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End-capped polystyrene with 8-hydroxyquinoline group by ATRP method

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Abstract

8-Hydroxyqunioline end-capped polystyrene was prepared through atom transfer free radical polymerization (ATRP) with 8-(5-chloromethyl) quinolyl acetate as initiator. The results indicated that this polymerization is a first order reaction with respect to monomer conversion. The molecular weight increased linearly with monomer consumption and very narrow distribution of molecular weight was obtained (polydispersity index less than 1.2). The FT-IR and NMR results show that the 8-hydroxyquinloine group was chemically bonded to the polymer end and there is nearly one 8-hydroxyquinoline group in per polymer chain. All those data show that polymerization of styrene at such conditions displayed living characters. The polymer with 8-hydroxyqquinoline end group reacted with triethylaluminum to form polymeric light-emitting complex and single layer LED was prepared by common spin-coating method. The peak wavelength of LED based on synthesized polymeric complex was around 570 nm.

Keywords: Atom transfer free radical polymerization; 8-(5-Chloromethyl)quinolyl acetate; Polystyrene

1. Introduction

End-capped oligomers and polymers play an important role in polymer design and find many applications in polymer industry [1]. Numerous methods have been developed to prepare end-functionalized polymer, such as ionic polymerization [2], free radical polymerization by chain transfer reagent [3]. Anionic polymerization has been widely utilized to synthesize the hydroxyl and carboxyl end-capped polymers for its easy controllability of polymer structure. But most anionic polymerizations always carried out at very low temperature and needed complete exclude the moisture and oxygen. Only a few monomers can be used and some side reaction took place to lower the functionality efficiency. Radical polymerization is another practical method to reach this goal. Chain transfer reagents, such as –SH group-containing organic compound, are always used to prepare various functional group end-capped polymer. But the molecular weight is always out of control and the average content of functional group per molecular chain is below unit. That means not all polymer chains are end-caped by expected functional group. In order to raise the functionality efficiency, some new method also developed to synthesize the end-functionalized polymer with well-defined polymer structure, such as iniferters [4], nitroxides [5], Co-based systems [6], degenerative transfer with alkyl iodides [7], the RAFT-process [8], and Ru [9], Ni-mediated polymerizations [10].

Most recently, atom transfer radical polymerization (ATRP) attracts much attention and various functional compounds with active C–X bond acted as initiator to initiate the polymerization [11]. ATRP can be carried out at normal free radical polymerization conditions and numerous kinds of monomer, such as styrene [12], acrylate [13] and methacrylate [14], polymerized smoothly under standard ATRP conditions. Some functional monomer, namely hydroxyethyl acrylate [15], glycidyl acrylate [16], can directly form functional polymer though ATRP method. By chosing functional initiator, end-capped polymer with well-defined structure can directly be obtained by ATRP. This method has been carefully reviewed by Matyjaszewski [17]. Up to now, many end-functionalized polymers were obtained by ATRP. Carboxylic acid group, hydroxyl group, epoxy group, double bond have been attached to the polymer end to form telecthelic polymer.

From 1990, organic and polymeric light-emitting diodes (LED) have been studied extensively by many research groups. Both organic compounds and conjugated polymers have been adopted to prepare the electroluminescent devices [18,19]. Among all light-emitting materials tris(8-hydroxyquinoline)-aluminum (AlQ3) complexes have been paid close attention because they can form stable thin films, exhibit high

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electron-transport mobility, and have good solid-state luminescent yields. Traditional method to prepare the AlQ3-based LED is vacuum-deposition procedure. Comparing with the spin-coating procedure suitable for polymer-based LED, the former method is complicated and not suitable for large-scale production. In order to improve the processability of AlQ3, some efforts have been paid to design and synthesize soluble AlQ3-containing polymer. In 2000 Hay's group reported the synthesis and properties of AlQ3-containing poly(arylene ether) [20]. They first prepared the poly(arylene ether) with 8-hydroxy-quinoline side group, then the precursor polymer reacted with organic aluminum and excess 8-hydroxyquinoline to obtain soluble AlQ3-containng poly(arylene ether). Then Weck's [21] group reported a novel route to prepare AlQ3-containing polymer. They first synthesized the functional AlQ3 monomer with polymerisable norbornene unit that can be polymerized using ring-opening metathesis polymerization (ROMP), then the AlQ3 monomer was copolymerized with norbornene derivatives to obtain the desired polymer. The concentration of AlQ3 in this polymer was higher than that in polymer reported by Hay. Here we reported a new and convenient method to prepare the 8-hydroxyquinoline end-capped polymer which can be used as polymeric ligand for aluminum ion.

2. Experimental section

8-Hydroxyquinoline, formaldehyde (36–38%), HCl acid were obtained from Shanghai Chemical Reagent Company, Ltd 8-hydroxyquinoline(Q) purified by recrystallization before use. Styrene (Fisher, Pittsburgh, PA) was purified by removing inhibitor by filtering through aluminum oxide column and then stirred with calcium hydride overnight and distilled under reduced pressure. The purified styrene was kept below -5 °C in inert atmosphere. Cu(I)Br (Acros, Pittsburgh, PA) was purified in a glove box by stirring with glacial acetic acid and filtering to remove any traces of Cu(II). The Cu(I)Br was then washed with ethanol and kept in a glove box to protect Cu(I)Br from oxidation. 2,2′-Bipyridine (J&K Chemical Ltd, Beijing) was recrystalliaztion befor use. Triethylaluminum (1.0 M in hexane), acetyl chloride (J&K Chemical Ltd, Beijing), anisole, tetrahydrofuran (THF; HPLC grade, unstabilized; JT Baker, Phillipsburg, NJ) were used as received.

2.1. Synthesis of 5-chloromethyl-8-hydroxyquinoline [22]

A mixture of 14.6 g (0.1 mol) 8-hydroxyquinoline, 16 ml of 32% hydrochloric acid and 16 ml (0.1 mol) of 37% formaldehyde at 0 °C was treated with hydrogen chloride gas for 6 h. The solution was allowed to stand at room temperature overnight without stirring. The yellow solid was collected on a filter and dried to give 5-chloromethyl-8-hydroxyquinline hydrochloride 21.6 g. ^{1}H NMR (250 MHz, CDCl3): 5.32(s, 2H), 7.53(m,1H), 7.58(m,1H), 8.12(m,1H), 9.12(m,1H), 9.28(m,1H).

2.2. Synthesis of 8-(5-chloromethyl)quinolyl acetate [23]

To a stirred solution of crude 5-chlromethyl-8-hydroxyquinoline hydrochloride (230 mg, 1 mmol) in dry DMF (5 ml) at 0 °C, pyridine (0.3 ml, 2.5 mmol) and cooled acetyl chloride (0.3 ml, 2.5 mmol) were added dropwise under Ar. After finishing addition the reaction mixture was stirred continuously and let the temperature raise to room temperature without heating and kept at this temperature for 2 h. After cooling to 0 °C, 10 ml cooled water was added, and the resulting mixture was stirred at 0 °C for 20 min. The mixture was then extracted with chloroform (3×20 ml). The combined organic layer was washed with saturated $NaHCO_3$ (2×20 ml), brine (2×20 ml) and dried over Na_2SO_4. Evaporation afforded the crude compound (180 mg, 75%) as a light brown solid and which was purified by recrystallization to get white product. Mp 121–122 °C, ^{1}H NMR (250 MHz, $CDCl_3$): 2.25(s, 3H), 4.98(s, 2H), 7.40(m,1H), 7.55(m,2H), 8.47(m,1H), 8.96(s, 1H). Anal. Calcd for $C_{10}H_{10}ClNO_2$: C, 61.16%; H, 4.28%; N, 5.94%. Found: C, 61.16%; H, 4.30%; N, 5.93%.

2.3. Polymerization procedure

The polymerization tube was cleaned by $K_2Cr_2O_7$–H_2SO_4 (Conc) solution for overnight at room temperature, then washed with distilled water thoroughly and dried over 200 °C and kept in a desiccator. In a glove box, appropriate amounts of Cu(I)Br and ligand were weighted into a 25 ml cleaned polymerization tube, equipped with a magnetic stirring bar and sealed with a rubber septum. The tube was then taken out of the glove box, attached to a vacuum line, and cycled between vacuum and nitrogen three times. Styrene and anisole were bubbled with nitrogen for 30 min just before use and then injected into the flask using degassed syringes. The flask was subjected to three freeze–pump–thaw cycles. The reaction tube was then immersed in a thermostated oil bath at 110 °C, and the mixture was stirred for 0.1 h to dissolve the copper salt complex. The weighted 8-(5-chloromethyl)quinolyl acetate in anisole was quickly injected into the solution via a 0.1 ml glass syringe to start the polymerization. The solution gradually turned dark green but remained homogeneous to the eye. At various time intervals, samples were taken via degassed syringes and diluted with THF and were used for measurements of monomer conversions and molecular weights.

2.4. Purification and hydrolysis of polymer

The polymer solution obtained as above was passed though alumina column for three times to remove any trace of copper ion. The purified solution was precipitated into methanol to get the polymer A. Then the precipitate was redissolved in THF (2% solution), a few drops of NaOH aqueous solution (1%) was added to the solution, which was stirred at room temperature overnight. Then the reaction mixture was concentrated by rotary evaporator and precipitated into methanol for three times. The white powder was placed in Soxhlet apparatus and extracted with methanol for 24 h to remove any 2,2′-bipyridine and low molecular weight polymer. The purified polymer B was dissolved in dry THF (1%) for next chelating reaction.

2.5. Preparation of polymeric complex with aluminum and fabrication of light-emitting diode (LED)

In a dry flask sealed with rubber septum desired amount of polymer-THF solution was added by dry syringe under Ar atmosphere at 0 °C. Then pre-cooled triethylaluminum in hexane was added into this stirred solution by dry syringe through rubber septum. Then let the temperature rise to room temperature slowly and stirred at this temperature overnight. The reaction mixture was concentrated on rotary evaporator to get solid product. Then the solid was thoroughly dried under vacuum for 24 h. Polymeric Alq3 used to prepare the light-emitting diode further purified by passing the THF solution through activated aluminum column to remove uncomplexed ligand.

Single layer diode, i.e. Ba(Al)/polymeric complex/ITO, was prepared by standard spin-coating method and chloroform using as the solvent. The polymeric complex was dissolved in chloroform at a concentration of approximately 30 mg/ml and filtered through a filter. Patterned indium tin oxide (ITO)-coated glass substrates were cleaned ultrasonically with acetone, detergent, distilled water, and 2-propanol. A thin film of electroluminescent polymeric complex was coated onto the anode by spin-casting inside a drybox. The film thickness of the active layers was around 50–70 nm, as measured with an Alfa Step 500 surface profiler (Tencor). A thin layer of Ba (4–5 nm) and subsequently 200 nm layers of Al were vacuum-evaporated subsequently on the top of an EL polymer layer under a vacuum of 1×10^{-4} Pa. Device performances were measured inside a drybox. Current–voltage (*I*–*V*) characteristics were recorded with a Keithley 236 source meter. EL spectra were recorded by Oriel Instaspec IV CCD spectrograph. Luminance was measured by a PR 705 photometer (photo research).

2.6. Measurements

FT-IR spectrum was recorded on Bruker EQUINOX 55 FT-IR system. Photoluminescent properties were recorded on Shimadzu RF-540, UV–vis spectrum was recorded on Shimadzu UV–vis 2550 and ^{1}H NMR analysis was carried out on Vanian Mercury Plus-400 instrument. Samples taken from the polymerization tube for monomer conversion were analyzed through a HP 5890 gas chromatography. Anisole was used as an internal reference. The remaining samples were filtered through aluminum oxide to remove the remaining copper species. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Agilent 1100 HPLC, Plgel MIXED-C type column, polystyrene standard purchased from waters, THF as eluent). The elemental analysis was performed on Vario EL elemental analysis instrument.

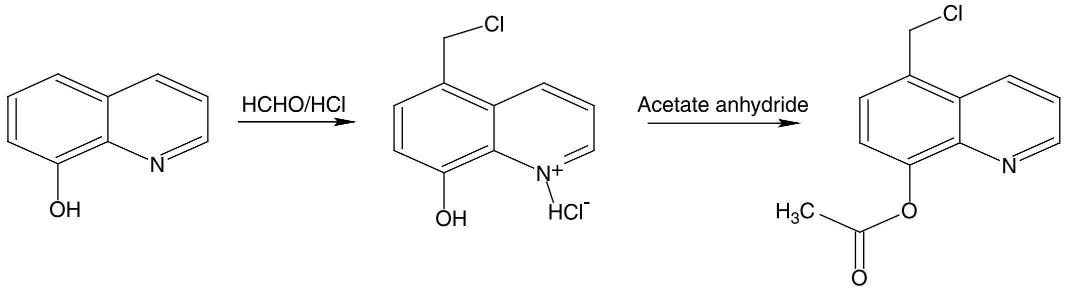
3. Results and discussion

3.1. Synthesis of functional initiator

The desired hydroxyl-protected 5-chloromethyl-8-hydroxyquinoline, namely 5-(chloromethyl)quinolin-8-yl acetate, was prepared as Scheme 1. First, the 8-hydroxyquinoline was chloromethylated with 37% formaldehyde solution under acid condition. Occasionally the reaction flask was cooled outside to keep the inner temperature below 10 °C. The dry HCl gas was bubbled through the reaction mixture all the time. After standing overnight at room temperature, the yellow precipitate was filtered and washed with dry ether. Then the vacuum dried product was acetylate with acetyl chloride to get 5-(chloromethyl)quinolin-8-yl acetate as the functional initiator. The purity of initiator was characterized by NMR and elemental analysis.

3.2. Living radical polymerization of styrene initiated by 5-(chloromethyl)quinolin-8-yl acetate

Well-controlled radical polymerization systems need some requirements: first order linear kinetic plots in semilogarithmic coordinates ($\ln[M]_0/[M]$ vs. time), linear evolution of molecular weight with respect to monomer conversion, polydispersities decrease with respect to monomer conversion for systems with slow initiation and slow exchange, end-functionalization not affected by slow initiation and exchange. Fig. 1 shows the relationship of $\ln[M]_0/[M]$ and monomer conversion with respect to polymerization time. The $\ln[M]_0/[M]$ increased almost linearly with polymerization time. This result indicates that the polymerization is first order kinetics



Scheme 1. Synthesis of 5-(chloromethyl)quinolin-8-yl acetate.

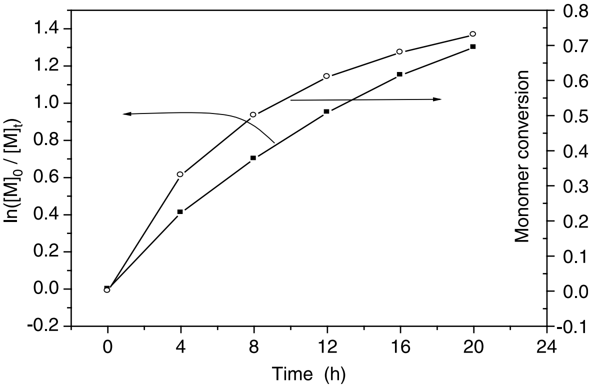


Fig. 1. Kinetic plot for the polymerization of St with 5-(chloromethyl)quinolin-8-yl acetate and CuBr/bipyridine in anisole solution (50/50, V/V) at 110 °C, [St]/[initiator]/[CuBr]/[bipyridine] = 100:1:1:2.

and the concentration of growing radical keeps constant during polymerization processing. At beginning of polymerization, the conversion increased rapidly and became slow after 8 h polymerization. After 20 h polymerization, the monomer conversion reached to 73%.

The effect of monomer conversion on average molecular weight and polydispersity index was shown in Fig. 2. The molecular weight measured by GPC increased almost linearly with the monomer conversion. The calculated molecular weight was very close to the data from GPC. This fact indicates that this polymerization was well-controllable at such polymerization condition. The polydispersity index was decreased lightly with increasing of monomer conversion and all values were less than 1.2. It means that all polymer obtained in this research have the characteristic of constant molecular weight distribution.

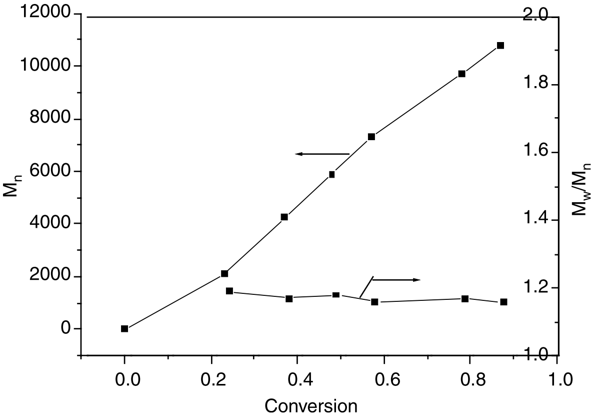


Fig. 2. Relationship of average molecular weight and polydispersity index with respect to monomer conversion for the polymerzation of St in anisole solution at 110 °C [St]/[initiator]/[CuBr]/[bipyridine] = 100:1:1:2.

The effect of monomer/initiator ratio on polymerization was listed in Table 1. With the increase in monomer/initiator ratio, the monomer conversion increased and the number average molecular weight from GPC decreased. The theoretical molecular weight is very close to the GPC results. The molecular weight estimated from elemental analysis was also very close to theoretical value. That means every polymer chain has nearly one 8-hydroxyquinoline. The polydispersity index also decreased with increasing of monomer/initiator ratio. All those experimental results indicate that the polymerization is well-controlled.

The effect of polymerization temperature on monomer conversion, molecular weight, polydispersity and initiator efficiency was summarized in Table 2. With the elevation of polymerization temperature, the monomer conversion, molecular weight from GPC and polydispersity index increased. Because at high polymerization temperature the dissociation of C–X bond is easier than that at lower temperature, more active species formed and initiated the polymerization to result in higher monomer conversion and molecular weight. At the same time, the termination reaction became very fast at higher temperature to bring about the wide molecular weight distribution.

3.3. Purification, hydrolysis and characterization of end-capped polystyrene with protected 8-hydroxyquinoline

8-Hyroxyqinoline metal–chelating complexes, such as Alq3, were thoroughly studied as an electroluminescent material with high luminescent efficiency. High purity of emitting materials is essential for high performance LED. Though Alq3 were widely used for assembling LED, the vacuum-deposition method for preparing the devices was a little tough process comparing with the spin-coating method for polymeric emitting materials. To synthesize soluble Alq3 with excellent film-forming properties will simplify the device-making procedure. End-capped polystyrene with

Table 1
Polymerization of styrene with various ratios of monomer and initiator

St/initiator	Conversion (%)	$M_{n,theo}$[a]	$M_{n,GPC}$	$M_{n,elem}$[b]	M_w/M_n (from GPC)	Initiation efficiency[c]
200/1	34.6	7197	8340	7350	1.35	0.86
100/1	49.3	5127	5960	5190	1.16	0.86
100/2	67.7	3520	3980	3620	1.13	0.88
100/3	89.7	3110	3560	3310	1.14	0.87
100/5	96.3	2003	2580	2170	1.28	0.78

Polymerization condition: 110 °C, 8 h, anisole as solvent.

[a] Average molecular weight calculated according to Ref. [11].

[b] Calculated by *N* content, supposing every polymer chain contained one hydroxyquinoline group.

[c] Initiation efficiency = ($M_{n,theo}$)/($M_{n,GPC}$).

Table 2
The effect of temperature on polymerization results

Temperature (°C)	Conversion (%)	$M_{n,thro}$	$M_{n,GPC}$	M_w/M_n (from GPC)	Initiation efficiency
130	87.7	9121	13,450	1.57	0.68
120	68.9	7166	8400	1.31	0.85
110	51.0	5304	6190	1.17	0.86
100	43.3	4503	5100	1.13	0.88
90	31.7	3297	3980	1.21	0.83

Polymerization conditions: [St]/[initiator] = 100:1, polymerization time 8 h, anisole as solvent.

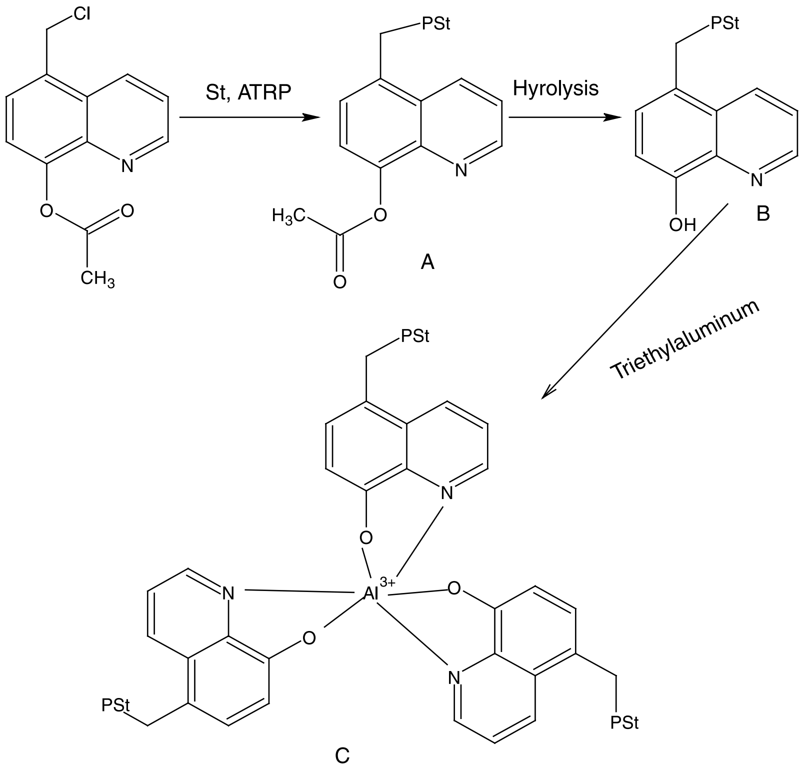
8-hydroxyquinoline maybe act as a polymeric ligand of aluminum ion. Scheme 2 showed the synthesis reaction.

The polystyrene obtained from this experiment was purified by passing the mixture though alumina column several times to remove any metal ions and the precipitated polystyrene was extracted with methanol to remove any bipyridine and low molecular weight product. Then the polymer was deprotected in THF with a few drops of acid water to remove acetate group and free 8-hydroxyquinoline—capped polystyrene was obtained as a white powder. The FT-IR spectra and NMR spectrum were shown in Figs. 3 and 4.

The polystyrene end-capped with protected 8-hydroxyquinoline shows two characteristic peaks at 1769 and 1199 cm^{-1} due to acetate groups. After hydrolysis, those two peaks disappeared and new broad peak around 3500 cm^{-1} appeared duo to phenolic hydroxyl group in 8-hydroxyquinoline ring.

From the ^{1}H NMR analysis, the signals at 8.9 and 8.6 ppm were due to 8-hydroxyquinoine rings. The purified 8-hydroxyquinline-end-capped polystyrene was utilized for polymeric ligand of aluminum ions. When the triethylaluminum solution was added to the solution of polymer B in THF, the colorless solution changed to lightly green. The solution was pass through an activated alumina column to remove any uncomplexed polymeric ligand. The polymeric Alq3 was vacuum-dried and used for characterization and devices preparation.

The molecular weight of polymeric Alq3 was list in Table 3. When the polymer ligands with low molecular weight was used, the molecular weight of polymeric Alq3 was very close to the theoretical value and the polydispersity index keep constant. Increasing the molecular weight of polymer ligand, the molecular weight of product was lower that of expected values and the polydispersity index was higher that



Scheme 2. Synthesis of 8-hydroxyquinoline end capped polystyrene and polymeric complex.

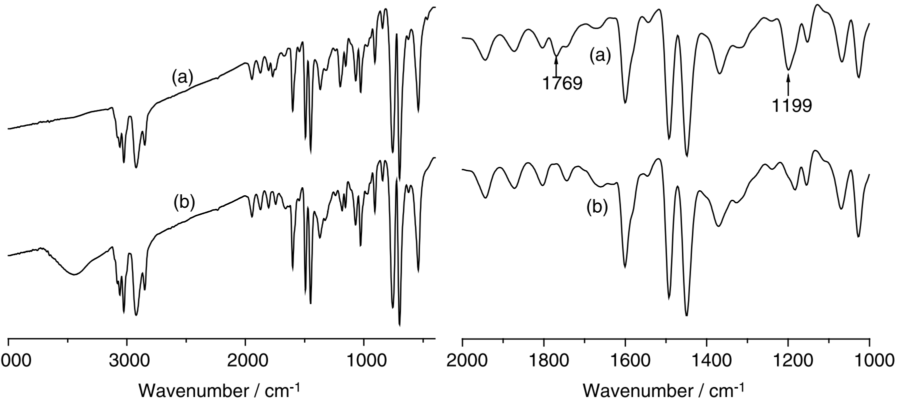


Fig. 3. FT-IR spectera of polymer (A) and polymer (B).

of starting polymeric ligand. That means a few uncomplexed ligands still left.

The reaction efficiency (RE) between polymer ligand and triethylaluminum was measured by molecular weight ratio of theoretical and found molecular weight of polymeric Alq3:

$$\mathrm{RE} = \frac{M_{\mathrm{n,th}}}{M_{\mathrm{n,GPC}}}$$

The more the value was close to unit, the higher the reaction efficiency. With increasing the molecular weight of ligand, reaction efficiency decreased for the steric hindrance effect. So the molecular weight of ligand should be carefully chosen to get high reaction efficiency. The percentage content of Alq3 by weight was also given in Table 3.

The UV–vis spectra of polymeric complex and $\mathrm{Alq_3}$ were shown in Fig. 5. Comparing with the absorbent spectrum of

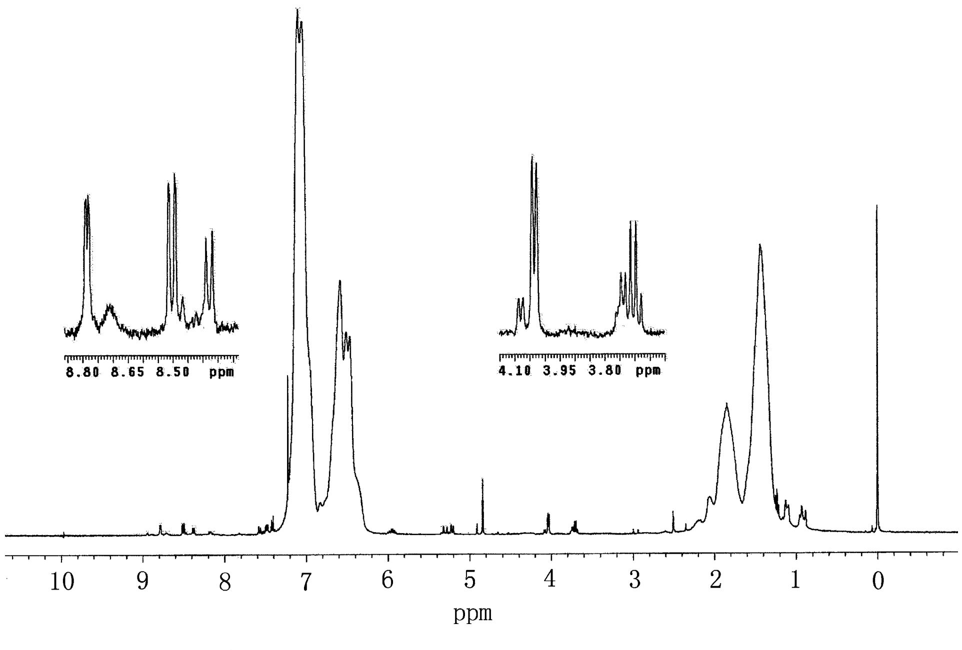


Fig. 4. ^{1}H NMR spectra of 8-hydroxyquinoline-end -capped polymer (B).

Table 3
Characterization of polymeric Alq3

	Q-PSt		$\mathrm{Alq_3(PSt)_3}$				
	M_n	PDI	$M_{\mathrm{n,th}}$	$M_{\mathrm{n,GPC}}$	$M_\mathrm{n}/M_\mathrm{w}$	RE	$\mathrm{Alq_3}$ (%)
1	2170	1.21	6534	6510	1.20	1.003	7.06
2	3310	1.14	9954	9900	1.14	1.005	4.64
3	5190	1.16	15,594	15,400	1.24	1.013	2.98
4	8400	1.31	25,224	24,380	1.49	1.035	1.88

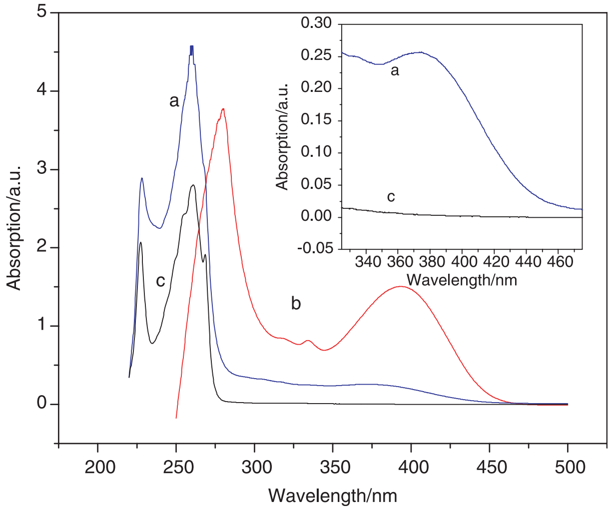


Fig. 5. UV–visible absorption spectra of Alq3, complex (C) and polystyrene (a) complex (C), (b) Alq3, (c) polystyrene.

polystyrene (Fig. 5), the polymeric complex showed an absorption peak at 380 nm, very close to the characteristic absorption of Alq_3. This fact indicated that chelating reaction took place between polymeric ligand and aluminum ion. The molecular weight of polymeric ligand affected slightly the photoluminescent properties. With increasing the molecular weight, the peak wavelength of photoluminescence shifted to short wavelength (Fig. 6).

The single layer LED Ba(Al)/polymeric Alq3/ITO was prepared by spin-coating method. The polymeric aluminum complex shows excellent solubility in most organic solvent, such as toluene, THF, chloroform. The basic electroluminescent characteristics were shown in Figs. 7 and 8. The electroluminescent wavelength of LED was near 570 nm. The details of electroluminescent characters of LED are now under investigation.

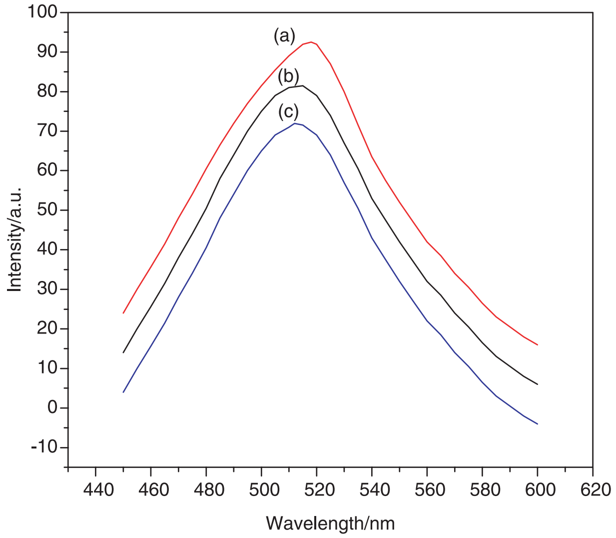


Fig. 6. Photoluminescent spectra of polymeric complex with various molecular weight (a) 2170, (b) 3310, (c) 5190.

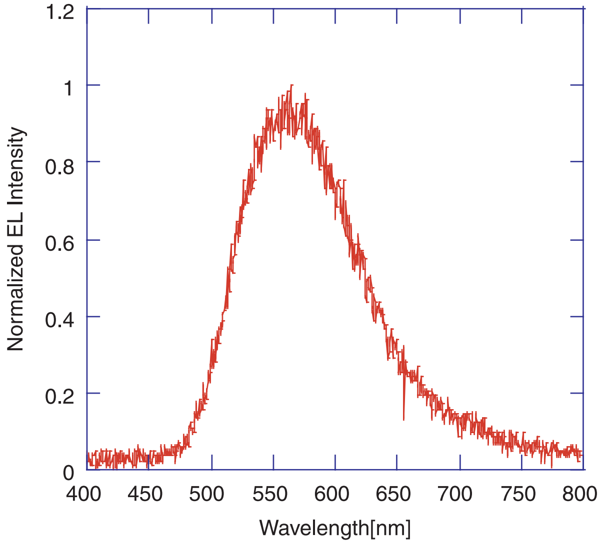


Fig. 7. Electroluminescent spectrum of Polymeric complex.

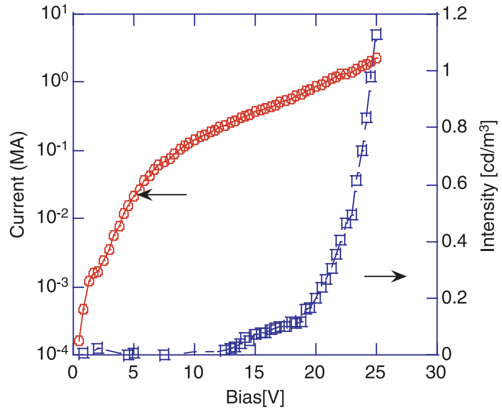


Fig. 8. Basic properties of single layer LED.

4. Conclusions

8-(5-Chloromethyl)quinolyl acetate was an efficient initiator for ATRP polymerization of styrene. 8-Hydroxyquinoline-end-capped polystyrene with desired molecular weight can be synthesized through this living polymerization method. The acetyl group was smoothly removed by hydrolysis with acid water in THF solution. This end-capped polystyrene can act as a polymeric ligand for aluminum ions. The resulting polymeric chelating compound was easily soluble in common organic solvent, such as THF, chloroform, toluene and dichloromethane. The single LED based on polymeric complex can be prepared by spin-coating method. Except the aluminum ion, the polymeric ligand can chelated with zinc ion, magnesium ion and other ions.

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