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Synthesis of oxyquinolyl end-functional PMMA by atom transfer radical polymerization

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Abstract: Oxyquinolyl end group functionalized PMMA was prepared by a new initiator 5-chloromethyl-8-hydroxyquinoline via atom transfer radical polymerization. Studying this polymer, we find it possesses stronger fluorescence and larger nonlinear third-order optical (NLO) coefficient than the PMMA initiated by ethyl α-bromoisobutyrate, and the polymer could be easily processed into film. The NLO coefficient of the polymer tested in the film is better than that in the solution.

1. Introduction

8-hydroxyquinoline and its derivatives are widely used as complexing agents in analytical chemistry for quantitative analysis of some trace amount metal ions. In 1987,Tang's group[1] reported a electroluminescent devices based on Aluminum tri(8-hydroxyquinoline) complex. The vacuum deposition technique by which small molecular weight complex were processed into film always made devices preparation complicated and difficult. Linking the small molecular weight complex to polymer chain might be a favorable way [2-3].

Atom transfer radical polymerization (ATRP) is a useful technique to prepared functional polymers for a large variety of vinyl monomers [4-5], with facile control of chain topology and able to synthesize block copolymer [6-7]. A large variety of compounds and halogenated polymer could be used as initiator (or macroinitiator) for ATRP [8]. Molecular weight of the obtained polymer could be easily controlled by mole ratio regulation of monomer and initiator.[9], In the present paper, 5-chloromethyl-8-hydroxyquinolin was synthesized and used as initiator of methyl methacrylate ATRP to prepare 8-hydroxyquinoline end group functionalized PMMA. The obtained polymer's properties, such as fluorescence and NLO was systematically studied.

2. Experimental

2.1. Materials

5-chloromethyl-8-hydroxyquinoline (5-$ClCH_2Q$) was prepared according to the known method[10-11]. MMA (AR grade from Shanghai Reagent Co. of China) was washed by 5% sodium hydroxide aqueous solution to remove inhibitor, dried over magnesium sulfate overnight and filtered, then distillated under reduced pressure. Copper chloride, CuCl (AR grade from Shanghai Reagent Co. of China) was dissolved in a few concentrated chlorhydric acid and deposited by a great deal of water, the result precipitate was dried under vacuum. All others reagents and solvents (Shanghai Reagent Co. of China) were used without further purification.

2.2 Polymerizations

CuCl (0.015 g, 0.15 mmol), 2,2'-bipyridineb, bpy (0.0702 g, 0.45 mmol), cyclohexanone (1.ml) and MMA (1.00 g, 10 mmol) were added to a reaction tube, The mixture was stirred till all solid materials were well distributed. Then 5-$ClCH_2Q$ (0.0097 g, 0.05mmol) was added. The reaction tube was degassed and pumped with N_2 for three times to remove trace oxygen. The reaction tube was then immersed in a preheated oil bath at 85℃. Samples for kinetic measurements were taken after desired time interval from the reaction tubes and the reaction was stopped by pouring the mixture to a large amount of methanol. The precipitated polymer was solved with THF, precipitated in methanol for the second time, and then dried under vacuum at 40℃ to constant weight.

2.3 Characterization

Percentage conversion was determined by gravimetry. The molecular weight and polydispersity of obtained PMMA were measured on Waters-1515 GPC with the calibration of the commercially available polystyrene standards and THF as solvent. ^{1}H-NMR spectra were performed on a INOVA-400 MHz spectrometer using $CDCl_3$ as solvent, and tetramethylsilane as internal reference. Fluorescence spectrum were performed on a Edinburgh-920 fluorescence spectra photometer. Third order NLO coefficient and delaying time were detected by PG401 psec YAG pulsed laser.

3. Results and discussion

3.1 Confirmation the living/controllable polymerization

Fig.1 is the mechanism of ATRP, according to the mechanism we can know the kinetic equation is just as follow:

$$R_P = -d[M]/dt = k_P[M][P\cdot] \qquad (1)$$

[P·] is invariable during the polymerization. So the equation (1) can convert to (2):

$$-d[M]/dt = k_p^{app}[M] \qquad (2)$$

Equation (2) can convert to the equation (3) by integral, (kp^{app} is apparent chain propagation rate constant[12])

$$\ln([M_0]/[M]) = k_p^{app}t \qquad (3)$$

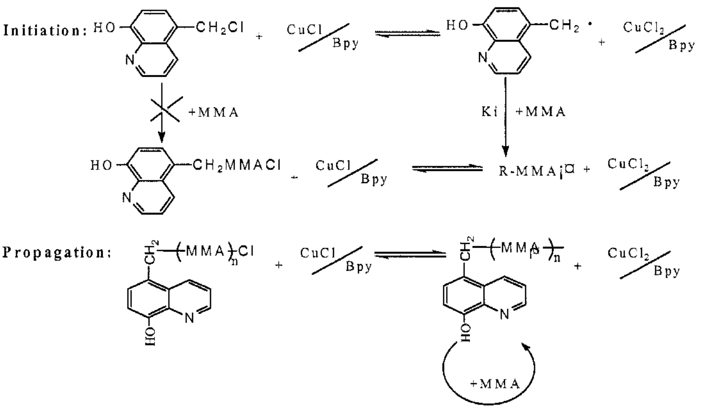

Fig.1 Mechanism of ATRP

Equation (3) indicates $\ln([M]_0/[M])$ increases linearly with the polymerization time, where $[M]_0$ and $[M]$ denote the initial and instantaneous monomer concentration respectively. Fig.2 is corresponding to equation 3, demonstrating that kinetics of polymerization was first order and the concentration of propagating radical is a constant.

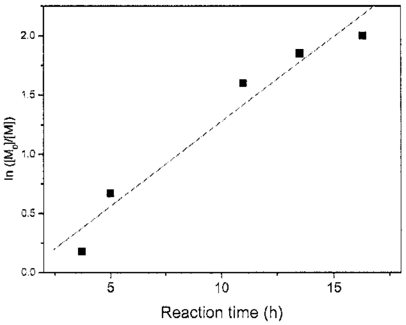

Fig.2 The relationship of ln([M0]/[M]) and polydispersity with Poly- time in the solution polymerization of MMA at 85□ onditions:MMA/ ClCH$_2$-Q/CuCl/Bpy=200/1/3/9 [M]

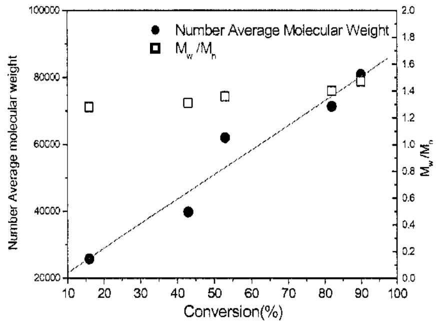

Fig.3 Dependence of molecular weight on conversion in the solution polymerization of MMA at 85℃ Conditions:MMA/ ClCH$_2$-Q/CuCl/Bpy=200/1/3/9 $[M]_0$=4.7mol/L

Fig.3 shows the molecular weights measured by GPC increase linearly with the conversion up to 88%. As shown in Fig.3, the polydispersities are all less than 1.55. From the two figures it could be concluded that the polymerization has the characteristics of living and controllability.

But the molecular weight measured by GPC is more greater than the theoretical molecular weight which is calculated according to Eq(4).

$$\overline{M}_{n.Theo.} = \frac{monomerAmount(g)}{initiator(mol)} \times conversion(\%) \qquad (4)$$

Table.1 shows the percentage yield, molecular weight, initiation rate and polydispersity index of the polymerized MMA as a function of the proportion of moner and initiator. At the proportion of moner and initiator being 200:1, the initiator rate reached the highest 0.22, and the rate decreased from 0.22 to 0.03 as the mole ratio decreased from 200:1 to 100:3. This result is similar to the system that using $ClCH_2$-Q as initiator to polymerize St. The reason was due to the fact that $ClCH_2$-Q has stronger ability of co-ordination than Bpy and it can rob the copper ion from the Bpy during the cause of polymerization. The $ClCH_2$-Q added more, the coper ion was robbed more and the complex of $ClCH_2$-Q/copper precipitated more as powder.

Table 1 Polymerization of MMA with different proportion of moner and initiator

MMA/$ClCH_2$-Q	Conversion/%	$Mn_{,cal}$	$Mn_{,GPC}$	Initiation rate	Mw/Mn
200:1	88	17600	81790	0.22	1.521
100:1	60	6000	73427	0.08	1.434
50:1	44	2200	54687	0.04	1.321
100:3	40	1333	40942	0.03	1.298

3.2 Terminal analysis

Fig.4 shows the ^{1}H-NMR spectrum of PSt-CH_2Q, The peak at 7.529 was assigned to the 3-H of 8-hydroxyquinoline and the peak at 2.38ppm assigned to methylene of the initiator.

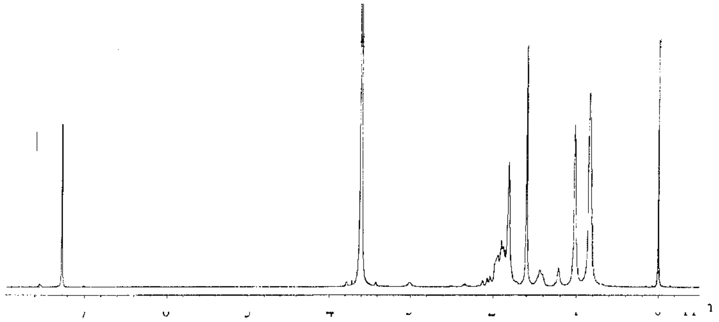

Fig.4 ^{1}H-NMR spectrum of PMMA synthesized with $ClCH_2$-Q/CuCl/Bpy initiating system with $CDCl_3$ as solvent

3.3 Fluorescence of the PSt-CH_2Q and its complex

Fig.5 shows the fluorescence intensity of the PMMA-CH_2Q. All these samples were the same mass concentration. The smaller molecular weight was, the stronger fluorescence intensity was. The reason was that in the same unit volume the smaller molecular weight was, the more end-functional groups were.

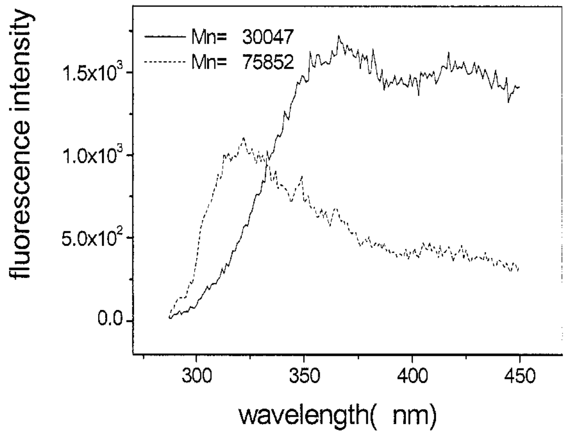

Fig.5 The fluorescence intensity of different molecular weight of the PMMA initiated with $ClCH_2$-Q/CuCl/Bpy system

Condition: Different samples have the same mass concentration and the same excitation

3.4 The third-order NLO properties of the PMMA-CH_2Q

Table.2 shows the third-order NLO properties of the polymers using different initiator. The NLO coefficient of the polymer which was initiated by functional intiator is bigger than the polymer initiated by commonly initiator.

Table 2 The $X^{(3)}$ value and delaying time of polymers initiated by different initiator

Sample	Mn	$X^{(3)}$ ($\times 10^{-13}$esu)	Delaying time ($\times 10^{-15}$s)
PMAA-EbiB (1)	55082	2.01	93.67
PMAA-CH_2Q(2)	54281	2.14	101.99

Table.3 shows the third-order NLO properties of the functional polymers which were tested in the different mediums. In the same medium the smaller molecular weight was, the bigger NLO coefficient was. The theory is just similar to what we had elaborated in the *3.2* part.

At the same time table.3 revealed that the properties measured in the film excelled to those measured in the solution. It is because that molecular orientation in film is better than in solution and the properties measured in film won't be influenced by solvent effect. Fig.6 and fig.7 are Gaussion fitting curves of the same sample respectively measured in solution and in film. Obviously the curve from film is smoother than that from solution. So the complex we have synthesized is easier to film-forming than those which have p-Л conjugate molecular chain and its' property of NLO can reach the same level[13].

Table 3 The $X^{(3)}$ value and delaying time of polymers

Test medium	Sample	Mn	$X^{(3)}$ ($\times 10^{-13}$esu)	Delaying time ($\times 10^{-15}$s)
Solution	PMAA-CH_2Q(3)	30047	0.950	185.4
	PMAA-CH_2Q(4)	72852	0.736	207.3
Film	PMAA-CH_2Q(5)	30047	1.49	142.38

	PMAA-CH_2Q(6)	72852	1.28	146.91

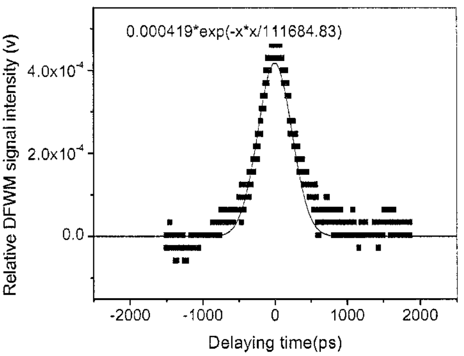

Fig.6 The NLO response curve of the polymer solution

Conditon:Mn=30050

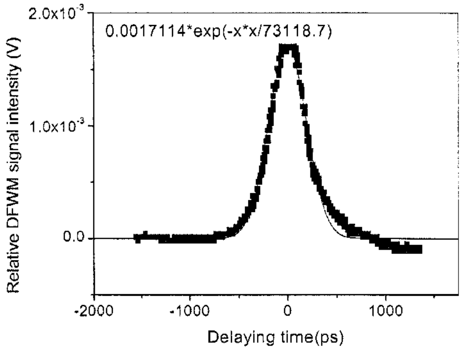

Fig.7 The NLO response curve of the polymer film

Condition:Mn=30050

Acknowledgement

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