

Synthesis and Fluorescent Properties of Zn(II) Complex with Functionalized Polystyrene Containing Salicylaldehyde End Group

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Summary

Functionalized polystyrene ligand containing schiff base end group (N-Salicyliden-(4-methoxy-Anilin)) was obtained by condensation of *p*-methoxyanilin with polystyrene containing salicylaldehyde end group which was prepared through atom transfer radical polymerization (ATRP). The polystyrene ligand was applied to prepare Zn(II) complex. The polystyrene ligand and its complex were characterized through ¹H-NMR, IR, UV-Vis and fluorescent spectra. Compared with analogous Zn(II) complexes with small molecular schiff base, the complex was soluble in common solvents, easy to form film and showed intensive fluorescence. When excited at 330 nm, the complex emitted intense fluorescence at 500 nm. The effects of different molecular weights, amount of solvent in coordination reaction and reaction methods including conventional heating and microwave irradiation on Zn contents and fluorescent intensity were also discussed.

Keywords

ATRP, salicylaldehyde, fluorescence, Zn(II) complex, microwave

Introduction

Various applications of metal-schiff base complexes that can be used as catalysts[1], sensors[2], liquid crystalline materials[3] and model systems for biological macromolecules[4] have been extensively demonstrated. Zinc chelates coordinated with salicylaldehyde schiff base have been attracted much attention due to their intense fluorescence, relatively high photoluminescence quantum efficiency and good thermal stability [5-6]. However the geometry rigidity of complexes results in insolubility of these materials in common solvents and difficulty in forming film[7]. To solve this problem, the introduction of a flexible chain into complex has been studied recently. Liang reported novel stable monolayer membranes containing a flexible long alkyl chain in schiff base[8-9]. Sukwattanasimitt designed soluble salen polymers containing various lengths of glycolic chains between the chiral salen

units[7]. Kaliyappan synthesized new polymeric schiff base and its metal complexes, but the molecular weigh and polydispersity of polymeric schiff base were out of control[10].

However, our previous research focused on functionalized polystyrene containing salicylaldehyde end group with controlled molecular weight and narrow molecular weight distribution through ATRP[11]. Based on this, by condensation of salicylaldehyde group with *p*-methoxyanilin, polystyrene containing schiff base end group was obtained here in. The polystyrene ligand coordinated with Zn(II) was probably a potential macromolecular fluorescence material that was soluble in common solvents and easy to form film.

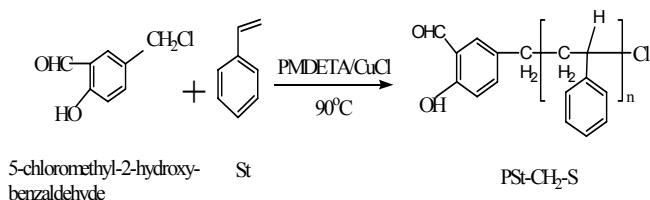
Experiment

Materials

p-methoxyanilin (chemical pure, Shanghai chemical Reagent Co.Ltd). N,N-Dimethylformide (DMF) (analytical pure, Shanghai chemical Reagent Co.Ltd) was distilled in vacuum. Tetrahydrofuran (THF) (AR, Changshu yangyuan chemical Reagent Factory) was dried with 4-Å molecular sieve. Zn(Ac)₂·2H₂O (CP, Suzhou jincheng chemical Reagent Factory). Styrene (CP, Shanghai chemical Reagent Co.Ltd) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with Magnesium sulfate anhydrous overnight, and finally distilled in vacuum. Copper(I) chloride (CuCl) (AR, Shanghai zhenxin chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with absolute ethanol and dried in vacuum. N,N,N',N',N'-pentamethyldiethyltriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuum. Cyclohexanone (AR, Shanghai chemical Reagent Co.Ltd) was dried with Magnesium Sulfate overnight and distilled in vacuum. Other agents were analytic pure and used without any purification. 5-chloromethyl-2-hydroxy-benzaldehyde obtained by chloromethylation of salicylaldehyde was used as initiator for the ATRP of styrene.

Preparation of PSt-CH₂-S through ATRP

CuCl, PMDETA, cyclohexanone (1.05g), initiator, styrene (1g) were added to a pressure tube. The tube was sealed under N₂ and placed in a 90°C oil bath. Samples were taken periodically for conversion and molecular weight analysis. Samples were dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.5, V/V), then filtrated and dried in vacuum.



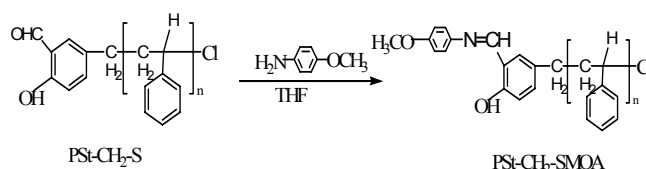
Scheme 1. ATRP of Styrene mediated by PMDETA/CuCl With 5-chloromethyl-2-hydroxy-benzaldehyde as initiator

Table 1. Percentage Yield, Molecular Weight and Polydispersity Index of Synthesized PSt (in cyclohexanone solution (50%v/v) at 90°C)

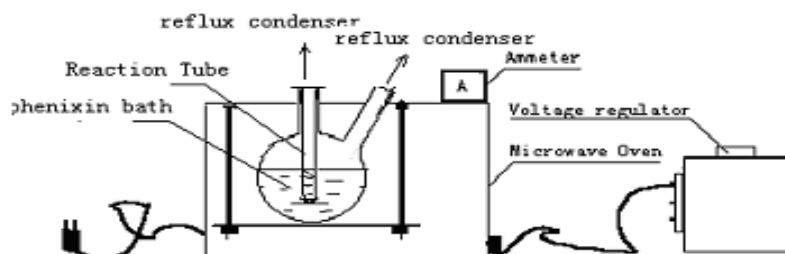
[St]/[initiator]/ [CuCl]/[PMDETA]	Polymerization h	Conversion %	Mn _{GPC}	Mw/Mn
100:1:1:1	5	26.7	4017	1.33
100:1:1:1	7	38.5	5800	1.37
200:1:1:1	9	45.5	9900	1.40

Condensation of PSt-CH₂-S with p-methoxyanilin

p-methoxyanilin (4mmol) was added to THF (20ml) solution containing 0.1mmol PSt-CH₂-S and refluxed for 24 hours. Then the sample was precipitated in a large amount of methanol, collected by filtration, dissolved in THF and precipitated in methanol again to remove residual *p*-methoxyanilin. The precipitation was filtrated and dried in vacuum. From the ¹H-NMR spectrum of PSt-CH₂-SMOA, we found the proton of -CHO completely disappeared. So the condensation reaction of salicylaldehyde with *p*-methoxyanilin was completed.

**Scheme 2.** Synthesis of PSt-CH₂-SMOA*Preparation of Zn based complex of PSt-CH₂-SMOA*

PSt-CH₂-SMOA (2*10⁻⁵mol) was dissolved in DMF (30ml), added Zn (Ac)₂·2H₂O (4*10⁻⁴mol) and stirred. The reactions proceeded at 25°C, 80°C or under microwave irradiation. The microwave-assisted coordination was performed in modified SAMSUNG M9D88 domestic microwave oven with electric current controller. The mixture was placed into a test tube, which had been dipped in a CCl₄ bath that was in a two-necked flask. The sketch map of the equipment was shown in Fig.1. After the reaction, the mixed solution was dropped into a large amount methanol and polymeric complex was precipitated, then filtrated, washed with deionized water and methanol respectively. The metal polymer was soluble in common organic solvents, such as THF, DMF, CH₂Cl₂, acetone, ether, etc.

**Figure 1.** Ketch map of the microwave assisted reaction equipment

Instruments

IR spectrum was measured by Perkin-Elmer577 FT-IR instrument (KBr pellet). $^1\text{H-NMR}$ was measured by INOVA 400MHz NMR instrument, with CDCl_3 as solvent. Element analysis was obtained by Carlo Erba-MOD1106 instrument. The purity of complex was analyzed by Waters 515 HPLC. Conversion for monomer was determined by gravimetry. Molecular weights and the molecular weight distributions of polystyrene were measured using waters 1515GPC with THF as a mobile phase at 30°C . UV-Vis spectrum was measured by Perkin-Elmer λ -17 UV-Vis instrument. Zn contents in the polymeric complex were determined by Leeman PLA-Specl induced coupled plasma (ICP) analysis. Emission and excitation spectrums of polymers were carried out in DMF solvent using Edinburgh-920 fluorescence spectra photometer at room temperature.

Results and discussion

Characterizations of polystyrene ligand (PSt- CH_2 -SMOA)

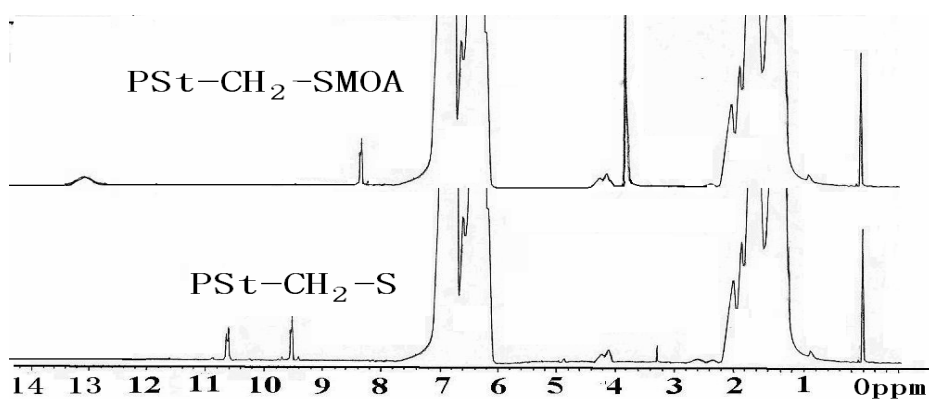


Figure 2. $^1\text{H-NMR}$ spectrum of PSt- CH_2 -S and PSt- CH_2 -SMOA ($M_{n(\text{GPC})}=5800$, $\text{PDI}=1.37$)

Fig.2 shows the $^1\text{H-NMR}$ spectrum of PSt- CH_2 -S and PSt- CH_2 -SMOA. In the $^1\text{H-NMR}$ spectrum of PSt- CH_2 -S, signals at 4.30-4.40ppm assign to the methine proton of $-\text{CH}_2\text{C}(\text{Ph})\text{H}-\text{Cl}$ at ω end. Signals at 9.72ppm, 10.82ppm are attributed to the protons of $-\text{CHO}$, $-\text{OH}$ respectively. So the end of polystyrene has functionalized by salicylaldehyde group and halide using 5-chloromethyl-2-hydroxy-benzaldehyde as initiator, CuCl as catalyst and PMDETA as ligand.

In the $^1\text{H-NMR}$ spectrum of PSt- CH_2 -SMOA, the signal at 9.72ppm disappears and new signals at 8.46-8.48ppm appear which assign to the methine proton of $-\text{CH}=\text{N}-$. The signal at 10.82ppm which assigns to the proton of $-\text{OH}$ shifts to 13.20ppm. Moreover, the signal at 3.83ppm assigns to the protons of $-\text{OCH}_3$.

As shown in the FT-IR spectrum of PSt- CH_2 -SMOA, the peak ($\nu(-\text{CHO})$) at 1657cm^{-1} disappears and the absorption band of the double $\nu(\text{C}=\text{N})$ bonds is observed at 1620cm^{-1} .

It is proved that the end group is changed from salicylaldehyde into N-Salicyliden-(4-Methoxy-anilin).

Characterizations of metal complex polymer (PSt-CH₂-SMOA-Zn)

UV-Vis spectrum

The UV-Vis spectrum of polystyrene ligand and its Zn(II) complex is showed in Fig.3. The $\pi-\pi^*$ transition occurs at 270, 330, 350nm for the pure ligand. When coordinated with Zn(II), the band at 350nm disappears and a new band at 410nm may be assigned to the charge transfers between central zinc atom and coordinated atoms.

IR spectrum

The IR spectrum of polystyrene ligand and its Zn(II) complex is showed in Fig.4. The band at 1620cm^{-1} ($\nu(\text{C}=\text{N})$) disappears and the absorption band of -OH shifts from 3436cm^{-1} to 3422cm^{-1} .

These indicate that the -CH=N, -OH are coordinated with the zinc(II) ion.

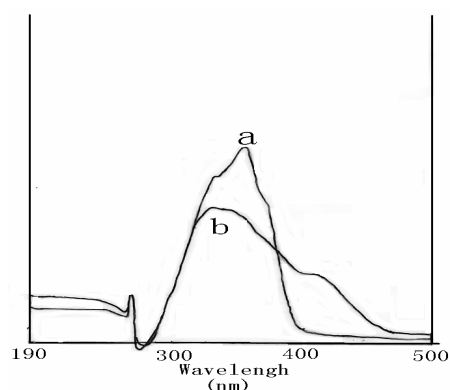


Figure 3. UV-vis spectrum of PSt-CH₂-SMOA(a) and PSt-CH₂-SMOA-Zn(b)

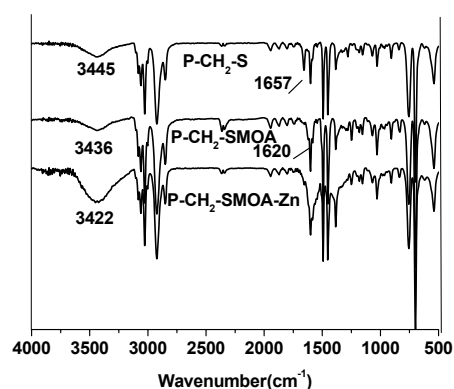


Figure 4. IR spectrum of PSt-CH₂-S, PSt-CH₂-SMOA and PSt-CH₂-SMOA-Zn

Structure study on PSt-CH₂-SMOA-Zn

In order to study the structure of PSt-CH₂-SMOA-Zn, we imitated the reaction of using N-Salicyliden-(4-Methoxy-anilin), which is the end group of the polymer to coordinate with Zn(II). N-Salicyliden-(4-Methoxy-anilin) was synthesized following the reported method[12]. Purity: 98.79%. Anal. Calcd(%) for SMOA: C, 74.10; H, 5.81; N, 6.17. Found: C, 74.01; H, 5.73; N, 6.17. ¹H-NMR: 3.78-3.84ppm(-OCH₃, 3H), 6.91-7.39ppm(phenyl protons, 8H), 8.61ppm(-CH=N-, 1H), 13.43ppm (-OH, 1H).

N-Salicyliden-(4-Methoxy-anilin) and Zn(Ac)₂·2H₂O were dissolved in absolute alcohol, stirred refluxed for 6h. The mixed solution was cooled in refrigerator for two days. Some red crystals were obtained. The result of element analysis of SMOA-Zn shows that experiment value(C 65.04%; H 4.70%; N 5.44%) is according with the theoretical value(C 64.99%; H 4.64%; N 5.42%) of the complex Zn(SMOA)₂.

UV-vis spectrum of SMOA-Zn shows the band at 350nm shifts to 410nm. And the IR spectrum of SMOA-Zn shows the absorption band of -OH shifts from 3437cm^{-1} to 3425cm^{-1} and the absorption band of -CH=N shifts from 1620cm^{-1} to 1613cm^{-1} . These indicate that the -CH=N, -OH are coordinated with the zinc(II) ion. Above results are consisted with that of the metal complex polymer.

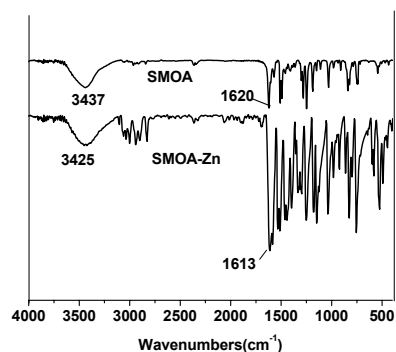


Figure 5. IR spectrum of SMOA and SMOA-Zn

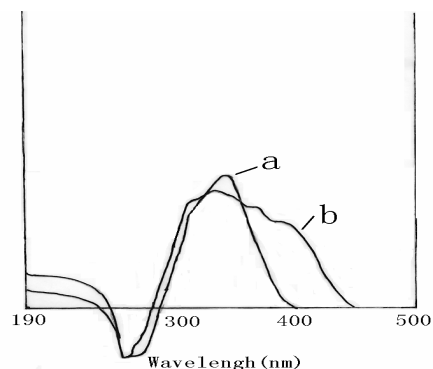


Figure 6. UV-Vis spectrum of SMOA(a) and SMOA-Zn(b)

Moreover, as shown in Fig.7, PSt-CH₂-SMOA-Zn and SMOA-Zn both emit fluorescence at 500nm with $\lambda_{ex}=330$ nm and the patterns are similar, though the fluorescent intensity of SMOA-Zn is slightly stronger than that of PSt-CH₂-SMOA which is probably caused by unsaturated coordination of polymer ligand owing to the curl of the chain of macromolecule.

It is also verified that PSt-CH₂-SMOA coordinated to Zn(II) in the similar way as in Zn(SMOA)₂. So it is presumed that one mole Zn(II) is coordinated to two mole polymer ligands in the metal complex polymer.

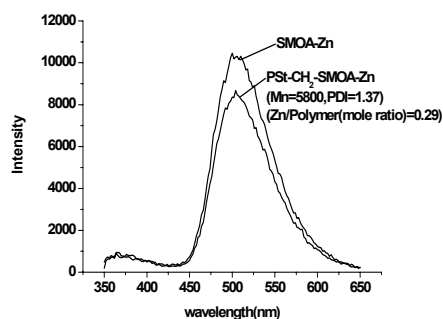


Figure 7. Comparison of fluorescent emission of PSt-CH₂-SMOA-Zn and SMOA-Zn in DMF (1.0×10^{-4} mol/L) with $\lambda_{ex}=330$ nm

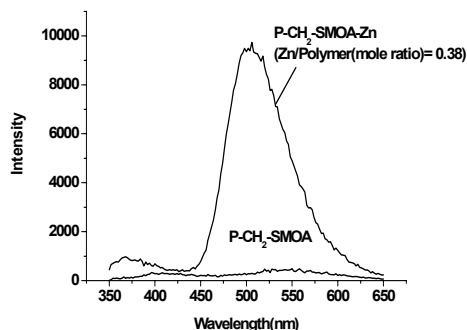


Figure 8. Comparison of fluorescent emission of PSt-CH₂-SMOA, PSt-CH₂-SMOA-Zn in DMF (1.0×10^{-4} mol/L) with $\lambda_{ex}=330$ nm ($M_{n(GPC)}=4017$, PDI=1.33)

Fluorescence spectrum

The fluorescent emission spectra of P-CH₂-SMOA and P-CH₂-SMOA-Zn are shown in Fig.8. When coordinated with Zn(II), the complex P-CH₂-SMOA-Zn emits obviously fluorescence at 500nm with $\lambda_{ex}=330$ nm. According to the previous research, the role of the Zn atom in the ligand of the complex is perhaps considered to be twofold[8,13.] First, the formation of the covalent bonds of N-Zn and O-Zn changes the emission energy which is caused by the lowering of the energy gap between π and

π^* owing to the enlarged conjugation length and enhance of electron flow. Second, the bonding of the ligand to Zn atom forms chelating rings which reduces the loss of energy via vibration motions and strengthens the emission. Compared with that of analogous reported complex $P(ZnL)$ [8], the emission of $P-CH_2-SMOA-Zn$ is obviously red-shift. It is probably explained that the phenyl and methoxy groups increase the electron density resulted in the decrease of the HOMO–LUMO band gap in the conjugated ligand.[14] The fluorescent intensity is also influenced by the conjugation length and variation of the substituents.

Effects of reaction conditions on Zn contents and fluorescent intensity

Effect of amount of solvent in coordination reaction

$PSt-CH_2-SMOA(2.0 \times 10^{-5} \text{ mol})$ and $Zn(Ac)_2 \cdot 2H_2O(4.0 \times 10^{-5} \text{ mol})$ were dissolved in different amount of DMF and stirred at 25°C for 12h. Fig.9 shows the evolution of Zn content in $PSt-CH_2-SMOA-Zn$ with amount of solvent in coordination reaction. With the increasing of amount of reaction solvent, the Zn content in $PSt-CH_2-SMOA-Zn$ increases. When solvent is 40ml, the Zn content reaches a maximum. While solvent continues to be added, the Zn content decreases. The reason is that dilute solution is helpful for the stretch of the chain of macromolecule. But the solution is too dilute, the collision probability of reaction is little.

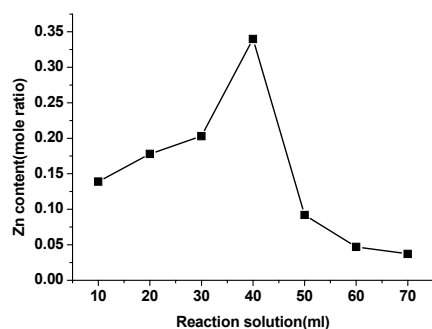


Figure 9. Evolution of Zn content in $PSt-CH_2-SMOA-Zn$ ($Mn_{(GPC)}=5800$, $PDI=1.37$) with amount of solvent in coordination reaction

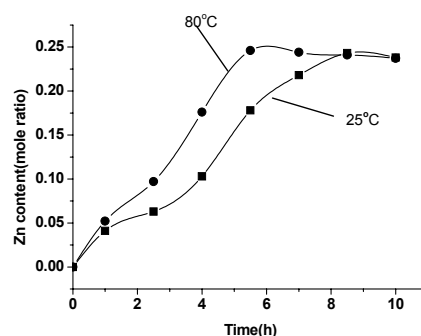


Figure 10. Evolution of Zn content in $PSt-CH_2-SMOA-Zn$ ($Mn_{(GPC)}=5800$, $PDI=1.37$) with reaction time at 25°C and 80°C

Effect of reaction method

$PSt-CH_2-SMOA(2.0 \times 10^{-5} \text{ mol})$ and $Zn(Ac)_2 \cdot 2H_2O(4.0 \times 10^{-5} \text{ mol})$ were dissolved in 30ml DMF and stirred at room temperature (25°C), 80°C and under microwave irradiation, respectively.

As shown in Fig.10, when the reaction proceeded at room temperature (25°C) and 80°C respectively, the Zn content all increases with the increasing of time and reaches equilibrium in the end. But it takes 8.5h to reach the equilibrium at 25°C , while 5.5h is needed at 80°C . So heating is helpful for the stretch of the chain of macromolecule.

Fig.11 shows the evolution of the Zn content with the reaction time under microwave irradiation. When electric current is 30mA, the Zn content increases rapidly in a short

time, while the reaction is carried for a longer time, Zn content decreases sharply. This is because the first stage is kinetics dominating, while the second stage is dynamic dominating. Microwave irradiation obviously accelerates the reaction rate. Maximum Zn content is got at only 80s which is bigger than that of in the equilibrium state with the other two reaction methods. Owing to the heating effect and irradiation effect, microwave irradiation causes the rapid shift of the dipole in the ligand. So it is helpful for the delivery of Zn(II) to polymer's end group that is embedded or surrounded by inert PSt chain in the polymer solution. Thus time for reaching maximum Zn content is shortened.

Fluorescence of different molecular weight of polystyrene ligand

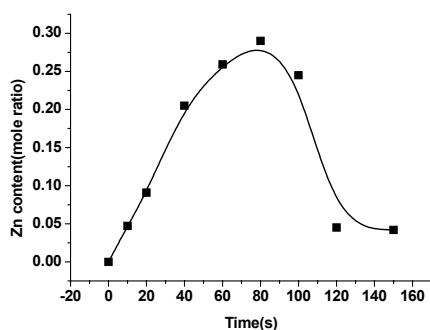


Figure 11. Evolution of Zn content in PSt-CH₂-SMOA-Zn(Mn_(GPC)=5800, PDI=1.37) with reaction time under microwave irradiation

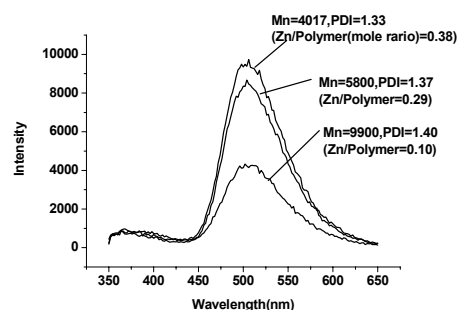


Figure 12. The fluorescent intensity of different molecular weight of the PSt-CH₂-SMOA-Zn with λ_{ex} =330nm in the same mass concentration (5mg polymer dissolved in 10 ml DMF)

Fig.12 shows the fluorescent intensity of different molecular weight of the PSt-CH₂-SMOA-Zn. All these samples are the same mass concentration. With increasing of molecular weight of the PSt-CH₂-SMOA, the Zn content in the complex decreases, accordingly and the fluorescent intensity reduces. It is probably attributed to the decrease of the amount of the end-functional group with the increasing of molecular weight of polystyrene ligand in the same unit volume and unsaturated coordination owing to the curl of the chain of macromolecule.

It can be concluded that the fluorescent intensity is in direct proportion to the Zn content.

Conclusions

Fuctionalized polystyrene containing salicylaldehyde end group was prepared through atom transfer radical polymerization (ATRP). Then polystyrene containing schiff base end group and its Zn(II) complex were synthesized. In the metal complex polymer, the mole ratio between Zn and polystyrene ligand might be 1:2. The polystyrene complex emitted very intensive fluorescence at 500nm with λ_{ex} =330nm. Choosing the suitable amount of solvent and small molecular weight of PSt could augment the fluorescent intensity. Microwave irradiation could accelerate the reaction rate. The metal complex polymer has good solubility and film-forming ability, which may be a prospective fluorescent material.

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