

Research Article

Synthesis and Characterization of Well-Defined Soluble Alq_3 - and Znq_2 -Functionalized Polymers via RAFT Copolymerization

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The reversible addition-fragmentation chain transfer (RAFT) copolymerizations of 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) with styrene (St) or methyl methacrylate (MMA) were successfully carried out in the presence of 2-cyanoprop-2-yl dithionaphthalenoate (CPDN). The polymerization behaviors showed the typical living natures by the first-order polymerization kinetics, the linear dependence of molecular weights of the polymers on the monomer conversions with the relatively narrow molecular weight distributions (M_w/M_n), and the successful chain extension experiments. The soluble polymers having tris(8-hydroxyquinoline)aluminum (Alq_3) and bis(8-hydroxyquinoline) zinc(II) (Znq_2) side chains were obtained via complexation of the polymers with aluminium isopropoxide or zinc acetate in the presence of monomeric 8-hydroxyquinoline, which had strong fluorescent emission at 520 nm. The obtained polymers were characterized by GPC, ^1H NMR, UV-vis, and fluorescent spectra.

1. Introduction

In recent years, organic electroluminescence (EL) display devices have attracted more intensive attention as a promising technology for flat panel display [1]. Many emitting materials, including low-weight molecules and polymers, have been designed and utilized in fabricating organic light emitting diodes (OLEDs) [2–5]. Among them, metal 8-hydroxyquinoline (Mq_n) chelates, especially for tris(8-hydroxyquinoline)aluminum (Alq_3), and bis(8-hydroxyquinoline) zinc(II) (Znq_2) have been extensively investigated for their high stabilities, good emissions, and electron-transporting properties [6–8]. Compared with low-weight 8-hydroxyquinoline (Mq_n) chelate, the polymers containing Mq_n pendant groups combine the fluorescent property of Mq_n and the processability of the polymer [6, 7, 9]. Up to now, two types of Mq_n -containing polymers (main-chain type and side-chain type) have been reported. Yamamoto and Yamauchi reported the synthesis

of poly(quinolinol) [10] and poly(aryleneethynylene) [11] containing 8-quinolinol moieties. On the other hand, various side-chain type polymers including poly(arylene ether) [12], copolymers of 7-allyl-, or 7-(2-methylvinyl)-functionalized derivatives of 8-hydroxyquinoline with styrene [13], functionalized polystyrene [14], and copolymers of methacrylates having 8-hydroxyquinoline moieties were also successfully prepared [15]. Furthermore, Mq_n -containing polymers were obtained by the reaction of the above polymers with metal compounds in the presence of monomeric 8-hydroxyquinoline. Meyers and Weck, reported the synthesis of an Alq_3 -functionalized polymer via ring-open metathesis polymerization of norbornene monomer containing Alq_3 unit [6]. Most recently, Liang et al. reported the formation of Al^{3+} complex micelles via self-assembly of diblock copolymers containing pendent 8-hydroxyquinoline units [16]. However, the molecular weights and molecular weight distributions of the obtained polymers containing Mq_n units were not well controlled in most cases.

The development of controlled/“living” radical polymerization (CRP) methods, such as atom transfer radical polymerization (ATRP) [17–19], nitroxide-mediated radical polymerization (NMRP) [20], reversible addition-fragmentation chain transfer (RAFT) [21] polymerization, and single-electron transfer mediated living radical polymerization (SET-LRP) [22] lead to unprecedented opportunities in design and synthesis of functional polymer materials. Among them, RAFT technique has been considered as one of the most advantageous techniques due to the mild reaction conditions, functional group compatibility, and versatility to monomers. Up to date, RAFT polymerization have been applied to a wide variety of monomers, including functionalized monomers, such as methyl methacrylate, styrene, methyl acrylate, acrylamide, 6-[4-(4-methoxyphenyl)phenoxy] hexyl methacrylate, and 3-[tris(trimethylsiloxy)silyl] propyl methacrylate [23]. However, the living radical polymerization of vinyl monomers containing 8-quinolinol moieties is rarely reported [16], although the common radical polymerization of vinyl monomers containing 8-quinolinol moieties have been successfully conducted [12–15].

From these points of view, we investigated the feasibility of preparation of 8-hydroxyquinoline-containing soluble polymers via RAFT technique. Furthermore, the well-defined side-chain M_{q_n} -containing ($M = Al$ and Zn) polymers were also prepared via complexation of the polymers with aluminium isopropoxide and zinc acetate, respectively, and their optical properties were also investigated.

2. Experimental Part

2.1. Materials. Styrene (St) and methyl methacrylate (MMA) (chemically pure, Shanghai Chemical Reagent Co. Ltd) were purified by extracting with a 5% sodium hydroxide aqueous solution, followed by washing with water and dried with anhydrous magnesium sulfate overnight, finally distilled freshly before use. 2,2'-Azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Co. Ltd, China, 99%) was recrystallized two times from ethanol. 2-Hydroxyethyl methacrylate (HEMA) (Alfa Aesar, 98%), 8-hydroxyquinoline (Alfa Aesar, 98%), aluminium isopropoxide (Alfa Aesar, 98%), sodium acetate (analytical reagent, Shanghai Chemical Reagent Co. Ltd), and zinc acetate (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were used as received. Carbon disulphide (analytical reagent, Shanghai Chemical Reagent Co. Ltd), 1-bromonaphthalene (Alfa Aesar, 98%), and tetrahydrofuran (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were dried by 4 Å molecular sieve before use. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) [24] and 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) [25] (Scheme 1) were synthesized according to the references, respectively. Unless otherwise specified, all other chemicals were purchased from Shanghai Chemical Reagents Co. Ltd and used as received without further purification.

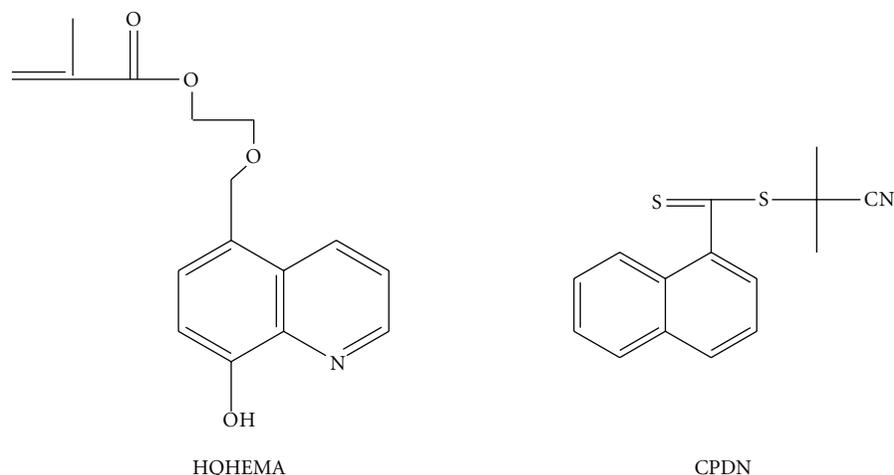
2.2. RAFT Copolymerization of HQHEMA with St or MMA. The typical procedures for the RAFT copolymerization are as

follows: 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) (0.251 g, 0.873 mmol), styrene (St) (1 mL, 8.73 mmol), 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) (26.02 mg, 0.096 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (1.57 mg, 0.0096 mmol), ($[M]_0/[CPDN]_0/[AIBN]_0 = 1000:10:1$, $M = (HQHEMA + St)$, $[St]_0/[HQHEMA]_0 = 10:1$) were added to a dry glass ampoule with a magnetic bar. The solution was bubbled with argon for approximately 10 minutes to eliminate the oxygen, and then the ampoule was flame-sealed under argon atmosphere and placed in the water bath at 70°C. At the designed time, the ampoule was opened, and the contents was diluted with about 2 mL THF, and precipitated into 250 mL methanol. The sample was obtained by filtration and dried to constant weight under vacuum. The conversion of the monomer was determined by gravimetry. The procedures of copolymerization of HQHEMA with MMA are similar to those described above.

2.3. Chain Extension Experiment with St or MA. The procedures of chain extension experiment are similar to those mentioned above except CPDN was substituted by poly(HQHEMA-co-St) or poly(HQHEMA-co-MMA) and the second monomer is St and methacrylate (MA), respectively.

2.4. Preparation of Alq_3 -Polymer Complex. To a 20 mL THF solution containing poly(HQHEMA-co-St) ($M_{n(GPC)} = 5400$ g/mol, $M_w/M_n = 1.17$, (St unit)/(HQHEMA unit) = 7:1 based on the 1H NMR spectrum) (4.32 g, 0.8 mmol) and 8-hydroxyquinoline (0.493 g, 3.4 mmol) was added dropwise a 10 mL THF solution of aluminium isopropoxide (0.265 g, 1.3 mmol). The reaction mixture was stirred at room temperature for 1 hour and at 50°C for another 17 hours. After being cooled to room temperature, the solution was poured into methanol. To remove any trace amounts of low molecular weight Alq_3 , the reprecipitation was repeated several times until the methanol solution was not colored anymore to yield the product as a light yellow solid (3.66 g, 85%). The similar procedures were used to prepare Znq_2 -polymer complex.

2.5. Characterization. 1H NMR spectra of the polymers were recorded on an INOVA 400 MHz NMR instrument, using $CDCl_3$ as solvent and TMS as the internal standard. The molecular weight and molecular weight distribution of the polymer was determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with poly(methyl methacrylate) standard sample. UV-vis absorption spectra were performed on a Shimadzu UV-240 recording spectrophotometer at room temperature in $CHCl_3$ solutions. The fluorescence emission spectra were obtained on a PerkinElmer LS-50B Fluorescence spectrophotometer in $CHCl_3$ at room temperature. The metal ion concentrations were determined by VISTA-MPX CCD Simultaneous ICP-AES, and the operation conditions are listed: plasma flow rate: 15 L min^{-1} ; carrier gas (Ar) flow rate: 1.5 L min^{-1} ; incident power (kW): 1.2 kW; vaporization press: 240 kPa.



SCHEME 1: The chemical structures of 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) and 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN).

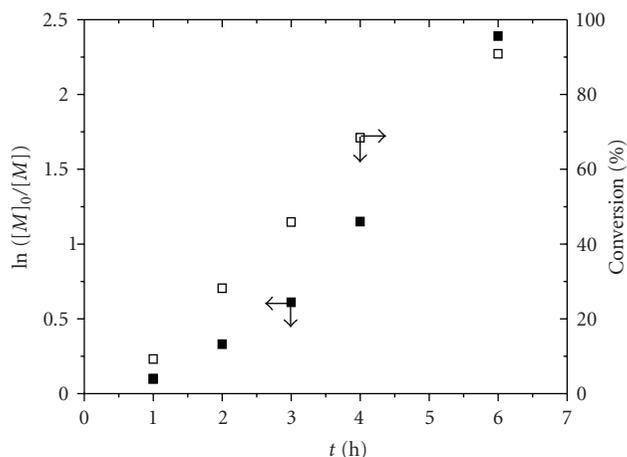


FIGURE 1: $\ln([M]_0/[M])$ and monomer conversion versus polymerization time. Kinetic plot of RAFT copolymerization of HQHEMA and MMA. Polymerization conditions: $[\text{Monomer}]_0/[\text{CPDN}]_0/[\text{AIBN}]_0 = 1000:10:1$, $[\text{Monomer}]_0 = [\text{MMA}]_0/[\text{HQHEMA}]_0 = 10:1$; $T = 70^\circ\text{C}$.

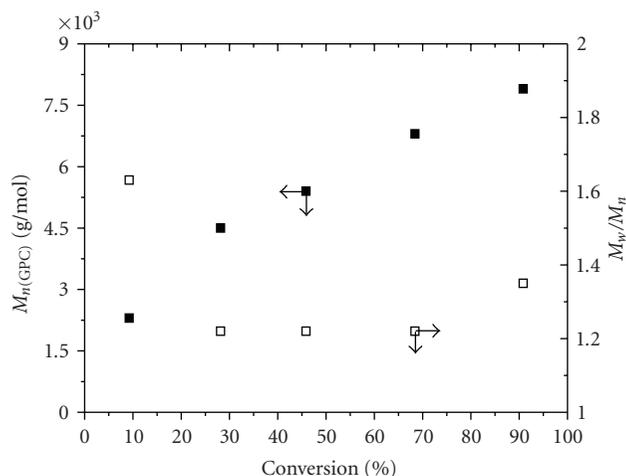


FIGURE 2: Dependence of molecule weights and molecule weight distributions on monomer conversions for RAFT copolymerization of HQHEMA and MMA. Polymerization conditions are the same as in Figure 1.

3. Results and Discussion

3.1. RAFT Copolymerization of HQHEMA and MMA. The monomer containing 8-hydroxyquinoline moiety, 2-((8-hydroxyquinolin-5-yl)methoxy)ethyl methacrylate (HQHEMA) was often used to prepare side-chain Mq_n -containing ($M = \text{Al}$ or Zn) polymers. However, the Mq_n -containing PHQHEMA was also difficult to be dissolved in common organic solvents. Takayama et al. [9] increased the solubility of the polymer via introducing alkyl side chain in 7-position of 8-hydroxyquinoline unit. We aimed to increase the processability of Mq_n -containing polymer by copolymerization of HQHEMA with other vinyl monomers. Firstly, we conducted atom transfer radical copolymerization (ATRP) of HQHEMA with St or MMA, however, no polymer was obtained, which may be due to the

coordination between 8-hydroxyquinoline and catalyst ($\text{CuBr}/\text{Ligand}$) used in ATRP and resulted in the catalyst ineffective [16]. RAFT copolymerizations of HQHEMA with MMA or St were successfully carried out in the presence of 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN). The results are presented in Figures 1–4 and Tables 1 and 2, respectively. Figure 1 illustrates the kinetic plot for the copolymerization of HQHEMA and MMA. The linear relationship between $\ln([M]_0/[M])$ and the reaction time can be observed, which indicated that the polymerization was first-order with respect to the monomer, and the radical concentration remained constant throughout the polymerization process. Figure 2 presents the dependence of the molecular weight and molecular weight distribution (M_w/M_n) on the monomer conversion for the RAFT copolymerization of HQHEMA and MMA. The molecular

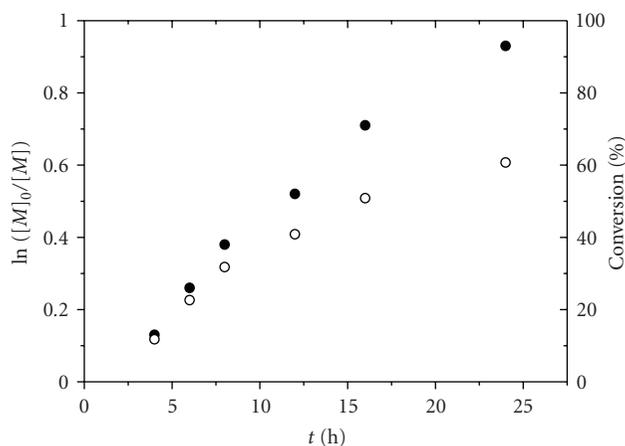


FIGURE 3: $\ln([M]_0/[M])$ and monomer conversion versus polymerization time. Kinetic plot of RAFT copolymerization of HQHEMA and St. Polymerization conditions: $[\text{Monomer}]_0/[\text{CPDN}]_0/[\text{AIBN}]_0 = 1000:10:1$, $[\text{Monomer}]_0 = [\text{St}]_0/[\text{HQHEMA}]_0 = 10:1$; $T = 70^\circ\text{C}$.

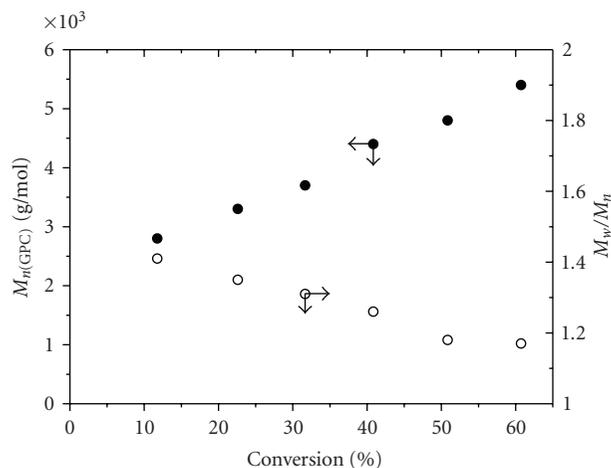


FIGURE 4: Dependence of molecule weights and molecule weight distributions on monomer conversions for RAFT copolymerization of HQHEMA and St. Polymerization condition are the same as in Figure 3.

weight of poly(HQHEMA-*co*-MMA) measured by GPC ($M_{n(\text{GPC})}$) increased linearly with the monomer conversion while keeping the relatively narrow molecular weight distribution ($M_w/M_n \leq 1.63$). The influence of the molar ratio of $[\text{CPDN}]_0/[\text{AIBN}]_0$ on the polymerization was also investigated. As shown in Table 1, the polymerization rate obviously decreased with increasing the initial concentration of CPDN in the polymerization system, which was agreed well with the RAFT polymerization mechanism [26].

3.2. RAFT Copolymerization of HQHEMA and St. The copolymerization of HQHEMA and St mediated by CPDN was also conducted and the results are given in Figure 3, Figure 4, and Table 2. Figure 3 shows the kinetic plot of $\ln([M]_0/[M])$ versus polymerization time. The resulting slope indicates this copolymerization proceeded with

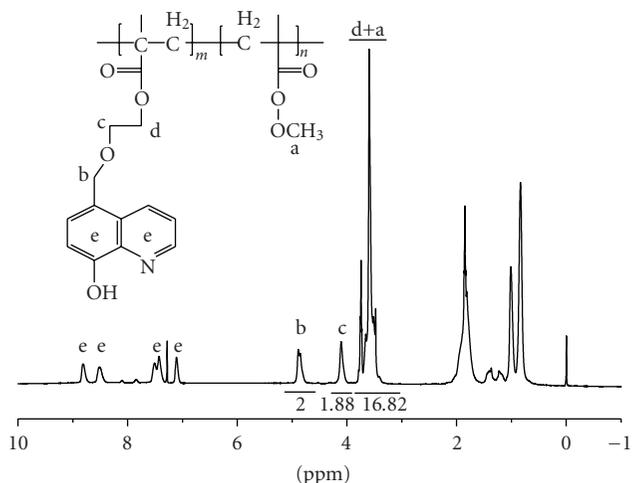


FIGURE 5: The ^1H NMR spectrum of random copolymer of HQHEMA and MMA (poly(HQHEMA-*co*-MMA)) in CDCl_3 .

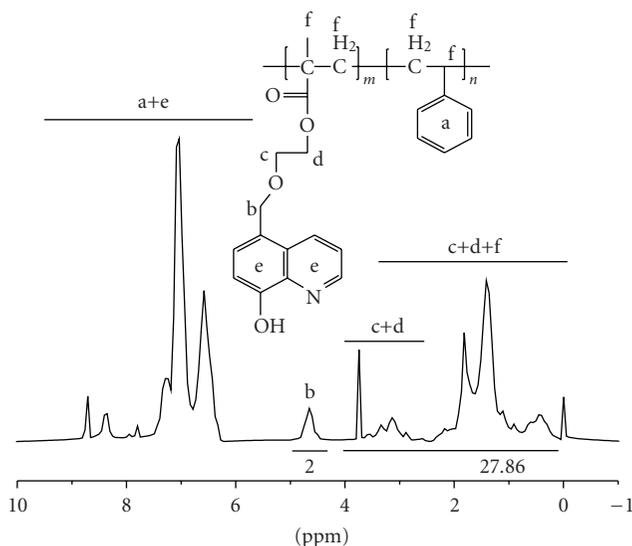


FIGURE 6: The ^1H NMR spectrum of random copolymer of HQHEMA and St (poly(HQHEMA-*co*-St)) in CDCl_3 .

approximately constant number of active species for the duration of the reaction. Figure 4 presents the molecular weight measured by GPC ($M_{n(\text{GPC})}$) and molecular weight distribution (M_w/M_n) of poly(HQHEMA-*co*-St) as a function of monomer conversion. Both the linear $M_{n(\text{GPC})}$ versus monomer conversion plot and the corresponding narrow molecular weight distribution imply the living nature of RAFT copolymerization. As expected, increasing the RAFT agent concentration (CPDN) decreased the polymerization rate as presented in Table 2 (entries 1–3).

3.3. Characterization of Copolymers and Chain Extension Experiment. The obtained copolymers were characterized by ^1H NMR spectra as shown in Figures 5 and 6. In Figure 5, the signal $\delta = 3.70$ ppm (a) was attributed to the methyl protons of the MMA units, and the signals $\delta =$

TABLE 1: RAFT copolymerization of HQHEMA and MMA with different CPDN concentrations.

$([\text{MMA}]_0 : [\text{HQHEMA}]_0) : [\text{CPDN}]_0 : [\text{AIBN}]_0$	t	T ($^{\circ}\text{C}$)	Conversion (%)	$M_{n(\text{GPC})}$ (g/mol)	M_w/M_n
1000(10 : 1) : 10 : 1	3	70	45.9	5500	1.22
1000(10 : 1) : 5 : 1	3	70	72.0	11500	1.52
1000(10 : 1) : 3 : 1	3	70	99.1	19100	1.27

TABLE 2: RAFT copolymerization of St and HQHEMA with different CPDN concentrations.

$([\text{St}]_0 : [\text{HQHEMA}]_0) : [\text{CPDN}]_0 : [\text{AIBN}]_0$	t (h)	T ($^{\circ}\text{C}$)	Conversion (%)	$M_{n(\text{GPC})}$	M_w/M_n
1000(10 : 1) : 10 : 1	12	70	40.8	4400	1.26
1000(10 : 1) : 5 : 1	12	70	66.3	7800	1.20
1000(10 : 1) : 3 : 1	12	70	71.1	10100	1.18

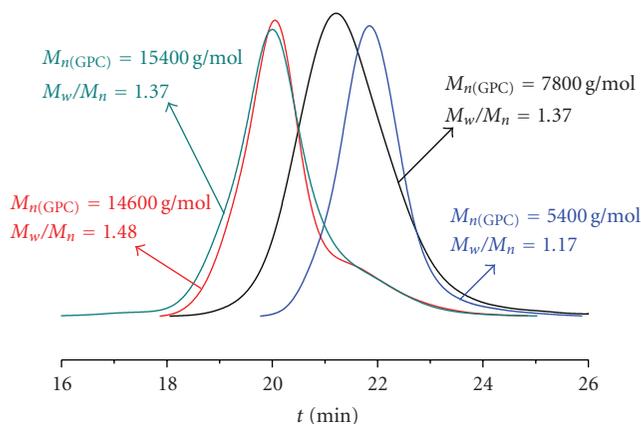


FIGURE 7: GPC curves of macro-RAFT agent (poly(HQHEMA-*co*-MMA) and poly(HQHEMA-*co*-St)) and polymers after chain-extension. Chain-extended experiment conditions: $[\text{St}]_0 : [\text{poly}(\text{HQHEMA-}co\text{-MMA})]_0 : [\text{AIBN}]_0 = 500 : 5 : 1$, $t = 24$ hour, $T = 70^{\circ}\text{C}$, conversion (%) = 68.6%; $[\text{MA}]_0 : [\text{poly}(\text{HQHEMA-}co\text{-St})]_0 : [\text{AIBN}]_0 = 500 : 5 : 1$, $t = 3$ hour, $T = 80^{\circ}\text{C}$, conversion (%) = 75.3%. Poly(HQHEMA-*co*-St) (-), poly(HQHEMA-*co*-MMA) (-), poly(HQHEMA-*co*-St)-*b*-PMA (-), poly(HQHEMA-*co*-MMA)-*b*-PS (-).

7.10 ppm (e), 7.44 ppm (e), 7.53 ppm (e), 8.54 ppm (e), and 8.83 ppm (3) demonstrate the existence of HQHEMA units, which confirmed that HQHEMA and MMA units were contained in the polymer chain. Based on Figure 5, we also can calculate that the ratio of HQHEMA unit to MMA unit is near 5 : 1 in the copolymer chain. In Figure 6, the signal $\delta = 6.40 - 7.10$ ppm (b) of protons of phenyl ring and the signals $\delta = 7.53$ ppm (e), 8.54 ppm (e), and 8.83 ppm (e) of protons of 8-hydroxyquinoline units indicate the polymer chain contains HQHEMA and St units. The near 7 : 1 ratio of HQHEMA to St unit is also calculated based on Figure 6. To further prove the “living” nature of RAFT polymerization, the obtained copolymers, poly(HQHEMA-*co*-MMA), and poly(HQHEMA-*co*-St) were both used as macro-RAFT agents to conduct chain extension reactions with St and MA as the second monomers, respectively. GPC curves for the block copolymers are shown in Figure 7. It can be seen from Figure 7 that the peaks shift to higher molecular weights from macro-RAFT agent to the chain-extended

block copolymers. The molecular weights increased from 7800 g/mol ($M_w/M_n = 1.37$) to 15400 g/mol ($M_w/M_n = 1.37$, 68.6% conversion) with poly(HQHEMA-*co*-MMA) as the macro-RAFT agent and St as the second monomer, and from 5400 g/mol ($M_w/M_n = 1.17$) to 14600 g/mol ($M_w/M_n = 1.48$, 79.3% conversion) with poly(HQHEMA-*co*-St) as the macro-RAFT agent and MA as the second monomer. These results reveal that almost all the macro-RAFT agents participate in the block copolymerization of MA or St, and block copolymers poly(HQHEMA-*co*-MMA)-*b*-PS and poly(HQHEMA-*co*-St)-*b*-PMA are formed in a controlled manner.

3.4. Synthesis of Alq_3 and Znq_2 -Containing Copolymer.

Formation of Alq_3 -containing copolymers was performed in THF using poly(HQHEMA-*co*-St) (8-hydroxyquinoline unit/St unit = 1 : 7), 8-hydroxyquinoline and aluminium isopropoxide in a ratio of 8 : 8 : 3. The use of excess 8-hydroxyquinoline and aluminium isopropoxide was adopted in order to minimize the formation of interchain cross-linked complexes. The obtained polymer complex was soluble in several common organic solvents, such as chloroform (CHCl_3), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF). The Formation of Znq_2 -containing copolymers was also successfully obtained via the similar procedures. As shown in Figure 8, the color of the polymer complex (solid and CHCl_3 solution) turned from slightly red to yellow, which demonstrated the successful coordination reaction between metal ion (Al^{3+} and Zn^{2+}) and 8-hydroxyquinoline units. The metal (Al and Zn) ion concentrations of final samples were also determined by VISTA-MPX CCD Simultaneous ICP-AES, and the results are 6.5×10^{-6} mol/L for Al^{3+} and 9.5×10^{-6} mol/L for Zn^{2+} , respectively. The above results demonstrated that the metal ions (Al^{3+} and Zn^{2+}) molar ratios to 8-hydroxyquinoline unit are both close to 1 : 3 and 1 : 2, respectively, which demonstrated that almost all 8-hydroxyquinoline units in the copolymer chains were successfully complexed to form Alq_3 and Znq_2 in the side chain.

UV-vis and fluorescent spectra of the Alq_3 - and Znq_2 -containing copolymers were investigated as shown in Figures 9 and 10. In Figure 9, the Alq_3 - and Znq_2 -containing copolymers had the absorption in the range of 300 nm and 450 nm, which were the typical UV-vis absorption of

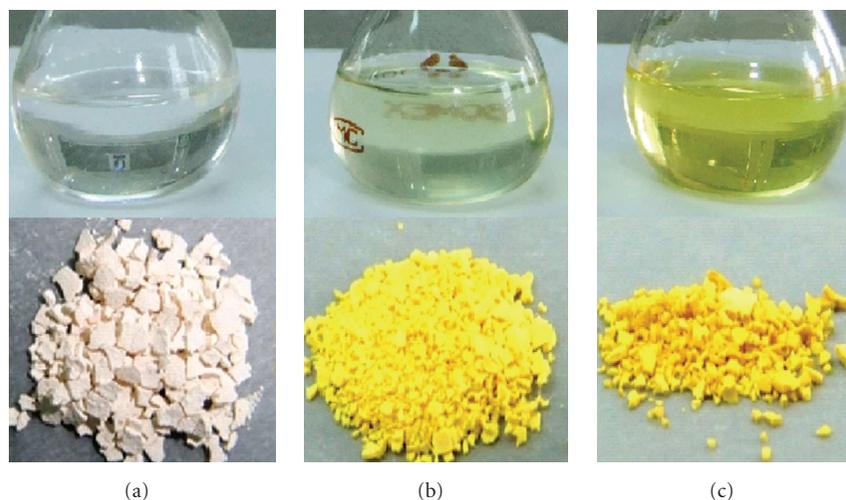


FIGURE 8: The images of poly(HQHEMA-*co*-St) and the corresponding Alq₃- and Znq₂-containing copolymers in solid and solution, respectively. (a) poly(HQHEMA-*co*-St); (b) Znq₂-containing poly(HQHEMA-*co*-St); (c) Alq₃-containing poly(HQHEMA-*co*-St). The concentration of 8-hydroxyquinoline moieties is 2.0×10^{-5} M for all the solutions.

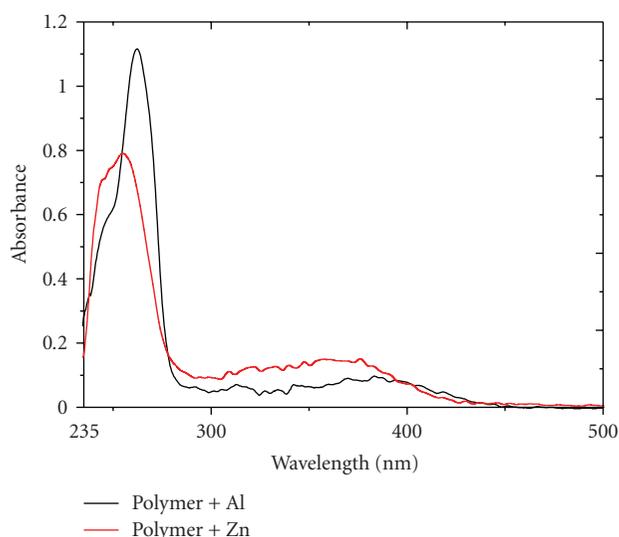


FIGURE 9: The UV-vis absorption spectra of Alq₃- and Znq₂-containing copolymers in CHCl₃. The concentration of 8-hydroxyquinoline moieties is 2.0×10^{-5} M.

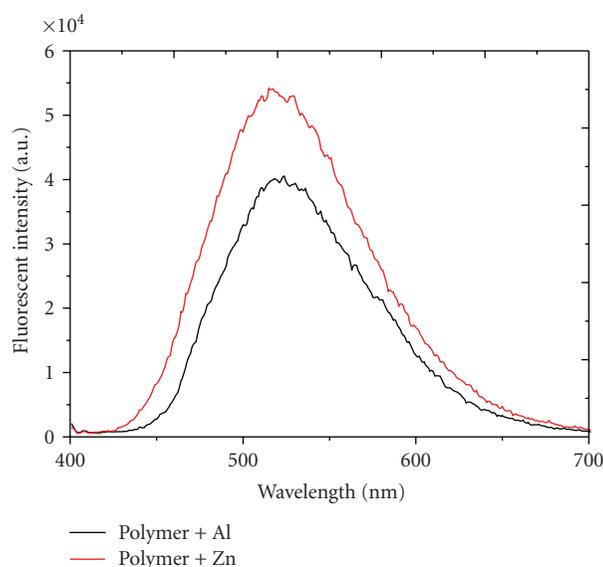


FIGURE 10: The fluorescence spectra of Alq₃- and Znq₂-containing copolymers in CHCl₃. The concentration of 8-hydroxyquinoline moieties is 2.0×10^{-5} M and excitation wavelength is 380 nm.

Alq₃- and Znq₂ complexes. Figure 10 presented the fluorescent spectra of Alq₃- and Znq₂-containing copolymers with an excitation wavelength of 380 nm. As expected, the Alq₃- and Znq₂-containing copolymers had strong emission at around 520 nm. These studies clearly show that the optical properties of Alq₃ and Znq₂ are preserved in the copolymers, respectively.

4. Conclusion

The well-defined poly(HQHEMA-*co*-MMA) and poly(HQHEMA-*co*-St) were successfully prepared via RAFT copolymerization of HQHEMA and MMA (or St)

mediated by a typical RAFT agent (CPDN). The soluble copolymers having Alq₃ and Znq₂ side chains were obtained via complexation of the polymers with aluminium isopropoxide and zinc acetate in the presence of monomeric 8-hydroxyquinoline, respectively, which had typical UV-vis absorption in the range from 300 nm to 450 nm and strong fluorescent emission at 520 nm.

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