

Synthesis and Characterization of High Molecular Weight Metaloquinolate-Containing Polymers

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ABSTRACT: In this article, a new method to synthesize novel metaloquinolate (AlQ₃, ZnQ₂)-containing polymers is reported. A model polymer with 8-hydroxyquinoline ligands can be obtained by free-radical copolymerization with methyl methacrylate (MMA), then metaloquinolate (AlQ₃, ZnQ₂)-containing polymers are prepared by coordinating reaction with di(8-hydroxyquinoline) aluminum (AlQ₂) chelates or mono (8-hydroxyquinoline) zinc (ZnQ) chelates without crosslinking. The structures of products are confirmed by NMR, FTIR, ultraviolet-visible, elementary analysis, photoluminescence spectrum, and gel permeation chromatography analysis. They are soluble in common solvents and suitable to form films. The use of AlQ₂ and ZnQ

avoided the crosslinking caused by the AlQ₃, ZnQ₂ formation between different polymer chains. Different from the traditional small organic molecules in organic light-emitting diodes (OLEDs) fabrication, the polymer can be processed by spin coating without phase separation. Compared to the PMMA or MMA-co-HEMA-CH₂-Hq, the *T_g* of the metaloquinolate-containing polymers was much higher. It should be of interest for OLED applications. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1945–1952, 2006

Key words: 8-hydroxyquinoline; organic light-emitting diodes (OLED); synthesis; metaloquinolate-containing polymer; electroluminescent materials

INTRODUCTION

Much progress has been made since the first efficient organic light-emitting device (OLED) was discovered from tri(8-hydroxyquinolinato) aluminum (AlQ₃)-based multiplayer thin-film by Tang and Van Slyke.¹ The flat panel display development based on OLEDs, has accelerated rapidly. The last ten years has been devoted to an intensive research into coordination compound light-emitting materials for application in next generation display technologies.^{2,3} Furthermore, the interest on other metal-chelate systems to produce EL in different spectra regions for display applications has considerably increased.⁴ Among these coordination compounds, 8-hydroxyquinoline metal chelates are presently considered as one of the most reliable electro-transporting and emitting materials applied in molecular-based OLEDs for their thermal stability, high fluorescence, and excellent electron-transporting mobility. However, in practice, metaloquinolates have some fatal deficiencies. As known, OLEDs are heterojunction devices, and the layers made of small molecular organic transport materials are usually amor-

phous thin solid films prepared by using vacuum deposition method. But, at times, isomerizations or oligomerizations occur upon high temperature sublimation.⁵ Furthermore, the crystallization takes place at the function time resulting in the decrease of work time. A convenient method is to prepare the mixtures of 8-hydroxyquinoline metal chelates and polymers,⁶ using the low-cost manufacturing techniques, such as soft processing and ink-jet printing.⁷ However, the solubility of the 8-hydroxyquinoline metal chelates is limited and phase separation often occurs in these systems, leading to the poor optical properties and short work-time.⁸

Several important methods to synthesize metaloquinolate (AlQ₃, ZnQ₂)-containing polymers have been reported. Jianping Lu first reported the attachment of AlQ₃ complexes as side chains to a polymer by postpolymerization step.⁹ According to the method mentioned earlier, Toshio Takayama synthesized AlQ₃-containing polymer with good solubility, but they could not eliminate the crosslinking, too.¹⁰ The macromolecular complexes possessing high fluorescence intensity can be obtained by the copolymerization of the monomeric metal complexes and some monomers, but the molecular weight of polymers and their solubility in solvents are very low. Amy Meyers's synthetic method is based on a fully functionalized monomer, which was polymerized in a controlled

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fashion by ring-opening metathesis polymerization (ROMP), eliminating the crosslinking.^{11–13} But the productive rate, solubility of the copolymer, and metaloquinolate (AlQ_3 , ZnQ_2) contents in the copolymer are limited.

In this article, we synthesized metaloquinolate (AlQ_3 , ZnQ_2)-containing polymers by a new method. High molecular weight model polymer containing 8-hydroxyquinoline ligands was first prepared and then it was coordinated (but not directly reacted) with di(8-hydroxyquinoline) aluminum (AlQ_2) chelates or mono(8-hydroxyquinoline) zinc (ZnQ) chelates to form the required polymer. This can avoid the crosslinking caused by the AlQ_3 or ZnQ_2 formation between different polymer chains. Therefore, there are several advantages of this method, such as: (1) High molecular weight polymers can be obtained by copolymerization. (2) Polymer is linear without crosslinking and can be dissolved easily in the common solvents. (3) The method is fit to synthesize the most of 8-hydroxyquinoline metal chelates-containing polymers by changing the polymer chains or metal central ion.

EXPERIMENTAL

Materials

Solvents and chemicals were obtained commercially. Some of them were used as received, such as 8-hydroxyquinoline, *p*-methoxyphenol, aluminum isopropoxide, zinc acetate, formaldehyde, and hydrochloric acid. Tetrahydrofuran (THF) and toluene were dried and distilled with sodium. Azobisisobutyronitrile (AIBN), anhydrous sodium acetate, MMA, and 2-hydroxyethyl methacrylate (HEMA) were purified and dried before use.

Characterization

The melting point of sample was observed by SGW X-4 micro-melting point apparatus (Shanghai PSE Co.Ltd). The molecular weight of polymers were determined by Water 515–410 GPC gel permeation chromatography, using THF as an eluent and polystyrene as the standard. ¹H-NMR spectra were recorded on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer. The FTIR spectra were carried out using a RFX-65A (Analects) Fourier Transform Infrared Spectrometer. Thermal analyses were performed on TA differential scanning calorimetry (DSC) 2910. 2550 Ultraviolet-visible spectrophotometer (Shimadzu) for UV absorption and Fluorolog-3 (JOBIN YVON) for Photoluminescence measurements were used. The Al-content was analyzed using ash test.

Synthesis

Synthesis of 5-chloromethyl-8-quinolinol hydrochloride (compound 1)

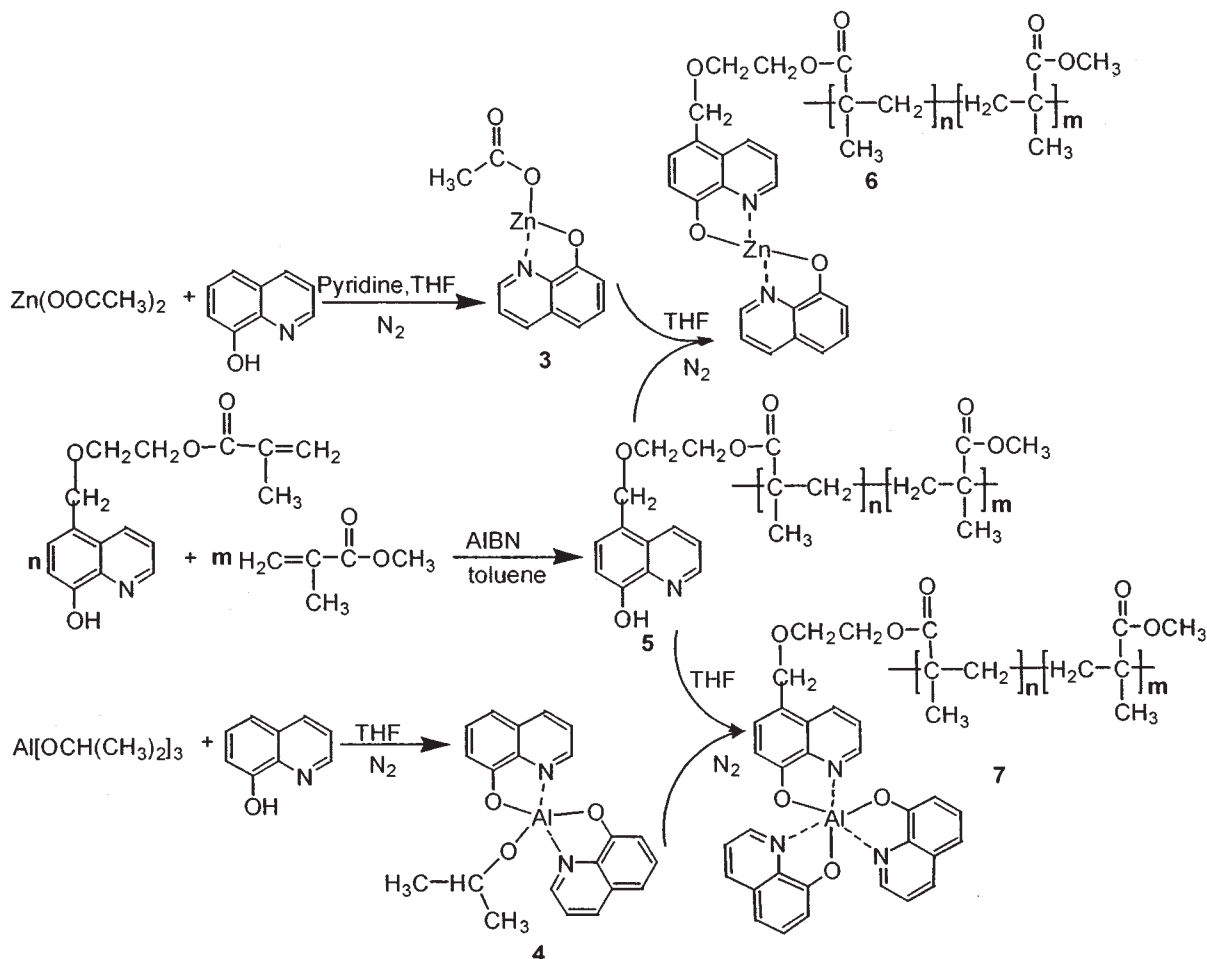
Compound 1 was obtained according to a well-known method,¹⁴ with slight modification. A mixture of 5.84 g (0.04 mol) of 8-quinolinol, about 50–70 mL of fuming hydrochloric acid, and 6.4 mL (0.08 mol) of 37% formaldehyde was added into a 250 mL three-necked flask with a magnetic stirrer, treated with hydrogen chloride gas about 10–12 h and allowed to stand overnight. The yellow solid was collected on a filter and washed with acetone for three or four times. After drying at 40°C in vacuum for 12 h, compound 1 was obtained as a bright yellow powder in a high yield (over 90%). m. p. 280°C (decomposition). ¹H-NMR (D_2O): 9.04–7.08 (5H, Ph—H), 4.85 (2H, s, —CH₂—Ph) (Fig. 1); FTIR (KBr, cm^{-1}): 3300 (—OH), 1625, 1596 (C—C and pyridine ring), 1550, 1492 (aromatic), 1390 (C—N), 698 (C—Cl); Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{NOCl HCl}$: C, 52.17; H, 3.91; O, 6.95; N, 6.08. Found: C, 52.50; H, 4.02; O, 6.78; N, 5.95.

Synthesis of 5-methyl (2-methacryloyloxyethoxy)-8-quinolinol (compound 2)

To a 500 mL three-neck round bottom flask fitted with a magnetic stirrer, a reflux condenser, and nitrogen inlet were added 20 g 2-hydroxyethyl methacrylate (HEMA), 0.2 g *p*-methoxyphenol and 1.78 g (0.0217 mol) sodium acetate. The reaction solution was stirred at 50°C for 1–1.5 h, and then 5 g (0.0217 mol) 5-chloromethyl-8-quinolinol hydrochloride was added into the solution. The suspension was heated at 80–90°C for 2 h. After cooling, the complex was poured into ice water and then neutralized with dilute ammonia. The precipitate was washed by a large amount of ice water, collected by filtration, and dried to give 5.8 g (93% yield) of milk-white solid (compound 2). After four recrystallizations from petroleum ether, the white flocculent solid was obtained, m.p. 86–87.5°C. ¹H-NMR (CDCl_3): 8.78–7.08 (5H, Ph—H), 6.03 (1H, s, =CH₂), 5.52 (1H, t, =CH₂), 4.87 (2H, s, —CH₂—Ph), 4.27, 3.69 (4H, t, —CH₂—O), 1.88 (3H, s, —CH₃) (Fig. 2). IR (KBr, cm^{-1}): 3300 (—OH), 2956 (—CH₃) 1718 (C=O), 1633 (C=C), 1613, 1581 (C—C and pyridine ring), 1506, 1475 (aromatic), 1384, 1319 (C—N). Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_4$: C, 66.90; H, 5.92; O, 22.30; N, 4.87. Found: C, 67.32; H, 6.00; O, 22.17; N, 4.75.

Synthesis of metal chelates (ZnQ) (coordinated compound 3)

To a 150 mL three-necked flask equipped with a nitrogen inlet and a magnetic stirrer was added zinc acetate 0.2195 g (0.001 mol) in about 30 mL anhydrous THF solution and stirred till it dissolved completely.



Scheme 1. Synthetic route to the metaloquinolate (AlQ_3 , ZnQ_2)-containing polymers.

Then the solution of 8-hydroxyquinoline (0.145 g, 0.001 mol) in about 50 mL anhydrous THF was slowly added dropwise into the flask to avoid the formation of ZnQ_2 . The yellow–white color appeared immediately. The reaction was kept at room temperature for 2–3 days. Then the mixture was concentrated under reduced pressure to get the white powder and washed 3 times with hot petroleum ether. After drying at 40°C in vacuum for 24 h, 0.246 g white solid was obtained (91.8% yield). $^1\text{H NMR}$ (CDCl_3): 8.62–6.79 (6H, Ph–H), 2.29 (3H, CH_3). IR (KBr, cm^{-1}), 2958 ($-\text{CH}_3$), 1602, 1575 (C–C and pyridine ring), 1502, 1465 (aromatic), 1385, 1327 (C–N).

Synthesis of metal chelates (AlQ_2) (coordinated compound 4)

To a 150 mL three-neck round bottom flask fitted with a magnetic stirrer, a reflux condenser, and nitrogen inlet were added aluminum isopropoxide 0.204 g (0.001 mol) in about 30 mL anhydrous THF solution. Then 8-hydroxyquinoline (0.290 g, 0.002 mol) in about 50 mL anhydrous THF was slowly added dropwise

into the solution to avoid the formation of AlQ_3 . A brilliant yellow solution was stirred at room temperature for 2–3 days. The mixture was filtered through a G4 funnel to remove insoluble AlQ_3 and the filtrate was precipitated from petroleum ether for 3 times. The precipitate was filtered off and dried at 40°C in vacuum. 0.3823 g yellow solid was obtained (63.6% yield). $^1\text{H NMR}$ (CDCl_3): 8.83–7.03 (12H, Ph–H), 3.72 (1H, $-\text{CH}-\text{O}$), 1.23 (6H, CH_3). IR (KBr, cm^{-1}), 3050 (Ph–H), 2956, 2980 ($-\text{CH}_3$, $-\text{CH}$), 1604, 1579 (C–C and pyridine ring), 1500, 1469 (aromatic), 1384, 1328 (C–N).

Synthesis of copolymer with 8-hydroxyquinoline ligands (polymer 5)

To a 100 mL three-neck round bottom flask fitted with a magnetic stirrer, a reflux condenser and nitrogen inlet were added MMA, HEMA- CH_2 -Hq monomer and AIBN in toluene solution, resulted in a very gradual rise in temperature. The solution was then kept at 60°C for 48 h. The resulted products were reprecipitated by methanol and washed for several times. After

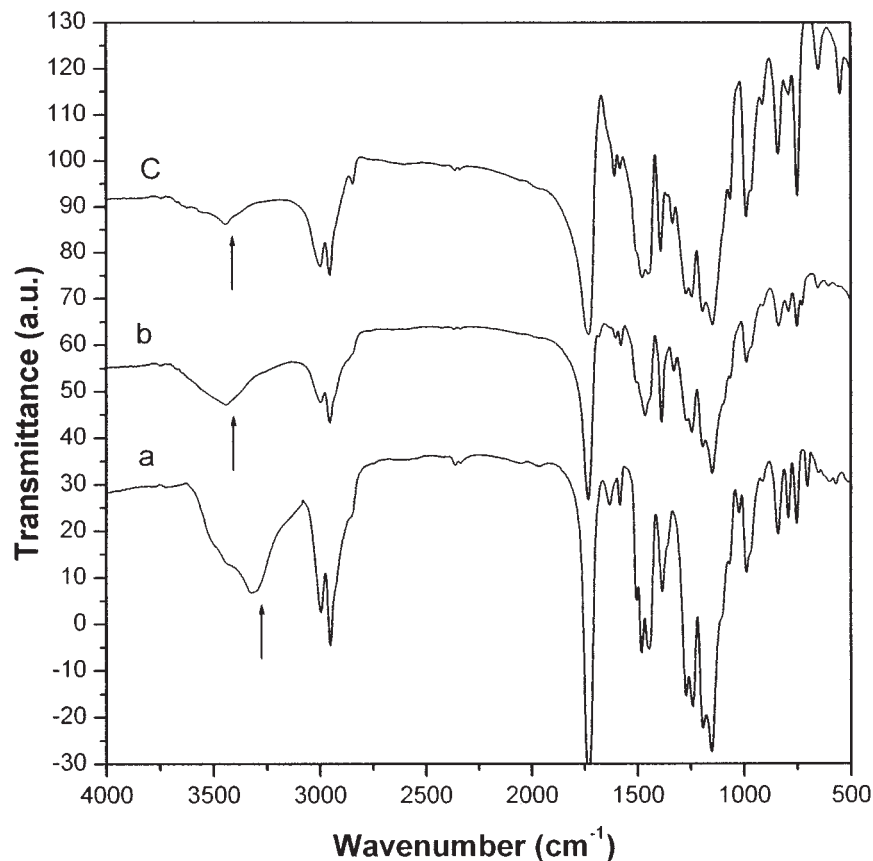


Figure 1 FTIR spectra of polymer 5, 6, 7 (a) polymer 5 (b) polymer 6, (c) polymer 7.

drying under vacuum at 50°C for 1 day, the 8-hydroxyquinoline ligands copolymer was obtained. IR (KBr, cm^{-1}), 3322 (O—H), 2952, 2997 ($-\text{CH}_3$), 1730 (C=O), 1632, 1582 (C—C and pyridine ring), 1504, 1481 (aromatic).

Synthesis of ZnQ_2 -containing polymer (polymer 6)

To a 150 mL three-neck round bottom flask fitted with a magnetic stirrer, a reflux condenser, and nitrogen inlet were added polymer 5 ([MMA]/[HEMA- CH_2 -Hq] = 10:1, 1.287 g, 0.001 mol) in about 20 mL anhydrous THF solution, resulted in a very gradual rise in temperature, then compound 3 (0.268 g, 0.001 mol) in about 50 mL anhydrous THF was slowly added dropwise into the solution, and the solution was kept at 75°C and refluxed for 48 h. The resulted product was reprecipitated by methanol and was washed for several times. Afterwards it was dried under vacuum at 50°C for 1 day. Then the product was dissolved in 20 mL DMF solution, reprecipitated by methanol and was washed for several times and dried under vacuum. Over three times repeatedly, the ZnQ_2 -containing polymer was obtained. IR (KBr, cm^{-1}), 3442 (—OH), 2954, 2998 ($-\text{CH}_3$), 1732 (C=O), 1630, 1578

(C—C and pyridine ring), 1504, 1466 (aromatic), 1387, 1329 (C—N).

Synthesis of AlQ_3 -containing polymer (polymer 7)

To a 150 mL three-neck round bottom flask fitted with a magnetic stirrer, a reflux condenser and nitrogen inlet were added polymer 5 ([MMA]/[HEMA- CH_2 -Hq] = 3:1, 0.587 g, 0.001 mol) in about 20 mL anhydrous THF solution, resulted in a very gradual rise in temperature, then compound 4 (0.374 g, 0.001 mol) in about 50 mL anhydrous THF was slowly added dropwise into the solution, and the solution was kept at 75°C and refluxed for 48 h. The resulted product was reprecipitated by methanol and was washed for several times. Afterwards it was dried under vacuum at 50°C for 1 day. Then the product was dissolved in 20 mL DMF solution, reprecipitated by methanol, washed several times, and dried under vacuum. Over three times repeatedly, the AlQ_3 -containing polymer was obtained. IR (KBr, cm^{-1}), 3444 (—OH), 3045 (Ph—H), 2952, 2993 ($-\text{CH}_3$), 1730 (C=O), 1639, 1551 (C—C and pyridine ring), 1500, 1466 (aromatic), 1391, 1335 (C—N).

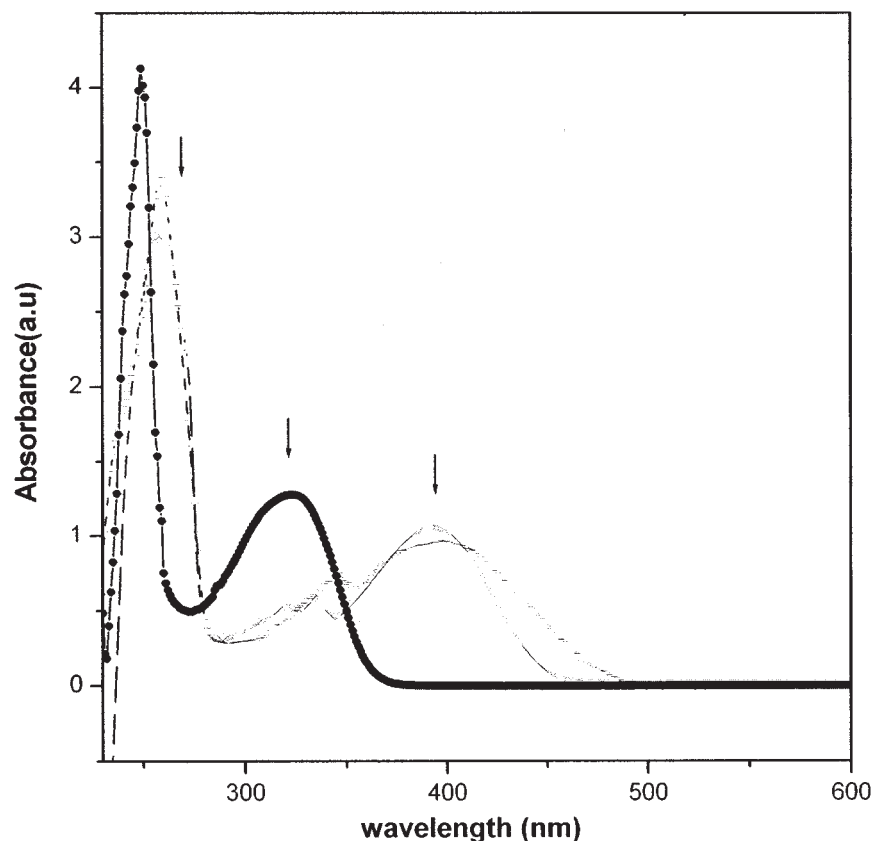


Figure 2 UV-vis absorption spectra in THF of polymer 5, 6, 7 (●) polymer 5, (—) polymer 6, (×) polymer 7.

RESULTS AND DISCUSSION

It was found that only low yield (%) was obtained for the chloromethylation of 8-hydroxyquinoline according to Burckhalter's method. In our work, the reaction condition was modified slightly by increasing the time and dose of hydrogen chloride gas from 90 min to 10–12 h and hydrogen chloride from 8 mL to about 50–70 mL, a high conversion was completed (over 90%).

For compound 2, It was synthesized based on Du's method.¹⁵ But the reaction time was shortened to 2 h by adding anhydrous sodium acetate as catalyst. As the reaction completed, the complex must be poured into a large amount of ice water, or the compound 2 will not be obtained, even if dilute ammonia solution

was added later. The pH of solution should be controlled about 7–8. If the pH < 7, the precipitation will not be completed, and the yield obtained was very low. On the contrary, the precipitate can partly dissolve again if the pH was >8.

For synthesis of AlQ_2 using aluminum isopropoxide and ZnQ using zinc acetate, the reactant conditions such as concentration, the sequence of dropping reactants, and dried atmosphere were very important. The reactions of aluminum isopropoxide (zinc acetate) and 8-hydroxyquinoline or its derivants were very fast, so 8-hydroxyquinoline should be added slowly and low Al^{3+} (Zn^{2+}) concentration must be kept in system for a proper yield. The resulted metal chelate solution can also be used directly for coordinating reaction with the

TABLE I
Al-Content in Polymer 5 (Doped or Coordinated with Al Complex)

	Al-content (before purification) (mol%)	Al-content (after purification) (mol %)		
		1	2	3
Polymer 5-HEMA- CH ₂ -AlQ ₃ (doped)	25.00 9.09	4.37 1.27	0.57 0.22	<0.1 <0.1
Polymer 5-AlQ ₂ (coordinated)	25.00 9.09	22.05 8.49	18.65 7.90	18.26 7.81

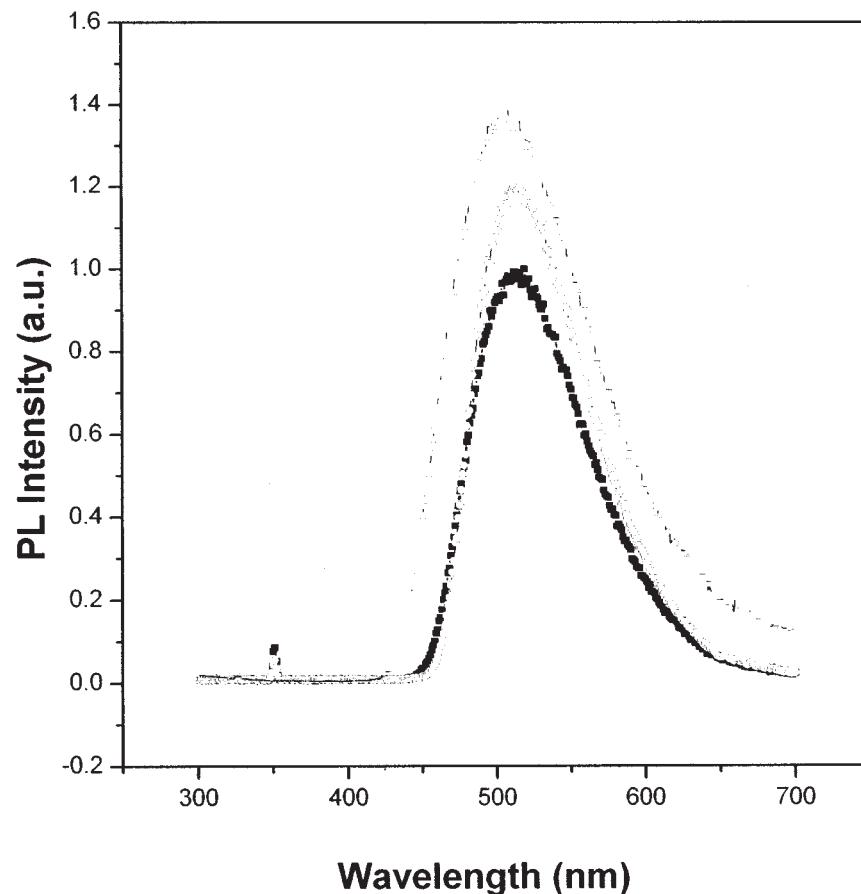


Figure 3 PL spectra in THF excited at 350nm of polymer 7 (—) small molecule AlQ_3 , (---) polymer 7 with AlQ_3 content about 22.65 wt %, (····) polymer 7 with AlQ_3 content about 6.84 wt %.

model polymer, AlQ_3 or ZnQ_2 formed before was finally removed by reprecipitating the metaloquinolate (AlQ_3 , ZnQ_2)-containing polymer.

From FT-IR measurements as shown in Figure 1, it was found that the strong peak at 3322 cm^{-1} from O—H stretching vibration and 1234 cm^{-1} from O—H deformation vibration of 8-hydroxyquinoline were markedly weakened due to the coordination of O—H, N with metal ion (Al^{3+} , Zn^{2+}), and the stretching vibration peak located at 1632 cm^{-1} was red shifted to 1604 cm^{-1} nearby, showing the coordination of metal ion with N. Coordinating with metal ion, leads to the

reduction of electron cloud and force constant. Then absorption frequency will red shift.

To confirm the reaction of di(8-hydroxyquinoline) aluminum (AlQ_2) and the model polymer containing 8-hydroxyquinoline ligands, the metal chelates (AlQ_2) was also doped in. Both systems (coordinated and doped) were extracted with solvents. The aluminum content that remained was analyzed. The results were given in Table I. As can be seen, the AlQ_3 doped was almost removed after extraction for three times, and the AlQ_2 in polymer 5 just little decreased. In other words, it had coordinated with polymer 5.

TABLE II
Metaloquinolate (AlQ_3 , ZnQ_2) Content of Different [MMA]/[HEMA- CH_2 -HQ] Mole Ratio

	[MMA]/[HEMA- CH_2 -HQ]		
	3	10	50
Polymer 5 Conversion (%)	69.32	80.41	90.02
Polymer 6 ZnQ_2 -content (wt %)	(44.40) ^a	22.54 (23.61) ^a	^a (6.43) 7.42
Polymer 7 AlQ_3 -content (wt %)	41.54 (50.94) ^a	22.65 (28.67) ^a	6.84 (8.19) ^a
Forming film properties	Bad	Good	Excellent

Copolymerization conditions: [M] = 2.04 mol/L, [AIBN] = 6.10×10^{-3} mol/L, toluene as solvent at 60°C for 48 h.

^a Those in parentheses indicate calculated values.

TABLE III
The Properties of a Series of Metaloquinolate (AlQ_3 , ZnQ_2)-Containing Copolymers

Sample No.	Metaloquinolate content (wt %)	T_g ($^{\circ}\text{C}$)	Film appearance
Polymer 5	00.0	105.02	—
Polymer 6	04.15	120.09	Transparent
Polymer 6	14.15	142.83	Transparent
Polymer 6	22.45	162.71	Transparent
Polymer 6	37.45	202.34	Non-transparent
Polymer 7	06.84	117.46	Transparent
Polymer 7	22.65	150.59	Transparent
Polymer 7	41.54	202.71	Non-transparent

The interaction between metal ion (Al^{3+} , Zn^{2+}) and 8-hydroxyquinoline was also supported by the UV-vis spectra. As can be seen from Figure 2, the absorption peak at 249 nm π - π^* electron transition from quinoline was red shifted and the n - π^* transition at 324 nm was disappeared or weakened. A new peak at 392 nm from AlQ_3 was found. So was ZnQ_2 (399 nm) in polymer. Also, the PL emission spectra showed that the polymer 7 had the same band as that in AlQ_3 , as given in Figure 3. PL emission peak at 510 nm were consistent with that of small molecular weight AlQ_3 complexes. The similar

result was found from PL emission peak of ZnQ_2 (541 nm) complexes.¹⁶

In general, it is difficult to obtain high molecular weight product by copolymerizing metal complex monomers directly with MMA (molecular weight was less than 2,0000) because of the inhibition of metal complex.¹⁷ Our work provided a new approach to synthesize this kind of high molecular weight polymers. The molecular weight (M_w) of polymer 7 was about 120,000 when AlQ_3 content was about 40% and little increased with $[\text{MMA}]/[\text{HEMA-CH}_2\text{-Hq}]$. In fact, the conversion, the film formation, and the T_g of polymer 7 were also affected by the $[\text{MMA}]/[\text{HEMA-CH}_2\text{-Hq}]$ mole ratio. As can be seen from Table II and III, the conversion was increased with the ratio. It is clear that polymerization was retarded by 8-hydroxyquinoline. Also, with the increase of MMA component in polymer, its solubility increased and the film cast became easy. In general, the film is transparent and tough if the AlQ_3 content was lower than 30 wt % (ZnQ_2 content < 25 wt %) in polymer. However, as expected, the T_g of polymer increased markedly with the increase of metaloquinolate (AlQ_3 , ZnQ_2) component because of the introduction of quinoline ring and metal ions. In other words, its thermal sta-

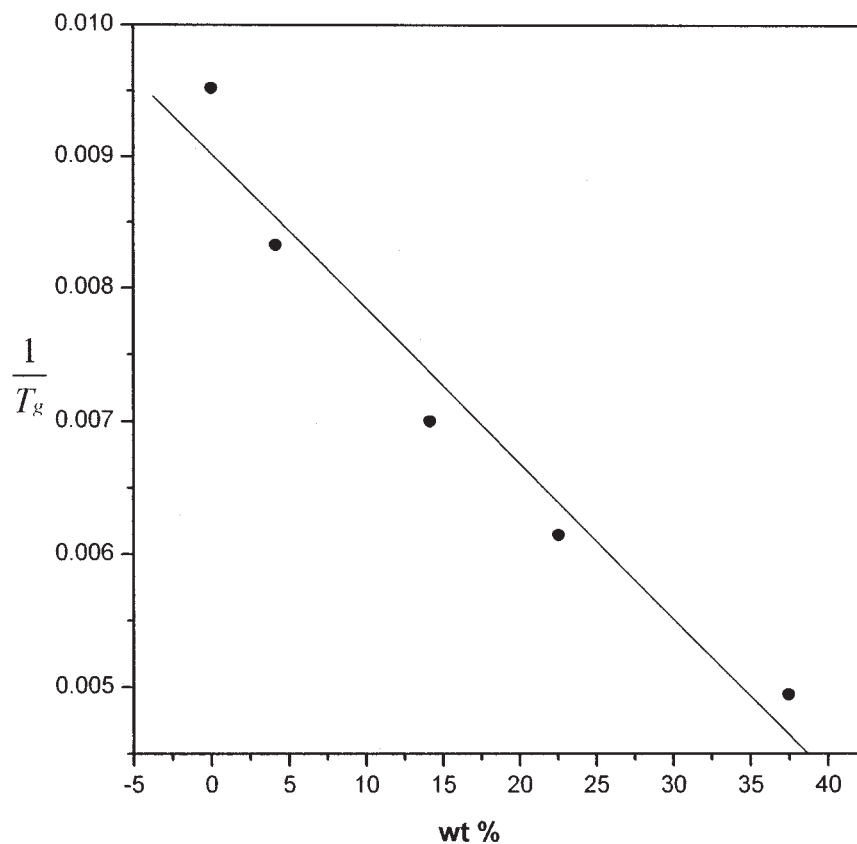


Figure 4 T_g varies with ZnQ_2 contents in polymer 6 Notes: W_A : metaloquinolate (AlQ_3 , ZnQ_2)-contant (wt %) in polymer, W_B : MMA contant (wt %) in polymer.

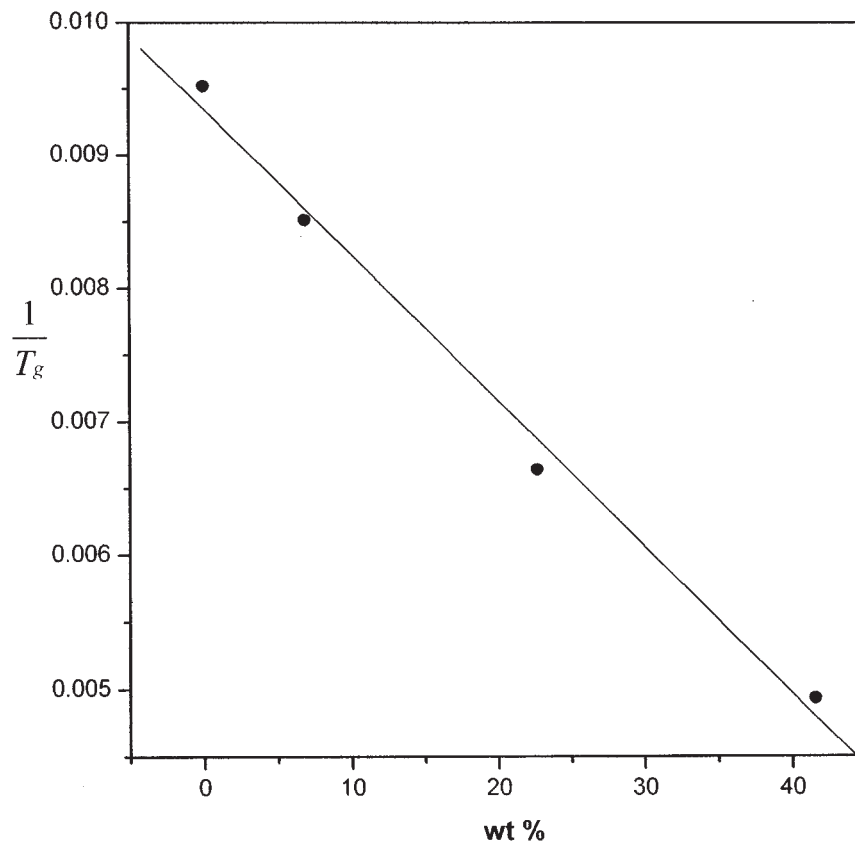


Figure 5 T_g varies with AlQ₃ contents in polymer 7.

bility can be improved as the introduction of metal complex. As shown in Figure 4 and 5, the T_g was in good agreement with Fox equation: $\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$, and indicated that the polymer containing ZnQ₂ or AlQ₃ is homogeneous. Their rate of slope are $-1.16929E-4$ and $-1.09585E-4$, respectively. It showed that the thermal stability of ZnQ₂-containing polymer can be more improved with increasing of the ZnQ₂ content than that of AlQ₃.

CONCLUSIONS

A novel thermally stable metaloquinolate (AlQ₃, ZnQ₂)-containing polymers were synthesized successfully by coordinating reaction with di(8-hydroxyquinoline) aluminum (AlQ₂) chelates or mono(8-hydroxyquinoline) zinc (ZnQ) chelates and a model polymer containing 8-hydroxyquinoline ligands without crosslinking. Preliminary study indicated that this polymer is soluble and easy to film-cast, even at high chromophore content. The glass-transition temperatures of the polymer is higher than the PMMA homopolymer or polymer 5. The polymer properties can be altered by controlling the monomer species and structures. The method is suitable for the most of 8-hydroxyquinoline metal chelates.

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