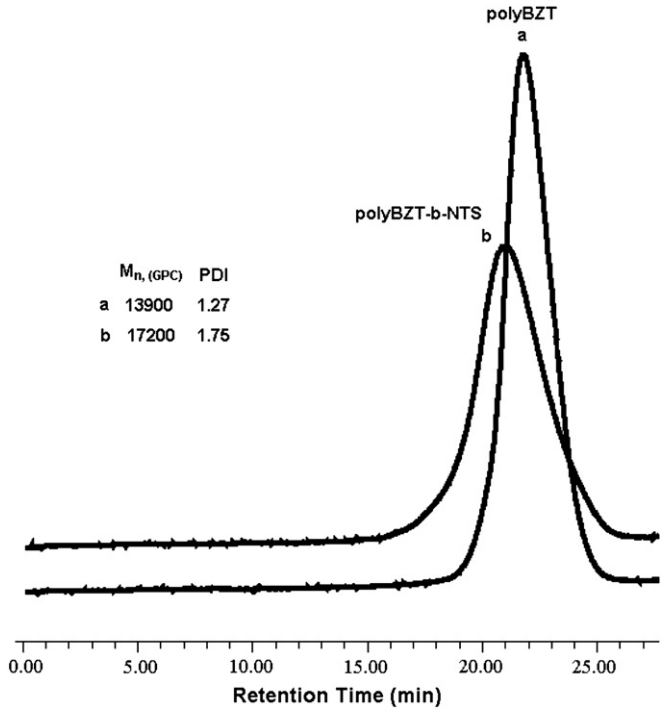


Fig. 1. GPC curves of polymers (a) before and (b) after chain extension of polyBZT.

2.5. Chain extension with PBVMA as a macroinitiator

A mixture of CuBr (2.86 mg, 0.02 mmol), BPY (4.68 mg, 0.03 mmol), cyclohexanone (5 mL), PBVMA (139 mg, 0.01 mmol) and MHNS (289 mg, 1 mmol) was stirred for 24 h at 80 °C under N_2 atmosphere. The sample was dissolved in THF and passed through an alumina column. Then the resulting solution was poured into an excess (about 150 mL) of vigorously agitated methanol. The precipitate formed was collected and the reprecipitation process was carried out three times. The purified polymer was dried under vacuum at room temperature.

2.6. Preparation of the polymer film

The polymer solution was obtained by dissolving the polymer (PBVMA) in $CHCl_3$ with the concentration of 0.1 g/mL. The thin film sample of PBVMA was prepared by spin-coating about 50 μL of the polymer solution onto a clean glass slide at 1500 rpm. The thickness of the film was controlled to be about 1.0 μm. After drying under vacuum for 24 h to remove the residual solvent, the film was stored in a desiccator for further study.

3. Results and discussion

3.1. Synthesis of BPBVE and BVMA

Scheme 1 shows the general procedures for the synthesis of BPBVE and BVMA. The intermediate acetic acid 4-(2-benzothiazole-2-yl-vinyl)-phenyl ester was obtained through condensation of 2-methylbenzothiazole and 4-hydroxybenzaldehyde using acetic anhydride as a condensing agent. The intermediate was hydrolyzed without any purification to obtain 4-(2-benzothiazole-2-yl-vinyl)-phenol. In comparison with the method mentioned in the previous literature [35], the procedure is relatively simple and gives good reproducibility with a high overall yield (62%). Esterification with either 2-bromo-2-methylpropionyl bromide or methacryloyl chloride was conducted, forming the functionalized ATRP initiator and monomer, respectively (Fig. 1).

Table 1
ATRP of BZT using ini-BZT as an initiator at 60 °C ($[BZT]_0/[ini\text{-}BZT]_0/[CuBr]_0/[Bpy]_0 = 100/1/2/3$).

No.	Time (min)	Conversion (%)	$M_{n,(GPC)}$	PDI
1	15	8.2	9500	1.22
2	30	32.0	13,900	1.24
3	60	53.5	19,600	1.29

3.2. ATRP of BVMA initiated by BPBVE and chain extension using PBVMA as the macroinitiator

BVMA was polymerized using BPBVE as an initiator to obtain a more well-defined polymer and minimize the influence of the end-group [36,37]. The polymerizations were conducted in cyclohexanone using CuBr complexed with BPY as the catalyst. The results are shown in Table 1.

According to the ATRP mechanism, the obtained PBVMA could be used as a macro-ATRP agent to prepare well-defined block copolymers. In this work, MHNS was used as the second monomer in the chain extension (Scheme 1). As shown in Fig. 2, the value of M_n of the polymer increased from 13,900 (a) to 17,200 (b). The block copolymer contains about 43 and 7 units of methacrylate monomers consisting of the blue fluorophore and the orange fluorophore, respectively. This suggests that the PBVMA had a ω-halogen (bromine) end group and that most of the PBVMA chains were still "living". However, the PDI of the obtained copolymer was broad (1.75), which was due to permanent premature termination of this polymerization, leading to a mixture of block copolymers and partial homopolymers. The block copolymerization may potentially be terminated by a large number of nitro-groups of MNHS [38].

3.3. ATRP of BVMA initiated by BPNHE

To further adjust the fluorescent property of PBVMA, ATRP of BVMA was also conducted using BPNHE as the initiator, CuBr/2,2′-bipyridine (BPY) as the catalyst and cyclohexanone as solvent at 60 °C. The ratio effect of $[M]_0/[I]$ on the ATRP of BVMA was investigated, and the results are presented in Fig. 2 and Table 2. As shown in Fig. 2, there is clearly a lag time on these polymerizations, and

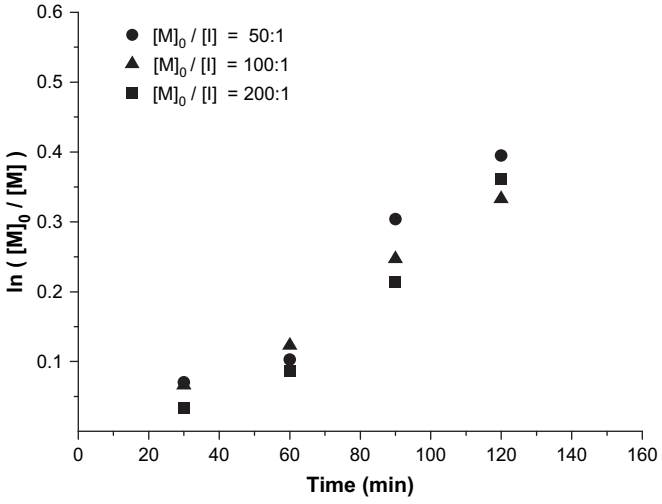


Fig. 2. Kinetic plots for ATRP of BZT with ini-NTS as an initiator in cyclohexanone solution at 60 °C for different $[M]_0/[I]$ ratios ($[ini\text{-}NTS]_0/[CuBr]_0/[Bpy]_0 = 1/2/3$).

Table 2
Conversion, $M_{n,\ (GPC)}$, and PDIs for ATRP of BZT with ini-NTS as an initiator in cyclohexanone solution at 60 °C for different $[M]_0/[I]$ ratios ($[\text{ini-NTS}]_0/[\text{CuBr}]_0/[\text{Bpy}]_0 = 1/2/3$).

$[M]_0/[I]$	Conversion (%)	$M_{n,\ (GPC)}$	PDI	$M_{n,\ (th)}$
50:1	6.8	6700	1.10	1100
	9.8	7100	1.12	1600
	26.2	7300	1.13	4200
	32.6	8100	1.13	5200
100:1	6.4	8400	1.15	2100
	11.6	9200	1.18	3700
	21.8	10,500	1.22	7000
	28.3	11,300	1.27	9100
200:1	3.2	10,300	1.21	2100
	8.3	12,700	1.26	5300
	19.3	13,800	1.30	12,400
	30.4	14,300	1.45	19,500

the corresponding plots of $\ln([M]_0/[M])$ *vs* the polymerization time are not quite linear for different $[M]_0/[I]$ ratios, which were attributed to some possible coupling between the nitrogen of BVMA and the catalytic metal center [39]. Table 2 shows the dependence of $M_{n,\ (GPC)}$ on the monomer conversions. The value of $M_{n,\ (GPC)}$ increases with monomer conversion. However, most of the $M_{n,\ (GPC)}$ values were higher than the $M_{n,\ (th)}$ values, which indicates low initiation efficiency. The low efficiency of this system was probably due to a mass of initiator radicals terminated in the initiation stage of the polymerization. Table 2 also shows the PDI values on the monomer conversion, and all of which were lower than 1.50. Instead of a continuing decrease in PDI with conversion (as often observed in other ATRP systems), an obvious increase in PDI occurred at higher conversions, and the deviations were presumably due to the slow initiation.

Fig. 3 shows the ^{1}H NMR spectrum of PBVMA initiated by BPNHE. Signals at 8.07 (a), 6.80 (b), 4.06 (d) and 3.88 (c) ppm are attributed to a partial fraction of the protons in the initiator units, which further confirms that the polymerization fit the mechanism of ATRP.

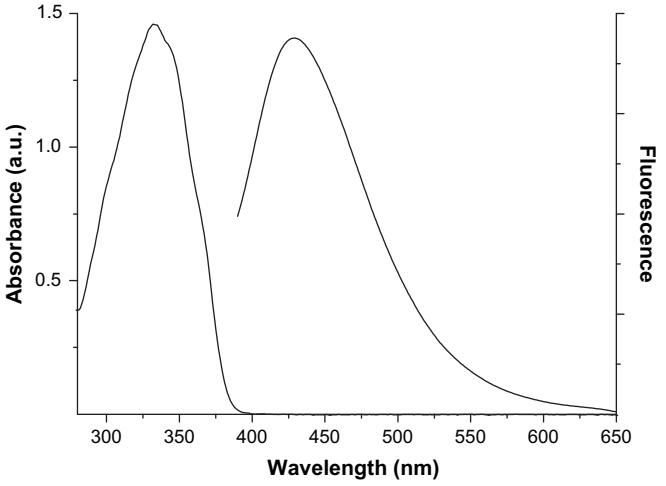


Fig. 4. Absorption and fluorescence spectra of polyBZT in DMF solution (32 mg/L) with $\lambda_{ex} = 380$ nm.

3.4. Fluorescent property of the homopolymer PBVMA and fluorescence adjustment through chain extension

As shown in Fig. 4, the UV–vis absorption peak of PBVMA appeared as the characteristic intense π–π* transition of benzothiazole at about 340 nm. The synthesized homopolymers were fluorescent and emitted an obvious blue light in DMF solution when irradiated with UV-light. The fluorescent emission spectra of BVMA, MHNS and PBVMA-b-PMHNS in DMF solution are presented in Fig. 5. The solution of PBVMA-b-PMHNS emitted orange fluorescence at about 610 nm. The emission spectrum of the block copolymer cannot be simply treated as a sum of the emission of the two segments. Generally, if the blue fluorophore and the orange fluorophore were combined in one macromolecule, the energy would transfer from the blue to the orange fluorophore, resulting in emission solely from the orange fluorophore [40].

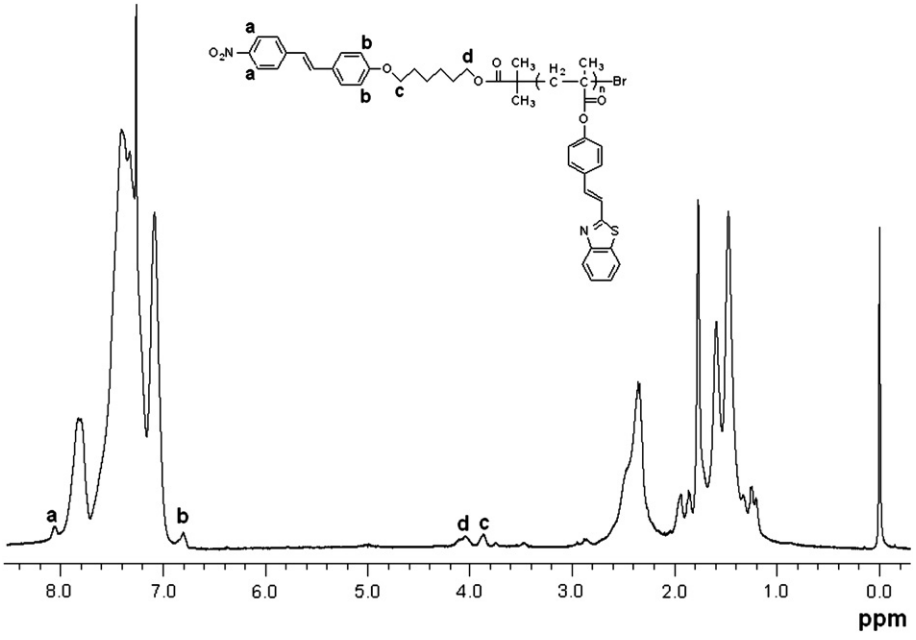


Fig. 3. ^{1}H NMR spectrum of polyBZT initiated by ini-NTS ($M_n = 7300$, PDI = 1.13).

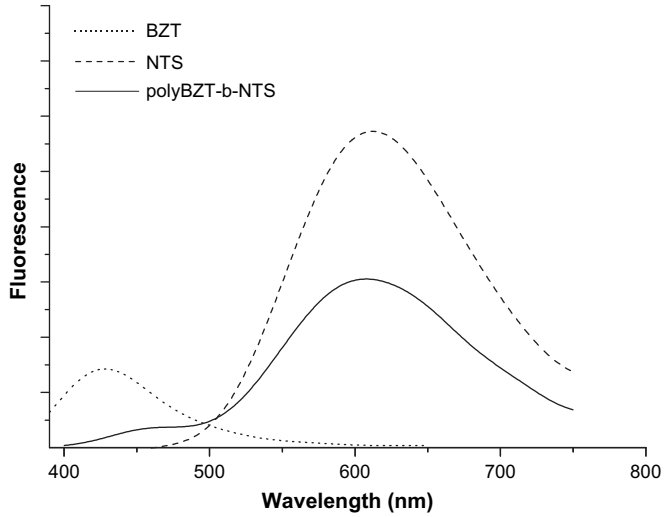


Fig. 5. Fluorescence spectra of BZT (10^{-4} mol/L), NTS (10^{-4} mol/L) and polyBZT-b-NTS (17.2 mg/L, $M_n = 17200$) in DMF solution with $\lambda_{ex} = 380$ nm.

3.5. Fluorescence adjustment of PBVMA through molecule weight control

ATRP of BVMA was also initiated with BPNHE to limit the intramolecular energy transfer since there is only one orange fluorophore in the end-group of the chain [6,10]. The fluorescence spectra of the polymers vary with different values of $M_{n,\,(GPC)}$ at the same concentration (10^{-6} mol/L). The intensity of the orange fluorescence decreased with increase in molecular weight of the polymers in all cases, which was due to the decreasing concentration of the initiator fluorophores attached to polymeric chains. On the contrary, the intensity of the blue fluorescence increased with increase in molecular weight. When the molecular weight increased to 15,900, the polymer exhibited relatively balanced intensities of the blue and orange emissions (Fig. 6), and the PBVMA solution emitted white fluorescence. The macromolecules of PBVMA in the film could aggregate, and the energy transfer was facilitated through both intra- and interchain pathways because of the shorter distances between the polymer chains [41], resulting in

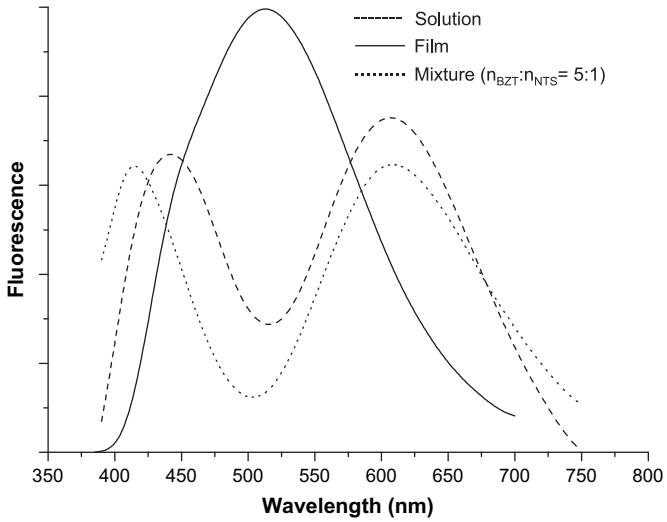


Fig. 6. Fluorescence spectra of polyBZT ($M_n = 15900$, PDI = 1.44) initiated by ini-NTS in DMF solution (10^{-6} mol/L) and in film and mixture (n_{BZT}:$n_{NTS} = 5:1$) with $\lambda_{ex} = 380$ nm.

the sole emission [42] covering the entire visible region. The fluorescence quantum yield (Φ) of the white fluorescence polymer was determined using quinine sulfate in 0.1 M sulfuric acid ($\Phi = 0.55$) as a standard [36,43], giving a value of 0.014. The low fluorescence quantum yield is ascribed to weak fluorescence emission of fluorophores in the polymer. Fluorescence spectra of a series of mixtures of BVMA and MHNS were also recorded. The optimum ratio for white emission is 5/1(n_{BVMA}/n_{MHNS}), as shown in Fig. 6.

4. Conclusions

The monomer BVMA and the initiator BPBVE containing benzothiazole were synthesized and characterized. ATRP of BVMA was carried out using CuBr/2,2′-bipyridine (BPY) as catalyst, cyclohexanone as solvent and BPBVE, PBVMA and BPNHE as initiators, respectively. The polymerizations showed "living"/controlled free radical polymerization behaviors. The fluorescent property of PBVMA could be adjusted through chain extension and molecular weight control. White fluorescence of PBVMA initiated by BPNHE was obtained with $M_n = 15900$. Further work include obtain fluoropolymer solution and prepare fluoropolymer film with both white emission and high fluorescence quantum yield.

Acknowledgements

This work was supported by the Chinese Natural Science Foundation (20571054 and 20876101), Project of Ministy of Education (20070285003), the Supporting Project of Jiangsu Province (Industry) (BE2008061), Great Project of Department of Education Jiangsu Province (08KJA430004) and Project of Qin Lan (Jiang Su).

References

[1] Luo J, Li XZ, Hou Q, Peng JB, Yang W, Cao Y. Adv Mater 2007;19:1113–7.
[2] Liu J, Xie ZY, Cheng YX, Geng YH, Wang LX, Jing XB, et al. Adv Mater 2007;19:531–5.
[3] Liu J, Shao SY, Chen L, Xie ZY, Cheng YX, Geng YH, et al. Adv Mater 2007;19:1859–63.
[4] Wu FI, Yang XH, Neher D, Dodda R, Tseng YH, Shu CF. Adv Fucnt Mater 2007;17:1085–92.
[5] Liu J, Guo X, Bu LJ, Xie ZY, Cheng YX, Geng YH, et al. Adv Funct Mater 2007;17:1917–25.
[6] Lee PI, Hsu SLC, Lee RF. Polymer 2007;48:110–5.
[7] Tu GL, Zhou QG, Cheng YX, Geng YH, Wang LX, Ma DG, et al. Synth Met 2005;152:233–6.
[8] Zhen HY, Xu W, Yang W, Chen QL, Xu YH, Jiang JX, et al. Macromol Rapid Commun 2006;27:2095–100.
[9] Kawamoto M, Tsukamoto T, Kinoshita M, Ikeda T. Appl Phys Lett 2006;89:121920.
[10] Lee SK, Jung BJ, Ahn T, Jung YK, Lee JI, Kang IN, et al. J Polym Sci Part A Polym Chem 2007;45:3380–90.
[11] Kido J, Shionoya H, Nagai K. Appl Phys Lett 1995;67:2281–3.
[12] Kim JH, Herguth P, Kang MS, Jen AKY, Tseng YH, Shu CF. Appl Phys Lett 2004;85:1116–8.
[13] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614–5.
[14] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721–3.
[15] Percec V, Barboiu B. Macromolecules 1995;28:7970–2.
[16] Wang XS, Armes SP. Macromolecules 2000;33:6640–7.
[17] Oh JK, Min K, Matyjaszewski K. Macromolecules 2006;39:3161–7.
[18] Yu Q, Zeng FQ, Zhu SP. Macromolecules 2001;34:1612–8.
[19] Chen XP, Sufi BA, Padias AB, Hall Jr HK. Macromolecules 2002;35:4277–81.
[20] Robinson KL, Khan MA, Báñez MVP, Wang XS, Armes SP. Macromolecules 2001;34:3155–8.
[21] Otazaghine B, Boutevin B, Desmazes PL. Macromolecules 2002;35:7634–41.
[22] Liu SS, Mishra MK. Macromolecules 2007;40:867–71.
[23] Ma IY, Lobb EJ, Billingham NC, Armes SP, Lewis AL, Lloyd AW, et al. Macromolecules 2002;35:9306–14.
[24] Du JZ, Chen YM. Macromolecules 2004;37:6322–8.
[25] Beers KL, Boo S, Gaynor SG, Matyjaszewski K. Macromolecules 1999;32:5772–6.
[26] Singha NK, Ruiter B, Schubert US. Macromolecules 2005;38:3596–600.
[27] Sumerlin BS, Tsarevsky NV, Louche G, Lee RY, Matyjaszewski K. Macromolecules 2005;38:7540–5.
[28] Tsarevsky NV, Braunecker WA, Brooks SJ, Matyjaszewski K. Macromolecules 2006;39:6817–24.

[29] Han YK, Dufour B, Wu W, Kowalewski T, Matyjaszewski K. Macromolecules 2004;37:9355–65.
[30] Heredia KL, Tolstyka ZP, Maynard HD. Macromolecules 2007;40:4772–9.
[31] Ando T, Kato M, Kamigaito M, Sawamoto M. Macromolecules 1996;29:1070–2.
[32] Lu JM, Xu QF, Yuan X, Xia XW, Wang LH. J Polym Sci Part A Polym Chem 2007;45:3894–901.
[33] Jin ZN, Xu QF, Li NJ, Lu JM, Xia XW, Yan F, et al. Eur Polym J 2008;44:1752–7.
[34] Chen L, Xia XW, Lu JM, Xu QF, Li NJ, Wang LH. Spectrosc Spect Anal 2009;29:176–9.
[35] Gilman H, Towle JL, Ingham RK. J Org Chem 1956;21:595–6.
[36] Yuan X, Lu JM, Xu QF, Wang LH. Polymer 2005;46:9186–91.
[37] Zhang L, Xu QF, Lu JM, Xia XW, Wang LH. Eur Polym J 2007;43:2718–24.
[38] Sun B, Zhu XL, Zhu J, Cheng ZP, Zhang ZB. Macromol Chem Phys 2007;208:1101–9.
[39] Pavinatto FJ, Barletta JY, Sanfelice RC, Cardoso MR, Balogh DT, Mendonça CR, et al. Polymer 2009;50:491–8.
[40] Liu J, Zhou QG, Cheng YX, Geng YH, Wang LX, Ma DG, et al. Adv Mater 2005;17:2974–8.
[41] Chuang CY, Shih PI, Chien CH, Wu FI, Shu CF. Macromolecules 2007;40:247–52.
[42] Yu XF, Lu S, Ye C, Li TC, Liu TX, Liu SY, et al. Macromolecules 2006;39:1364–75.
[43] Arimori S, Bell ML, Oh CS, Frimat KA, James TD. J Chem Soc Perkin Trans 1 2002:803–8.