

Synthesis and fluorescence properties of polystyrene via atom transfer radical polymerization using a coumarin derivate as initiator

K. Zhao · Z. P. Cheng · Z. B. Zhang · N. C. Zhou ·
X. L. Zhu

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Abstract Well-defined polystyrene was successfully synthesized via atom transfer radical polymerization, using a novel coumarin derivate, 2-bromo-2-methyl-propionic acid 4-methyl-2-oxo-2H-chromen-7-yl ester (BMP), synthesized in our lab as an initiator, and CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalyst at 110 °C. The kinetics of the polymerization was studied in detail. The fluorescence properties of the resultant polystyrenes were studied in *N,N*-dimethylformamide (DMF). It is very interesting that the adding of Fe³⁺ has significant effect on the fluorescence intensities, which decreased with increasing the concentration of iron in solutions. The obtained polystyrenes can be used as fluorescent probe molecules for Fe³⁺.

Keywords Polymer synthesis · ATRP · Iron ion · Fluorescence probe

Introduction

The development of atom transfer radical polymerization (ATRP) constitutes one of the key developments in the field of synthetic polymer chemistry due to its precise control over the compositions and structures [1–7]. Various functional initiators have been successfully employed to initiate well-controlled ATRP for syntheses of functional polymers. The fluorescence characteristics of polymers have been intensively studied with respect to application as fluorescent materials. At first, polymers have gained tremendous recognition in the field of artificial sensor in the goal of gaining better selectivity and fast measurement [8–11]. Second, fluorescent

K. Zhao · Z. P. Cheng · Z. B. Zhang · N. C. Zhou · X. L. Zhu (✉)

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China
e-mail: xlzhu@suda.edu.cn

polymers have widely been studied as functional materials [12–19]. Moreover, many reports described that fluorescence characteristics of polymer systems affected by metal ions and this behavior has gained tremendous attention in recent years [20, 21]. For example, Fan et al. [22] founded varying fluorescence “turn-on” behavior of polymers in the presence of cations including Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , H^+ , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} . Wang et al. [23] reported that a fluorescent polymer, poly(acrylic acid)-poly(pyrene methanol) (PAA-PM) could be used as a sensing material for metal ions (Fe^{3+} and Hg^{2+}).

This article reports the synthesis of novel well-defined polystyrene end-capped with 2-methyl-propionic acid 4-methyl-2-oxo-2H-chromen-7-yl ester via ATRP. The aim of this research is to create a precise molecular environment for fluorescent polymer, and to investigate the effect of trivalent iron (Fe^{3+}) on the fluorescence intensity of the polymer. The mechanism of observed fluorescent phenomena was discussed.

Experimental section

Materials

Styrene (St) (99%, Shanghai Chemical Reagent Co., LTD) was washed with an aqueous solution of sodium hydroxide (5%) and then with deionized water until neutral, dried with anhydrous sodium sulfate overnight, and then distilled under vacuum. The distillates were stored at $-18\text{ }^{\circ}\text{C}$ before use. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4 Å molecular sieve and distilled under vacuum. CuBr (Aldrich, 98%) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried under vacuum. 7-Hydroxy-4-methylcoumarin (97%) was purchased from Acros and used as received. Ammonium ferric sulfate ($\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$) (analytical reagent, Shanghai Chemical Reagent Co., LTD), Tetrahydrofuran (THF) (analytical reagent, Shanghai Chemical Reagent Co., LTD), Dimethylformamide (DMF) (analytical reagent, Shanghai Chemical Reagent Co., LTD) and all the other chemicals were also used as received.

Synthesis of 2-bromo-2-methyl-propionic acid 4-methyl-2-oxo-2H-chromen-7-yl ester (BMP)

A solution of 2-bromo-2-methyl-propionyl bromide (2.30 g, 0.01 mol) in 10 mL of chloroform was slowly dropped into a solution of 7-hydroxy-4-methylcoumarin (1.76 g, 0.01 mol) in 100 mL of CHCl_3 at $0\text{ }^{\circ}\text{C}$. The resulting solution was stirred overnight. After filtration, the solution was evacuated off, the crude product was purified by recrystallization from ethanol twice, and a white crystal (BMP) was obtained (1.90 g, 56%). ^1H NMR (CDCl_3 , 400 MHz, δ): 7.15–7.49 (3H, Ar_H), 6.29 [1H, =CH], 2.45 (3H, =C(CH_3)), 2.09 (6H, C(CH_3) $_2$). Elem. Anal. Calcd.: C, 62.2%; H, 6.2%. Found: C, 61.9%; H, 6.3%.

Polymerization

A typical ATRP procedure was carried out as follows: a dry glass tube was quantitatively filled with BMP 0.028 g (0.087 mmol), CuBr 0.012 g (0.087 mmol), PMDETA 54 μL (0.26 mmol), and St 2 mL (0.0174 mol) in sequence. After the reaction mixture was bubbled with argon for 20 min, the tube was sealed under argon and then immersed in a thermostated oil bath at 110 °C. The polymerizations were stopped at a desired time by cooling the tubes with cold water. Afterward, the tube was opened and the contents were diluted with THF. Then the solution was poured into a large amount of methanol/HCl (100/5, volume ratio) mixture. The polymers were filtered and dried under vacuum.

Solution preparation

Solutions of polystyrenes were diluted at a concentration of 1×10^{-4} mol/L in DMF. Solutions of cationic salts with the concentration of typically 1×10^{-4} mol/L were prepared in DMF. Solutions were prepared for fluorescence or UV analyses by adding needed cationic solution to 1 mL of polymer solution, and DMF was added to obtain 10.0 mL of solutions.

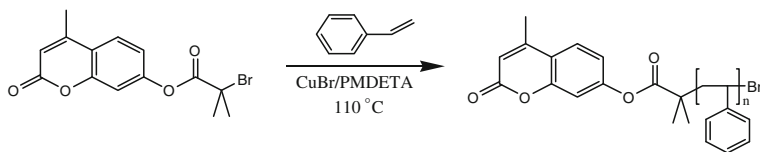
Characterizations

Conversion of monomer was determined by gravimetry. The molecular weights and molecular weight distributions (M_w/M_n s) of the polymers were determined on a Waters 1515 gel permeation chromatograph (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 column with molecular weight range 100–500000 calibrated with polystyrene standard samples. THF was used as an eluent at a flow rate of 1.0 mL/min and operated at 30 °C. ^1H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument at ambient temperature using CDCl_3 as a solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis of C and H was measured with an EA1110 CHNO-S instrument. The fluorescence spectra of polymers and mixture of polymer and iron(III) in DMF solution were recorded by HITACHI F-2500 Fluorescence Spectrophotometer. Atomic absorption spectrometry was detected by Varian Spectra 220FS Atomic Absorption Spectrometer.

Result and discussion

ATRP of styrene using BMP as initiator

The new coumarin derivate initiator, 2-bromo-2-methyl-propionic acid 4-methyl-2-oxo-2H-chromen-7-yl ester (BMP, Scheme 1), was used in the bulk polymerization



Scheme 1 Synthetic pathway for the fluorescent polymer

of styrene. The polymerizations were carried out at 110 °C via ATRP with $[St]_0:[BMP]_0:[CuBr]_0:[PMDETA]_0 = 200:1:1:3$ and $400:1:1:3$ (Scheme 1).

The first-order kinetic plots of polymerization of styrene indicate a constant radical concentration throughout polymerization process under both cases, as shown in Fig. 1. However, two induction periods (~ 25 or 35 min) were observed. These may be explained by slow establishment of the equilibrium between active and dormant species and the impurities in the reaction systems.

Evolution of M_n s with conversion was found to be linear as shown in Fig. 2. Experimental M_n values were higher than the theoretical values throughout the polymerizations. This phenomenon may indicate inefficient initiation of BMP. However, the narrow molecular weight distributions ($1.1 < M_w/M_n < 1.3$) of polymers remained as shown in Fig. 2.

Chain extension

According to the mechanism of ATRP, if the end of the polymer chain has a halogen atom, it can be used as a macroinitiator to initiate the polymerization of a fresh feed of monomer in the presence of ATRP catalyst, such as CuBr/PMDETA. Figure 3 shows the GPC traces of the polymers before (PS) and after chain-extension (PS-*b*-PMMA) with methyl methacrylate (MMA). The molecular weight increases from

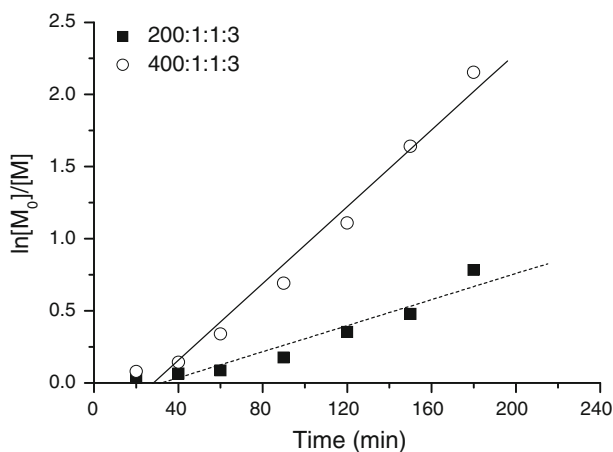


Fig. 1 Kinetic plots for the bulk polymerizations of styrene with different molar ratios at 110 °C. $[St]_0:[BMP]_0:[CuBr]_0:[PMDETA]_0 = 200:1:1:3$ (filled square); $[St]_0:[BMP]_0:[CuBr]_0:[PMDETA]_0 = 400:1:1:3$ (open circle), $St = 2$ mL

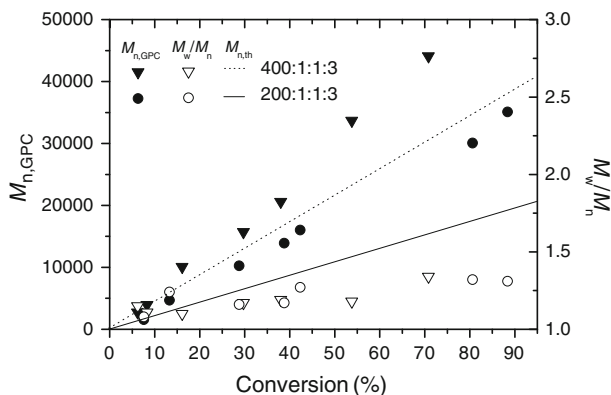


Fig. 2 Evolution of M_n and M_w/M_n with conversion for the bulk polymerization of styrene with different molar ratios at 110 °C. $[St]_0:[BMP]_0:[CuBr]_0:[PMDETA]_0 = 200:1:1:3$ and $400:1:1:3$, $St = 2$ mL

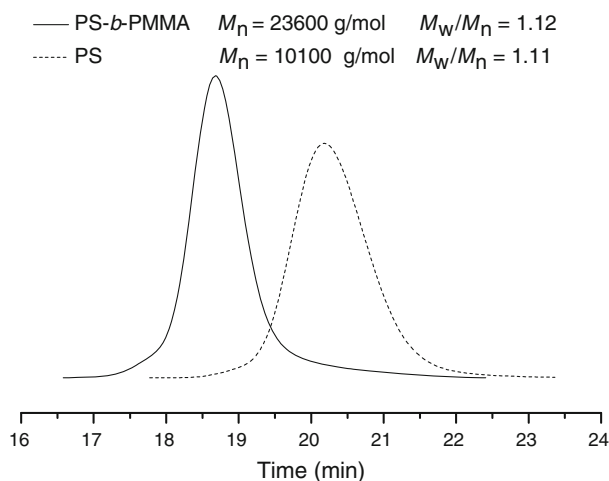


Fig. 3 GPC traces of PS before chain-extension and PS-*b*-PMMA, after chain-extension. Polymerization condition: $[MMA]_0:[macro\ initiator]_0:[CuBr]_0:[PMDETA]_0 = 1000:1:1:3$, $MMA = 2$ mL, conversion = 31.2%, temperature = 110 °C

10100 g/mol for PS to 23600 g/mol for block copolymer PS-*b*-PMMA, and the corresponding M_w/M_n remains narrow, from 1.11 to 1.12, indicating the original PS obtained end-capped with BMP moiety is “living”.

Figure 4 shows the 1H NMR spectra of initiator BMP (Fig. 4a), PS macro-initiator (Fig. 4b), and PS-*b*-PMMA diblock copolymer (Fig. 4c) in $CDCl_3$. The typical proton signals (*a*, 2.40 ppm) of the BMP can be seen in Fig. 4a. These signals can also be seen in the PS (Fig. 4b) and PS-*b*-PMMA (Fig. 4c), which indicates that the moieties in BMP was successfully attached to the ends of PS and PS-*b*-PMMA. Furthermore, the signals at 4.4–4.6 ppm in Fig. 4b are assigned to the protons of $-CH-$ group in polystyrene adjacent to bromine in the end chain. And the

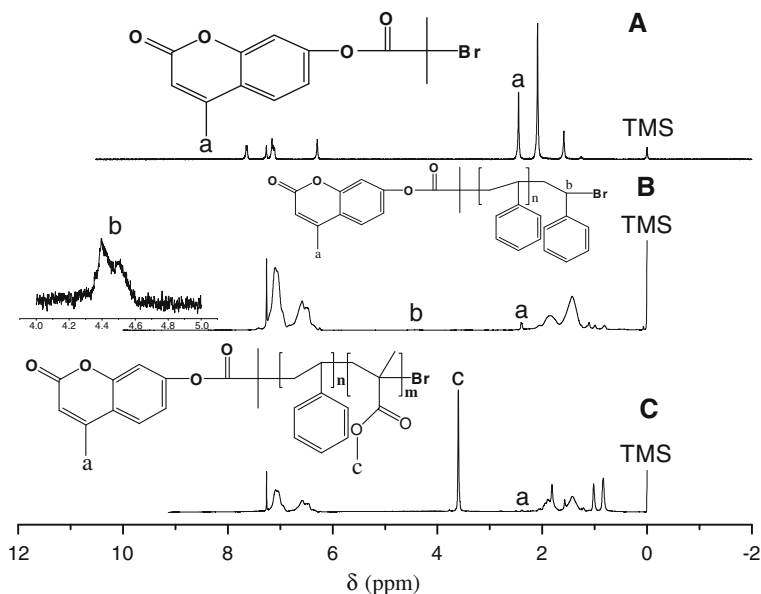


Fig. 4 ¹H NMR spectra of initiator BMP (a), PS macroinitiator ($M_{n, \text{GPC}} = 10100$ g/mol, $M_w/M_n = 1.1$) (b), and PS-*b*-PMMA diblock copolymer ($M_{n, \text{GPC}} = 23600$ g/mol, $M_w/M_n = 1.12$) (c) in CDCl_3

signal at 3.60 ppm is a characteristic chemical shift of methoxyl group in PMMA block. These results confirmed that the polymer chains were end-functionalized by 2-methyl-propionic acid 4-methyl-2-oxo-2H-chromen-7-yl chromophore and bromine moieties.

Fluorescent characteristic of the polystyrene

Same as the coumarin derivate initiator, the polystyrene with chain end of coumarin shows fluorescence emission characteristics. However, it is more important that Fe^{3+} can affect the fluorescence spectrum. Figure 5 displays the fluorescence spectra of polystyrene with chain end of coumarin before and after addition of Fe^{3+} ion in solution of DMF. A strong fluorescence emission band centered at 440 nm was observed in the polystyrene spectrum in the absence of Fe^{3+} (dashed line), and a new weak fluorescence emission band centered at around 401 nm with a blue shift has been observed when Fe^{3+} was added in this system (solid line). Experimental results in Figs. 5 and 6 indicated that the fluorescence intensity of polystyrene in existence of Fe^{3+} decreased with increasing concentration of Fe^{3+} added upon this system, and that there is a relationship of linearity between fluorescence intensity and concentrations of iron (III) added ($\text{Fe}^{3+} = 1 \times 10^{-6}$ – 1×10^{-4} mol/L). In order to investigate the selectivity, various metal ions including Ca^{2+} , Mg^{2+} , Cu^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , and Pb^{2+} were added into polystyrene solution in DMF to study the change of fluorescence intensity. However, almost no any changes were observed as compared with that of the obtained polystyrene. These results indicated that the as-prepared polystyrene is both sensitive and selective chemosensor for the

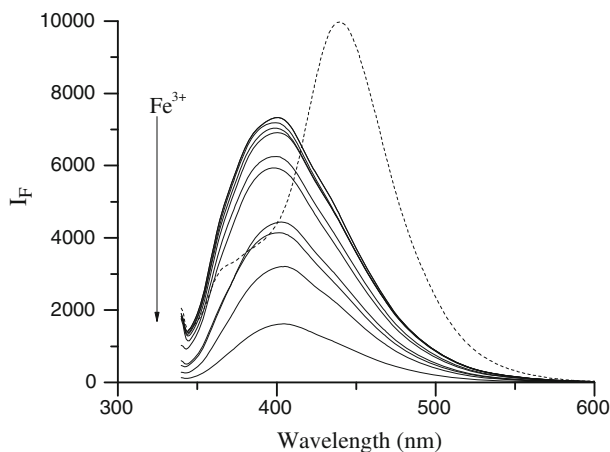


Fig. 5 Fluorescence spectra of the obtained polystyrene before (*dashed line*) and after (*solid line*) addition of different amounts of Fe^{3+} . $\lambda_{\text{ex}} = 325$ nm, solvent = DMF, PS, $M_{n,\text{GPC}} = 30100$ g/mol, $M_w/M_n = 1.31$, concentrations of Fe^{3+} from top to bottom ($\times 10^{-6}$ mol/L): 2, 4, 6, 8, 10, 20, 40, 60, 80, and 100

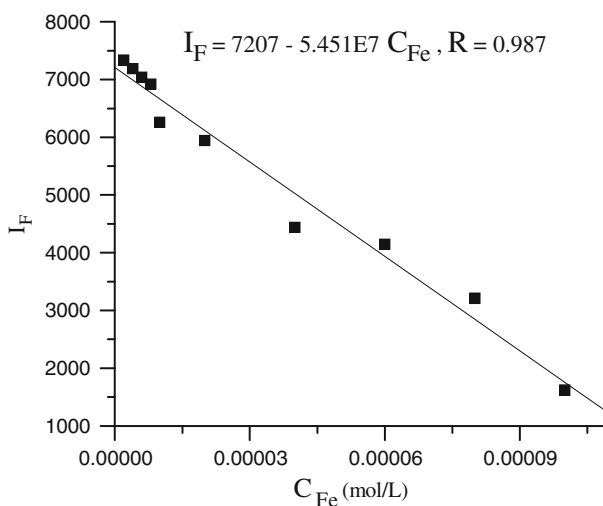


Fig. 6 Fluorescence intensities of polystyrenes (1×10^{-5} mol/L) added with different concentration of Fe^{3+} in DMF solution

Fe^{3+} ion. Based on both the properties, there are potentials for fluorescence probe and analytical detections.

Plausible mechanism for decrease of fluorescence intensity

According to fluorescence theory [24], the fluorescent decrease should result from static quenching of forming complex. In this study, a complex between Fe^{3+} ions

and coumarin derivate groups in the chain end of polystyrene may be formed, which can quench the emission from the polymers. In order to confirm the formation of the complex, the following experiment was carried out. 50 mL of DMF solution of 1×10^{-3} mol/L ammonium ferric sulfate was mixed with 50 mL of DMF solution of polystyrene (1×10^{-3} mol/L) in a flask under stirring. The mixture was refluxed for 24 h at 65 °C. Then the solution was poured into a 200 mL of methanol/HCl (100/5, volume ratio) mixture. The precipitate was filtered off. Finally, the filtrate was detected by atomic absorbance spectrophotometer, and no Fe^{3+} was found. Therefore, this experiments supports that a complex of coumarin in the chain end of polystyrene and Fe^{3+} was formed although we can not confirm the structure of the complex by experiment.

Conclusion

A functional fluorescent initiator BMP was successfully used as an ATRP initiator to synthesize fluorescent polymers. Well-defined BMP end-capped polymers were obtained. The polymerizations were well controlled with a linear increase of molecular weights of polymers with monomer conversions and relatively low polydispersities ($1.1 < M_w/M_n < 1.3$) throughout the polymerizations. The obtained PS can be used as fluorescent probe molecules for Fe^{3+} .

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