DOI: 10.1002/cjoc.201400181

Preparation of Fluorescent Polystyrene *via* ATRP with Dimethylamino Chalcones as Initiator

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4-(3-(4-(Dimethylamino)phenyl)acryloyl)phenyl-2-bromo-2-methylpropanoate (APPBr) was used for the heterogeneous atom transfer radical polymerization (ATRP) of styrene (St) with copper(I) bromide/ *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA) catalytic system. The functional end group was characterized *via* UV-Vis and ^{1}H NMR spectra. The polymerization showed a first-order kinetic characteristic and each of the obtained polymers had well-controlled molecular weight and relatively low polydispersity index (PDI). Furthermore, the obtained end-functionalized polystyrene (PS) in solution showed strong green-light emission which is further affected by mixing different metal cations. In particular, the fluorescent intensity of the polymer was decreased in the presence of Ag^+, Cu^{2+} and Fe^{3+}.

Keywords fluorescence, end-functionalized, metal ions

Introduction

Living and controlled polymerization techniques are appropriate tools to achieve polymers with well-controlled architecture.[1-10] Among them, atom transfer radical polymerization (ATRP) provides a simple route to many well-defined (co)polymers with predetermined molecular weight and narrow molecular weight distribution.[11-14] It has been effectively applied to the preparation of polymers with precisely controlled functionalities, topologies, and compositions.[15,16] Furthermore, a wide range of fluorophores can be introduced into the end of polymer chains by using fluorophore-containing initiators if the functional groups remain intact during the living radical polymerizations.

Dimethylamino chalcones are well known as fluorescent compounds with high quantum yields and widely used as fluorescence probes or photosensing material.[17-19] Most of these small molecules enjoy low thermal decomposition temperature and easy crystallization. To solve these problems, polymers with high molecular weight were considered as a good candidate owing to their high thermal decomposition temperature and good film-forming ability by simple processing techniques such as spin-coating, static casting and ink printing.[20] Danko and coworkers investigated spectral properties of chalcone containing triphenylamino structural unit in polymer matrices such as polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). It indicated that the fluorescence became more intense when the molecule was incorporated in a polymer matrix.[21] As we all know, the doping system is easy to phase separation. The idea of stimulating a single chromophore on a polymer chain and amplifying its effect through the polymer chain has motivated the evolution of new exciting research areas in polymer science.[22-29] Moreover, as one of controlled radical polymerization method, it is possible to place a single chromophoric unit at a defined position with a polymer chain *via* ATRP technique.

In this paper, we reported the ATRP of styrene (St) using 4-(3-(4-(dimethylamino)phenyl)acryloyl)phenyl-2-bromo-2-methylpropanoate (APPBr) as an initiator. The thermal decomposition temperature of initiator and the obtained polymer, PS-APPBr, were discussed. In addition, we also investigated the end-functional PS's recognition properties to metal ions, which bring the difference in fluorescence intensity.

Experimental

Materials

Styrene (St, 98%; Sinopharm Chemical Reagent Co., Ltd) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with

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Received March 25, 2014; accepted May 24, 2014; published online June 5, 2014.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201400181 or from the author.

water and dried with anhydrous sodium sulfate overnight, finally distillated under vacuum. Cuprous bromide (CuBr, 98.5%; Sinopharm Chemical Reagent Co., Ltd) was purified in acetic acid, washed with methanol and dried under vacuum to afford a white powder. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA), 4'-hydroxyacetophenone, 4-dimethylaminobenzaldehyde, 2-bromo-2-methylpropionyl bromide (97%; Alfa Aesar) were used as received. All other reagents and solvents were analytically pure and used as received.

Instrument and physical measurements

^{1}H NMR and ^{13}C NMR spectra were measured by INOVA 300 MHz NMR spectrometer, $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature. The purity was determined with a Waters515 HPLC apparatus: a mixture of methanol and water (methanol∶water＝80∶20, *V*∶*V*) was used as the eluent at a flow rate of 0.8 mL•min^{-1} at 30 ℃ with a C18 column and with a Waters 996 detector. Molecular weights and the polydispersity (PDI) relative to PS were measured using Waters1515 GPC with THF as a mobile phase at a flow rate of 1 mL•min^{-1} and with column temperature of 30 ℃. UV-Vis absorption spectra of the polymers and initiator in DMF solutions were determined on a Shimadzu RF540 spectrophotometer. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer.

General reaction procedure

Synthesis of initiator Initiator is prepared in two steps and characterized by ^{1}H NMR and ^{13}C NMR.

Synthesis of 3-(4-(dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-one (APPO) The solution of acetic acid (60 mL) containing 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol) was added into the solution of sulfuric acid (2 mL) including 4'-hydroxyacetophenone (2.72 g, 20 mmol). The obtained mixture was stirred at room temperature for 24 h, and was poured into the ice-water. The pH of the solution was adjusted to neutral with 0.1 mol•L^{-1} NaOH. The crude powder was collected by filtration. The pure powder (3.76 g, 14 mmol) was recrystallized from the mixture solution of ethanol and water. Yield 70%; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.30 (s, 1H), 8.02 (d, J＝8.5 Hz, 2H), 7.68 (d, J＝8.7 Hz, 2H), 7.61 (s, 2H), 6.87 (d, J＝8.6 Hz, 2H), 6.74 (d, J＝8.5 Hz, 2H), 3.00 (s, 6H).

Synthesis of 4-(3-(4-(dimethylamino)phenyl)acryloyl) phenyl-2-bromo-2-methylpropanoate (APPBr) APPO (2.67 g, 10 mmol) in THF (20 mL) was placed into a 50 mL round-bottom flask with triethylamine (2.0 g, 20 mmol). The reaction mixture was cooled to 0 ℃ in an ice/water bath and 2-bromopropionyl bromide (3.45 g, 15 mmol) in THF (10 mL) was added to a 50 mL pressure equalizing addition funnel fitted to the flask. After being added dropwise, the reaction mixture was stirred overnight and allowed to warm to room temperature of its own accord. The crude product was isolated by evaporating the solvent, and purified by using recrystallization from the mixture solution of ethanol-water. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.22 (d, J＝7.1 Hz, 2H), 7.70 (dd, J＝16.2, 8.6 Hz, 4H), 7.35 (d, J＝8.4 Hz, 2H), 6.76 (d, J＝9.0 Hz, 2H), 3.02 (s, 6H), 2.07 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 187.91, 169.82, 153.91, 152.45, 145.95, 136.84, 131.36, 130.52, 121.92, 116.30, 112.30, 57.39, 30.45.

Synthesis of polymer St was initiated by APPBr as the following procedure: St (2.08 g, 20 mmol), initiator (4.15 mg, 0.01 mmol), CuBr (1.43 mg, 0.01 mmol) and PMDETA (3.46 mg, 0.02 mmol) were dissolved in cyclohexanone and the mixture was placed into a two-neck round-bottomed flask. The flask was sealed and cycled between vacuum and argon for three times. 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 methanol. The precipitation was filtrated and dried under vacuum. The conversion of styrene was determined by gravimetry.

Results and Discussion

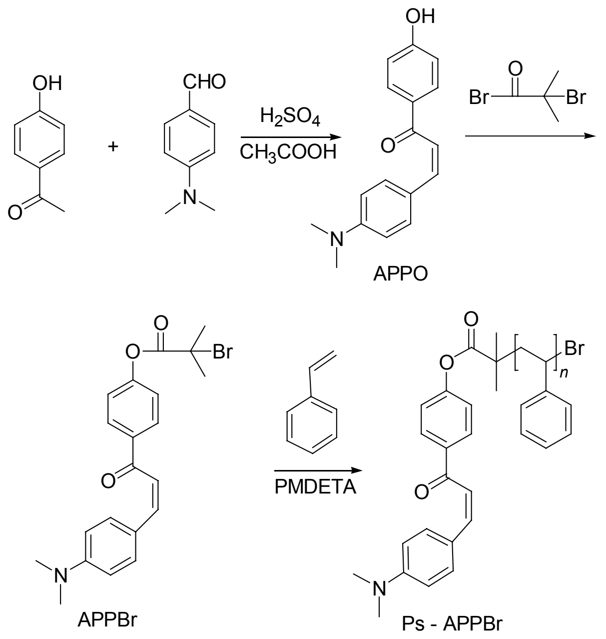
ATRP of St initiated by APPBr

The preparation of initiator and polymer was presented in Scheme 1. Initiator is easy to dissolve in common organic solvents such as acetone, THF, DMF, *etc*. The ATRP of St was carried out using APPBr as initiator in cyclohexanone at 80 ℃ with $[St]_0$∶$[APPBr]_0$∶$[CuBr]_0$∶$[PMDETA]_0$＝2000∶1∶1∶2, $[St]_0$＝0.5 mol•L^{-1} and the results are shown in Figure 1 and Figure 2. According to Figure 1, the linearity of the semilogarithmic plot of $\ln([M]_0/[M])$ versus the polymerization time indicated that the polymerization was first-order with respect to monomer. The number average molecular weights (M_ns) increase inearly with the conversion and the PDIs keep relatively narrow in all cases (M_w/M_n＝1.19－1.22), indicating the polymerization is well-controlled (Figure 2). The $M_{n(GPC)s}$ were similar to the corresponding $M_{n(th)s}$, in which the $M_{n(th)}$ was calculated according to $M_{n(th)} = M_{w,initiator}([St]_0/[initiator]_0) \times M_{w,St} \times Conversion$ ($M_{w,nitiator}$ and $M_{w,St}$ are the total molecular weight of initiator and St, and $[St]_0$ and $[initiator]_0$ mean the initial concentrations of St and initiator, respectively). The GPC chromatograms (Figure 3) displaying narrow, single peaks demonstrate that there are no low molecular weight trails indicative of transfer processes.

Characterization of polymerization

According to the mechanism of ATRP, initiator group is incorporated at α-end of the polymer chain, while ω-end remains a terminal halide. It can be verified by ^{1}H NMR spectrum (Figure 4). Signals at δ 8.00－7.50 are attributed to partial of the protons in initiator

Scheme 1 Synthetic scheme of initiator and its polymers



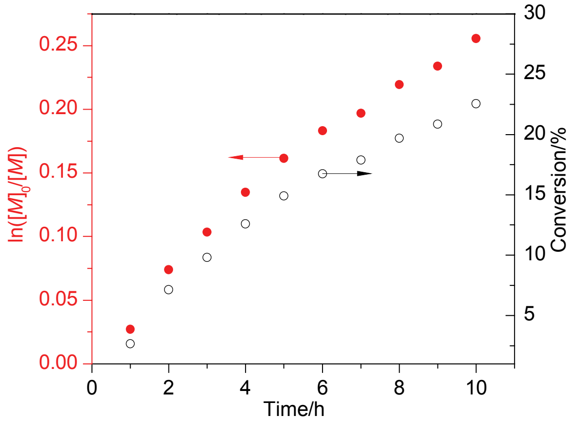


Figure 1 Kinetic plot for ATRP of styrene initiated by APPBr in cyclohexanone solution at 80 ℃.

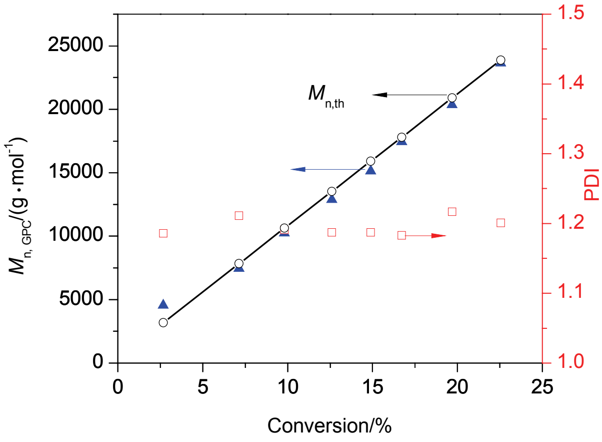


Figure 2 The evolution of M_n and PDI with conversion for the polymerization of PS-APPBr.

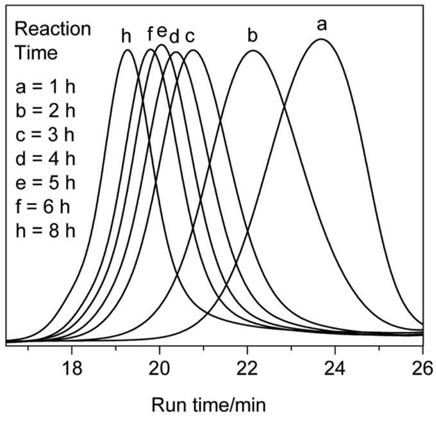


Figure 3 The GPC traces of the PS-APPBr. (a) M_n=4550 g•mol^{-1}, (b) M_n=7460 g•mol^{-1}, (c) M_n=10250 g•mol^{-1}, (d) M_n = 12880 g•mol^{-1}, (e) M_n = 15140 g•mol^{-1}, (f) M_n = 17430 g•mol^{-1}, (g) M_n=20370 g•mol^{-1}, (h) M_n=23660 g•mol^{-1}.

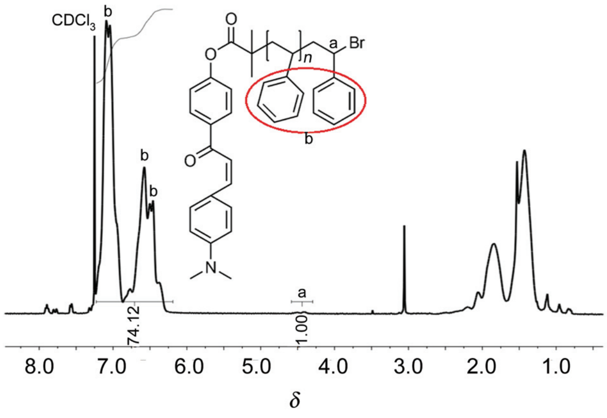


Figure 4 ^{1}H NMR spectrum of polymer ($CDCl_3$) at r.t.

units. The signals of hydrogen atom from the vinyl group (*δ* 5.5—6.0) disappeared and a broad signal of methylene below *δ* 2.0 was formed and then the protons of the CH-Br resonate at *δ* ~4.50, confirming that the initiator has indeed been incorporated at *α*-end of the polymer chain. The molecular weight could be estimated by comparing the resonance signals in the aromatic part (*δ* ~6.2—7.25) with those of the CH-Br protons (*δ* ~4.50). The molecular weight of PS-APPBr estimated by the ^{1}H NMR analysis was 8110 g•mol^{-1}, which was in good agreement with that determined by the GPC analysis (7460 g•mol^{-1}). Using the calibration curve drawn from the UV absorption data (Figure S1), the degree of labelling in PS-APPBr is determined to be 5.04% (by weight), corresponding to the molecular weight (8230 g•mol^{-1}).

The thermal properties of polymer and initiator were examined by thermogravimetric analysis (TGA, Figure 5a) and differential scanning calorimetry (DSC, Figure 5b). The PS-APPBr exhibits better thermal stability than initiator's, with a glass transition temperature about 105 ℃ and an onset decomposition temperature about 350 ℃, which is higher than initiator's (190 ℃).

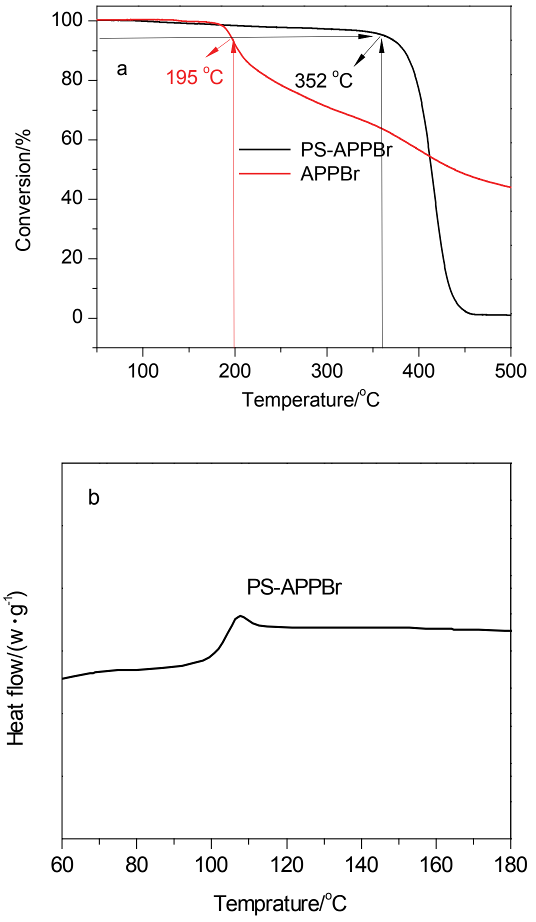


Figure 5 TGA (a) and DSC (b) curves of initiator and polymer collected under N_2 at a heating rate of 10 ℃•min^{-1}.

As shown in Figure 6, the absorption spectra of end functional polymer were measured in different solvents at the same concentration. The absorption maximum of end functional polymer was at 425 nm in DMF solution, ascribed to a localized aromatic π-π* transition. The blue-shift of the absorption band was both observed in acetone (423 nm) solution and THF (406 nm) solution respectively due to decreased dielectric constants of solvent. Such obvious solvatochromism is associated with the lowering of energy level caused by increasing dipole-dipole interaction between the solute and solvent. Therefore, charge-transfer states are effectively stabilized in polar media such as DMF.

As shown in Figure 7, the fluorescent property of the polymer has been investigated in DMF solution with different concentration. The peak position of the fluorescent emission of the polymer does not vary with different concentration. The relative intensity was increased with increasing concentration of the polymer. The intensity reached to maximum with concentration of 10^{-4} mol•L^{-1}. The fluorescent intensity was quenched while we kept on improving the concentration of polymer. The fluorescent emission spectra of polymer in different solvents at the same concentration were shown in Figure 8. The emission peak of polymer was red-shifted with the enhancement of the solvent polarity, and the relative fluorescence intensity was enhanced, with increasing the polarity of the solvents.

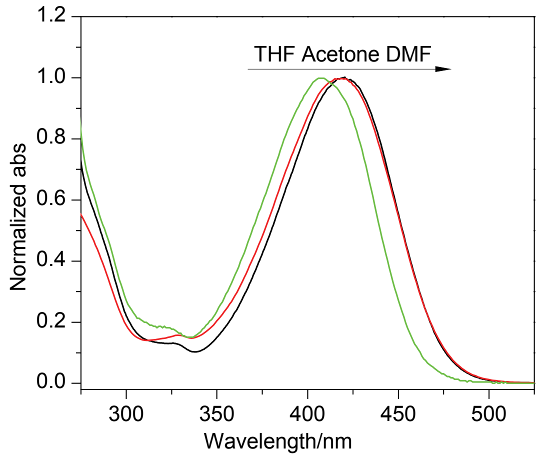


Figure 6 Absorption spectra of polymer in different solvents.

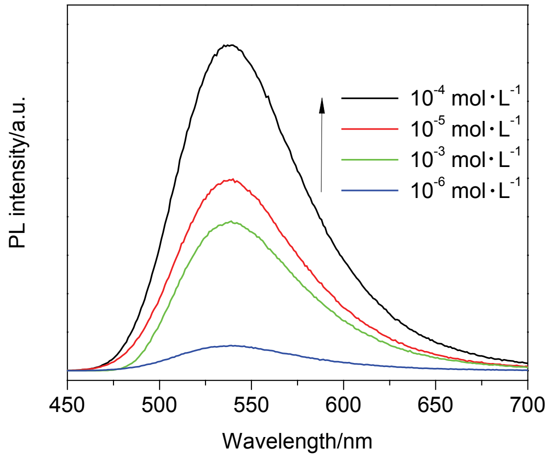


Figure 7 The PL spectra of the polymer in DMF solution with different concentrations.

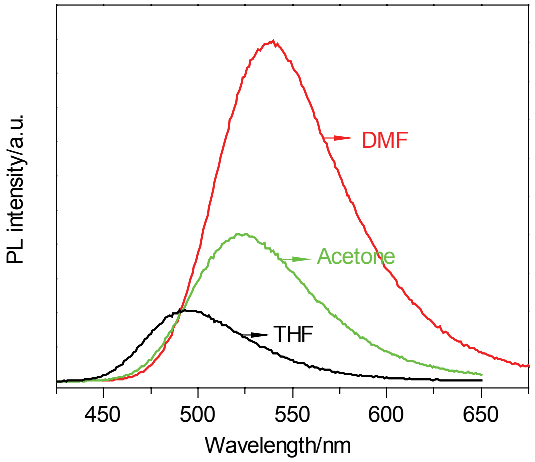


Figure 8 The PL spectra of the polymer in different solvents with the same concentration (10^{-5} mol•L^{-1}, λ_{ex}=410 nm).

Binding affinities of polymer toward transition metal ions, Al^{3+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Cu^{2+} and Fe^{3+}, were evaluated by fluorescent spectroscopy measurements. Addition of metal cations leads to no obvious changes (Al^{3+}, Mg^{2+}, Ca^{2+}) or decrease (Ag^{+}, Cu^{2+}, Fe^{3+}) of the fluorescent intensity of the polymer dissolved in DMF solution and the fluorescent spectra were shown in Figure 9. The decrease of fluorescent intensity could be ascribed to the formation of the transition metal (Ag^{+}, Cu^{2+}, Fe^{3+}) complexes because the unoccupied d orbits of transition metals incline to coordination. The coordination occurring in the core of the end-group is followed by a photoinduced electron transfer (PET) process or energy transfer to the periphery of the molecule, which is known as the fluorescence changing mechanism. The fluorescent spectra of polymer change more significantly upon addition of metal ions (Metal/PS-APPBr=50) than upon addition of metal ions (Metal/PS-APPBr=10). These results indicate that PS-APPBr have high binding affinity toward these metal ions. This work provides a method to prepare polymer-containing fluorescent probe. The research to improve their fluorescent property and prepare a film-typed probe is ongoing in our lab.

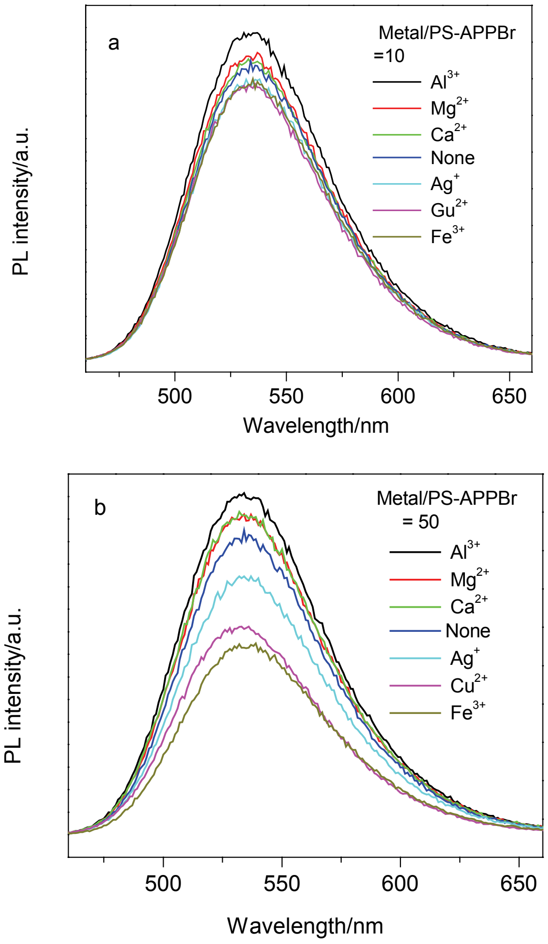


Figure 9 The PL spectra of the end-functionalized PS ($\lambda_{ex}=410$ nm) in DMF solution in the presence of metal cations. (a) Metal/PS-APPBr=10; (b) Metal/PS-APPBr=50.

Conclusions

The polymerizations of St initiated by APPBr were well-controlled with the characteristics of controlled/ "living" polymerization. The obtained end-functionalized PS in solution showed strong green-light emission which was further affected by mixing different metal cations. In the presence of metal cations (Al^{3+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Cu^{2+} and Fe^{3+}), the fluorescent intensity of the PS-APPBr solution was different. The fluorescent intensity of the polymer showed no obvious changes in the presence of Al^{3+}, Mg^{2+}, Ca^{2+}, but the fluorescent intensity of the polymer was decreased in the presence of Ag^{+}, Cu^{2+}, Fe^{3+}. Although the emission mechanism of polymer in the presence of metal cations is still glancing, it might be a novel approach for designing new fluorescent probe for Al^{3+}, Mg^{2+}, Ca^{2+}, Ag^{+}, Cu^{2+} and Fe^{3+}.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Nos. 21336005, 21371128 and 21176164).

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(Pan, B.; Qin, X.)