Synthesis and Coordination of Oxyquinolyl End-Functionalized Polystyrene by Atom Transfer Radical Polymerization

Xiang Guo,[1] Jianmei Lu,[1,2] Hua Li,[1] Shechun Yao,[1] Lihua Wang[1]

[1]*Department of Chemistry and Chemical Engineering, Suzhou, Key Laboratory of Organic Synthesis University, Suzhou 215006, China*
[2]*Jiangsu Polytechnic University, Changzhou 213016, People's Republic of China*

ABSTRACT: The end-functionalized polystyrene is synthesized by a new initiator, 5-chloromethyl-8-hydroxyquinoline (5-ClCH$_2$Q), via atom transfer radical polymerization. The existence of the oxyquinoline group on the chain end was confirmed by ^{1}H-NMR. The polymers can be easily changed into films with good fluorescence property and nonlinear third-order optical property. Coordinating the oxyquinoline group with Eu^{3+} and La^{3+}, the fluorescent intensity and third-order nonlinear optical coefficient will be enhanced much more. The proportion of the oxyquinoline group coordinating and rare-earth metal is 3:2 determined by titrimetric analysis. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2067–2071, 2005

Key words: oxyquinoline; ATRP; fluorescence; NLO; terminal functionalization

INTRODUCTION

8-Hydroxyquinoline possesses advantages, such as fluorescence and good capacity for coordination with rare-earth metal.[1] However, for the small molecular complex, there are some defects such as difficulty to form film, ease of crystallization to reduce the product's life, and complicated preparation techniques. To solve these problems, there are some reports to try to attach 8-hydroxyquinoline to the polymer.[2,3]

Atom transfer radical polymerization (ATRP) is a new technique to synthesize functional polymers. It can be used for a large variety of monomers,[4,5] allowing facile control of chain topology and block copolymer,[6,7] and can be initiated by a wide range of halogenated initiators and macroinitiators.[8] Utilizing the ATRP method, the end-functional polymer can be prepared by selecting initiators that contain specified groups. Many initiators have been successfully used such as arenesulfonyl halides,[9] 2-hydroxyethyl 2-bromoisobutyrate,[10] and 2-(2,4-dinitrophenylthio)ethyl 2-bromo-2-methylpropionate.[11] These illuminate us to change 8-hydroxyquinoline into halogenated initiators and use the ATRP method to attach it to the polymers. After coordinating with rare-earth metal, it can be developed to a novel optical material.

EXPERIMENTAL

Materials

5-chloromethyl-8-hydroxyquinoline (5-ClCH$_2$Q) was prepared according to a known method.[12,13] Styrene obtained commercially (Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was washed by 5% sodium hydroxide aqueous solution to remove inhibitor, dried over magnesium sulfate overnight and filtered, and then distilled under reduced pressure. Lanthanum chloride and europium chloride (Shanghai Chemical Reagent Co., Ltd.) were self-made from their oxides by dissolving in 6M hydrochloric acid and then evaporating at 90°C. Copper chloride (CuCl) obtained commercially (Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was dissolved in a small amount of thick hydrochloric acid and deposited by a great deal of water; the resulting precipitate was dried in a vacuum-drying oven. All others reagents and solvents were analytical pure and used without purification.

Polymerizations

CuCl (0.015 g, 0.15 mmol), 2,2'-bipyridine (0.0702 g, 0.45 mmol), cyclohexanone (1.0 ml), and styrene (1.04 g, 10 mmol) were added to a pressure tube. The mixture was stirred until all solid materials were well distributed. Then 5-ClCH$_2$Q (0.0097 g, 0.05 mmol) was added. After the tube was sealed and cycled between vacuum and high-purity nitrogen four times, the reaction tube was then immersed in a preheated oil bath at 120°C. Samples for kinetic measurements were car-
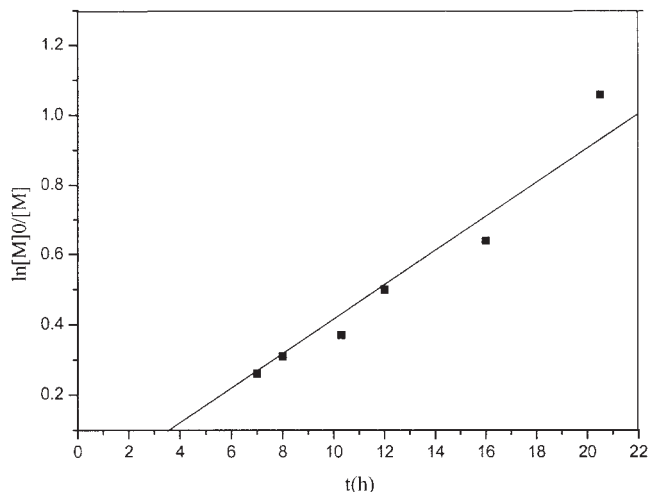
Figure 1 The relationship of $\ln([M]_0/[M])$ with polymerization time in the solution polymerization of St at 120°C, Conditions: St/ClCH$_2$-Q/CuCl/Bpy = 200/1/3/9; $[M]_0$ = 4.7 mol/L.

Figure 2 The relationship of molecular weight and polydisperity with conversion in the solution polymerization of St at 120°C, Conditions: St/ClCH$_2$-Q/CuCl/Bpy = 200/1/3/9; $[M]_0$ = 4.7 mol/L.

ried out after the desired time interval from the reaction tubes. Polystyrene was precipitated by a large amount of methanol. After solving in THF and precipitating for the second time, the polystyrene was dried under vacuum at 40°C until its weight was constant.

Coordination with rare-earth metal

The end-functional polystyrene and excess EuCl$_3$ or LaCl$_3$ were dissolved in dimethyl formamide (DMF) and stirred overnight. The content in the beaker was precipitated by methanol and washed by anhydrous ethanol three times to ensure that the EuCl$_3$ or LaCl$_3$ is absolutely removed. Then, the product was dried under vacuum at 40°C until its weight was constant.

Characterization

Percentage conversion was determined by gravimetry; molecular weight and polydispersity index were measured by a Waters 1515 GPC (Waters Corporation, Milford, MA) with the calibration of the commercially available polystyrene standards and THF as solvent. ^{1}H-NMR spectra were performed on an INOVA 400-MHz spectrometer (Varian Company, San Francisco, CA) by using CDCl$_3$ as solvent and tetramethylsilane as internal
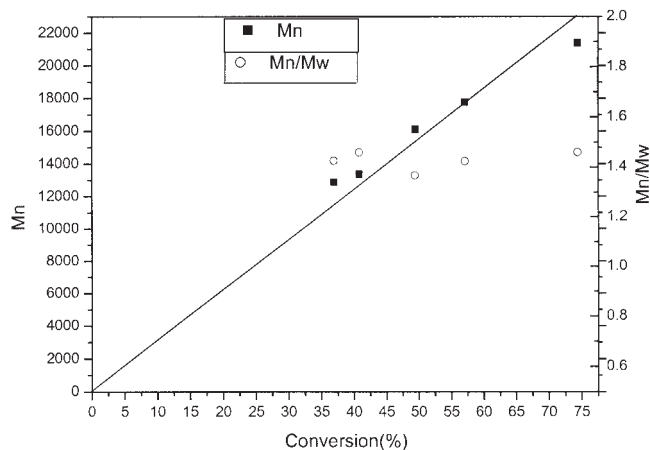
reference. FIIR spectra were obtained on a Mangna 550 infrared spectrometer (Nicolet Analytical Instruments Company, Madison, WI). UV spectra were obtained on a UV-240 spectrometer (Shimadzu Corporation, Kyoto, Japan). Fluorescence spectra were performed on a Edinburgh 920 fluorescence spectra photometer (Edinburgh Instrument Corporation, Edinburgh, UK). Third-order NLO response of polymers was probed by phase-conjugated forward three-dimensional degenerated four wave mixing (DFWM) technique with PG401-ps YAG pulsed laser (The Solid-state Laser Company, USA).

RESULTS AND DISCUSSION

Confirmation of the living/controllable polymerization

Figure 1 shows the semilogarithmic kinetic plot and polydispersities with time for the ATRP of styrene initiated by 4-chloromethyl benzoic acid. Figure 2 shows the molecular weights with conversion for the ATRP. Figure 1 indicates that $\ln([M]_0/[M])$ increases linearly with the polymerization time, where $[M]_0$ and $[M]$ denote the monomer concentrations at time 0 and t. This shows the polymerization is first-order kinetics. In Figure 2, the molecular weight of the polymer increases linearly with the monomer conversion. Fur-

TABLE I
Polymerization of St with Different Proportions of Monomer and Initiator

St/ClCH$_2$-Q	Conversion (%)	M_n (cal)	M_n (GPC)	Initiation efficiency	M_w/M_n
200 : 1	65.4	13,800	21,380	0.65	1.495
100 : 1	39.4	3940	17,760	0.22	1.366
50 : 1	39.4	1970	16,140	0.12	1.327
100 : 3	13.5	448	4020	0.11	1.328

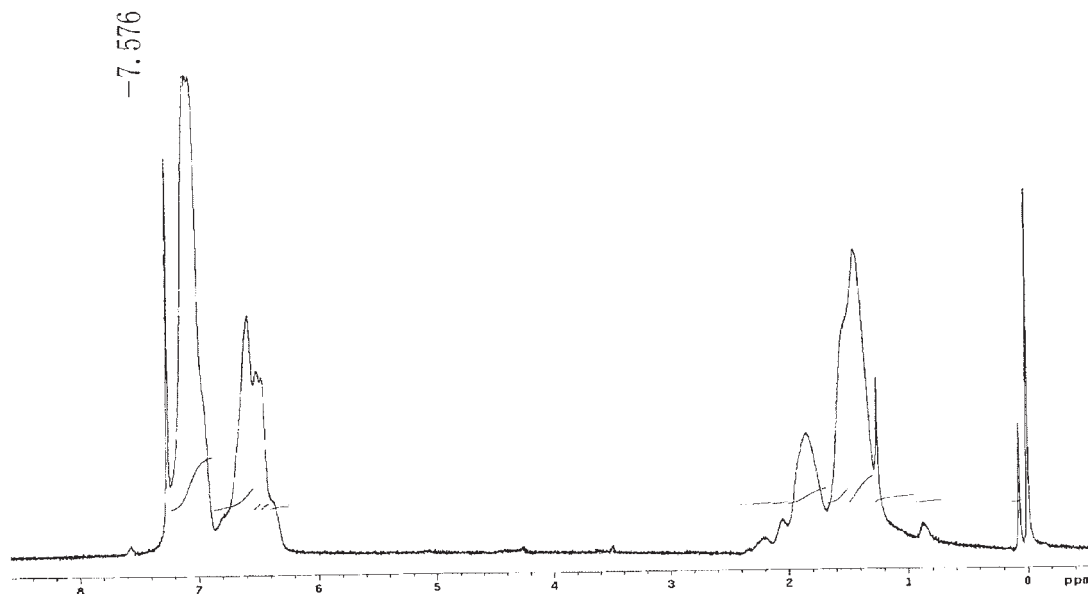Polymerization temperature, 120°C; St : CuCl : Bpy = 200 : 3 : 9; reaction time, 20.5 h; $[M]_0$ = 4.7 mol/L.

Figure 3 ^{1}H-NMR spectrum of PSt initiated by ClCH$_2$-Q/CuCl/Bpy system, CDCl$_3$ as solvent.

thermore, polydispersities of polymer are less than 1.5. Figures 1 and 2 show that the polymerization is a living/controllable polymerization.

Table I shows the effect of the proportion of monomer and initiator on the ATRP process. From Table I, we found that, with the proportion of monomer and initiator decreasing, the conversion, molecular weight, initiation efficiency, and polydispersity index will all decrease. This result is similar to using the same catalysis system to polymerize methyl methacrylate. It may be due to the fact that ClCH$_2$Q has the ability of coordinating with the copper atom, so it can rob the copper from the 2,2'-bipyridine (Bpy) during polymerization.

Terminal analysis

Figure 3, the ^{1}H-NMR spectrum of polystyrene initiated by 5-ClCH$_2$Q, shows the peak at 4.30 ppm, which

corresponds to the proton (H$_1$) near the ω-chlorine, and the peak at 7.58 ppm, which is indicative of aromatic protons (H$_2$, H$_3$) from initiator, oxyquinoline. The top two peaks testified that the polymerization is ascribed to ATRP and the oxyquinoline group was attached to the polymer chain.

The complex of PSt-CH$_2$Q and rare-earth metal ion

IR spectrum of the complex

The IR spectrum of PSt-CH$_2$Q and its complex is shown in Figure 4. It revealed that, after PSt-CH$_2$Q
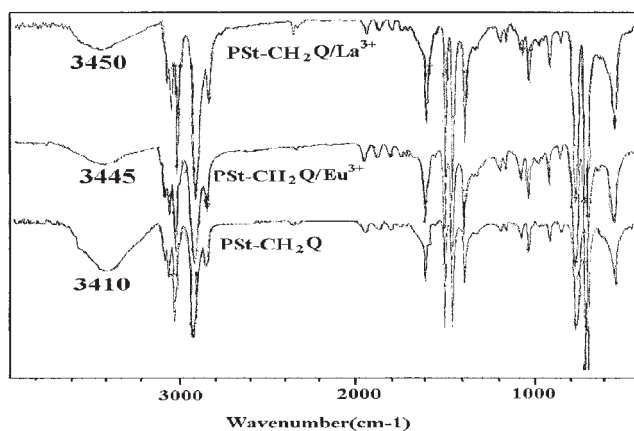

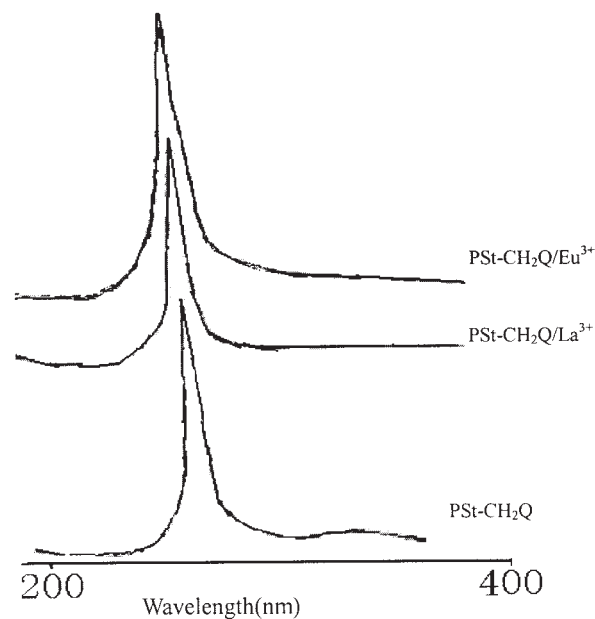**Figure 4** IR spectrum of PSt-CH$_2$Q and its' complex.

Figure 5 UV-spectrum of the polymer and complex.

Sample	M_n	$W_{complex}$ (g)	V_{EDTA} (ml)	$N_{rare\text{-}earth}$ (10^{-6} mol)	N_Q (10^{-6} mol)	$N_Q/N_{rare\text{-}earth}$
La[a]	12,950	0.0667	0.16	3.32	5.13	1.54
		0.0505	0.12	2.49	3.90	1.57
Eu[b]	18,800	0.0435	0.08	1.66	2.31	1.39
		0.0681	0.12	2.49	3.62	1.45

[a] La, the complex of PSt-CH$_2$Q/La^{3+}.
[b] Eu, the complex of PSt-CH$_2$Q/Eu^{3+}.
M_n, the average molecular weight received from GPC; N_Q, the amount of oxyquinolin in the complex; $N_{rare\text{-}earth}$, the amount of the rare-earth in the complex; $W_{complex}$, the amount of the complex. The concentration of EDTA is 0.02073 mol L^{-1}.

was coordinated with EuCl$_3$ or LaCl$_3$, the wavenumber of O—H red-shifted about 30 cm^{-1}. It indicated that the oxyquinoline group coordinated successfully with the rare-earth metal.

UV spectrum of the complex

Figure 5 is the UV spectra of PSt-CH$_2$, the complex of PSt-CH$_2$Q/Eu^{3+} and the complex of PSt-CH$_2$Q/La^{3+}. It indicated that the polymer itself had one strong absorption peak at 260 nm and one weak peak at 330 nm. They belong to the π–π^* electronic transition of phenyl from monomers and oxyquinoline group from initiator, respectively. However, the peak at 330 nm disappeared after the polymer coordinated with the rare-earth metal ions. This illustrated that the rare-earth metal was coordinated with oxyquinoline group and the way of the π–π^* electronic transition of quinoline was changed.

Coordination structure confirmed by titrimetric analysis

It is important to find out the structure of the complex compound by confirming the coordination number. Table II showed the data determined by complexometry using EDTA. It showed that the proportion of

functional group and the rare-earth metal ions in the complex was ~1.5, so we could confirm that the ratio of oxyquinoline group and rare-earth metal was 3 : 2, and the probable structure of the complex was just like Ra$_2$(QCH$_2$PSt)$_3$ (Ra is rare-earth metal ion).

Fluorescence of the PSt-CH$_2$Q and its complex

Figure 6 shows the fluorescence intensity of the PSt-CH$_2$Q and its complex. All these samples were the same concentration. The fluorescence intensity of PSt-CH$_2$Q with small molecular weight was stronger than the large one. It may be that, in the same unit volume, the smaller the molecular weight was, the more end-functional groups there were. Otherwise, after PSt-CH$_2$Q coordinates with the rare-earth ions, the fluorescence intensity of the complex enhanced more. It is because the electron structure of Eu^{3+} is just like [Xe]4f^6 and -unsteady, it is very easy to accept a electron from the ligand to become steady. The fluorescence emitted during the course that the charge transition state damped to the excited state of f-configuration (metastable state) and then circled to ground state under irradiation condition.

The third-order nonlinear third-order optical (NLO) properties of the PSt-CH$_2$Q and its complex

Table III shows the third-order NLO properties of the polymers using different initiators. The NLO coefficient of the polymer, initiated by 5-ClCH$_2$Q, is bigger than the one initiated by ethyl-2-bromideisobutyrate.
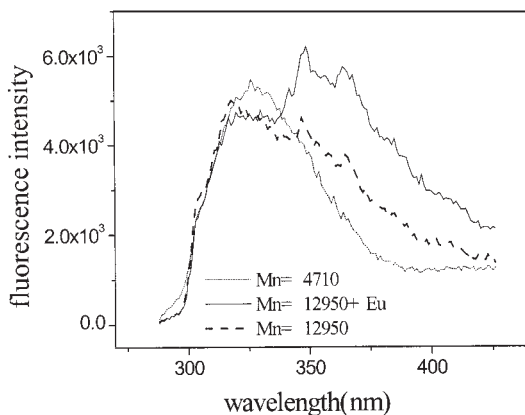

Figure 6   The fluorescence intensity of different molecular weight of the PSt-CH$_2$Q and it's rare-earth metal complex.

TABLE III
The χ^3 Value and Delaying Time of Polymers Initiated by Different Intiators

Sample	M_n	χ^3 ($\times 10^{-13}$ esu)	Delaying time ($\times 10^{-15}$ s)
PSt-EbiB[a]	9100	1.94	92.06
PSt-CH$_2$Q[b]	8940	2.07	72.74

[a] EbiB, ethyl-2-bromideisobutyrate.
[b] Q 8-hydroxyquinoline.

TABLE IV
The χ^3 Value and Delaying Time of Polymers and Its Complex

Test medium	Sample	M_n	χ^3 ($\times 10^{-13}$ esu)	Delaying time ($\times 10^{-15}$ s)
Solution	PSt-CH$_2$Q	4710	0.80	174.6
	PSt-CH$_2$Q	12,950	0.65	182.7
	PSt-CH$_2$Q	16,140	0.54	194.4
	PSt-CH$_2$Q-La	12,940	0.81	94.2
Film	PSt-CH$_2$Q	4710	1.34	147.4
	PSt-CH$_2$Q	16,140	0.83	152.3
	PSt-CH$_2$Q-La	12,940	1.41	143.4

Table IV shows the third-order NLO properties of the functional polymers and coordination polymers, which were measured by solution and film, respectively. In the same unit volume, the polymer with small molecular weight attached more end-functional groups. So we can see that the smaller the molecular weight was, the bigger the NLO coefficient was. After the functional groups coordinated with La^{3+}, the NLO coefficient enhanced markedly. This is attributed to the fact that La^{3+} possessed multielectron F orbit and plenty of energy levels, so it is easy to influence the π-conjugation system to enlarge the conjugate space and increase the conjugated electron. All these were advantageous to enhance the third-order NLO properties of the complex.

Obviously, by ATRP method, we get the polymer that end-attached the functional group. By coordinating the functional group with rare-earth metal, we get the coordination polymer, which is easier to film-form than those p–π-conjugated polymer chains by our previous research but its property of NLO can reach the same level.[14] To the polymer with same molecular weight, the third-order NLO coefficient of film is larger than that of solution. It is because molecular orientation in film is better than in solution. Figure 7 shows the Gaussion fitting curve of the film.

CONCLUSION

In summary, ATRP is a convenient way to prepare the functional polymer. By selecting 5-chloromethyl-8-hydroxyquinoline as initiator to initiate polymerization of styrene, we can get the PSt, which end-attached the oxyquinoline group. The polymers show good fluorescence property and NLO property with good film-forming ability. Chelating the oxyquinoline group with Eu^{3+} and La^{3+}, the fluorescent intensity and third-order nonlinear optical coefficient of this coordination polymer will be enhanced much more. The proportion of oxyquinoline group coordinating with rare-earth metal is determined 3 : 2 by titrimetric analysis.
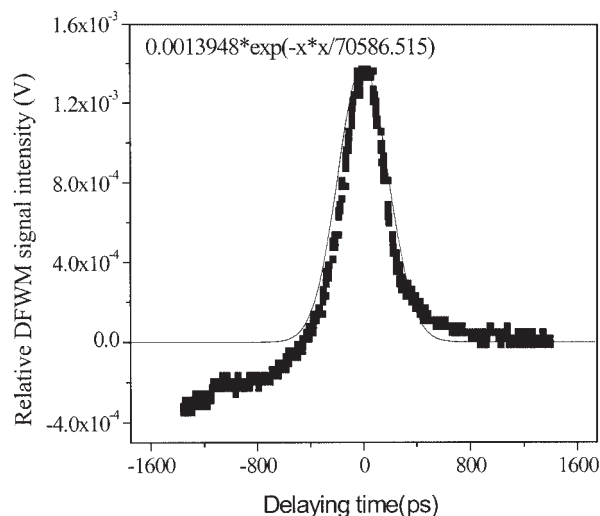
Figure 7 The NLO reponse curve of the polymer film (Condition: Mn = 4710).

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