

Synthesis, Characterization, and Fluorescence of End-Functionalized Polystyrene Initiated by 4-Chloromethyl benzoic acid and Ethyl 4-chloromethyl benzenecarboxylate via ATRP

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ABSTRACT: End-functionalized polystyrene (PSt) was synthesized via atom-transfer radical polymerization (ATRP) by using 4-chloromethyl benzoic acid (CMBA) and the ethyl-protected carboxylic acid, ethyl 4-chloromethylbenzenecarboxylate (ECBC), as initiators respectively. The structure of PSt proved the living-radical polymerization. Results exhibit both ATRP initiators afforded well-controlled polymerization with high initiator efficiencies. However, the study also shows the controllability of ATRP can be obvi-

ously influenced by using different initiator in different catalyst system. Furthermore, the terminal group of the PSt, benzoic acid, can coordinate with Europium(III) ion to obtain the polymeric Eu(III) complex, which shows both emissions of polymer and Eu(III) ion. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 75–80, 2007

Key words: 4-chloromethyl benzoic acid; 4-chloromethyl benzenecarboxylate; initiator; ATRP; styrene

INTRODUCTION

Atom-transfer radical polymerization (ATRP) is a relatively novel versatile method in the synthesis of polymers with controlled molecular weights and low polydispersities.^{1–5} In an ATRP, initiator always plays an important role to initiate the polymerization and determine the α -end of polymer.^{6–11} Nowadays, various functionalized polymers with kinds of functional group at α -end have been obtained by using different initiators. For example, pyrene, anthracene end-functionalized macromonomers can be obtained by using initiators containing pyrene, anthracene group.^{12–13} They are potential optical materials due to their special electrical and optical properties. In addition, if the initiators contain donor atoms such as sulfur, oxygen, and nitrogen, the terminal of obtained polymers can be an ideal ligand to form polymeric complex. Our interest is focused on the design and synthesis of differ-

ent functional initiators to initiate the ATRP of vinyl monomers.

In our previous research, PMMA with oxyquinolyl end group was synthesized via ATRP. The Europium(III) (Eu(III)) complex was verified to coordinate with the oxyquinolyl end group of PMMA and emitted obvious red fluorescence.¹⁴

In this study, an initiator 4-chloromethyl benzoic acid (CMBA) was allowed to initiate the polymerization of styrene via ATRP. The end-functionalized polystyrene (PSt) with carboxylic acid group can further coordinate with lanthanide ion to form polymeric lanthanide(III) complex. The PSt with CMBA end group shows obvious fluorescent emission between 375 and 450 nm, while the corresponding emission band of its Eu(III) complex is much stronger and a characteristic band of Eu(III) ion at 616 nm was also found in emission spectrum. Because of the good film-forming ability of PSt, the new end-functionalized PSt and their complexes will be potential optical film materials.

In addition, ATRP of St initiated by the ethyl-protected carboxylic acid, ethyl 4-chloromethylbenzenecarboxylate(ECBC), was also discussed to better compare the initiation of unprotected and protected carboxylic acid. Results exhibit both ATRP initiators afforded well-controlled polymerization with high initiator efficiencies. However, the controllability of ATRP can be obviously influenced using different initiator in different catalyst system. For example, well-

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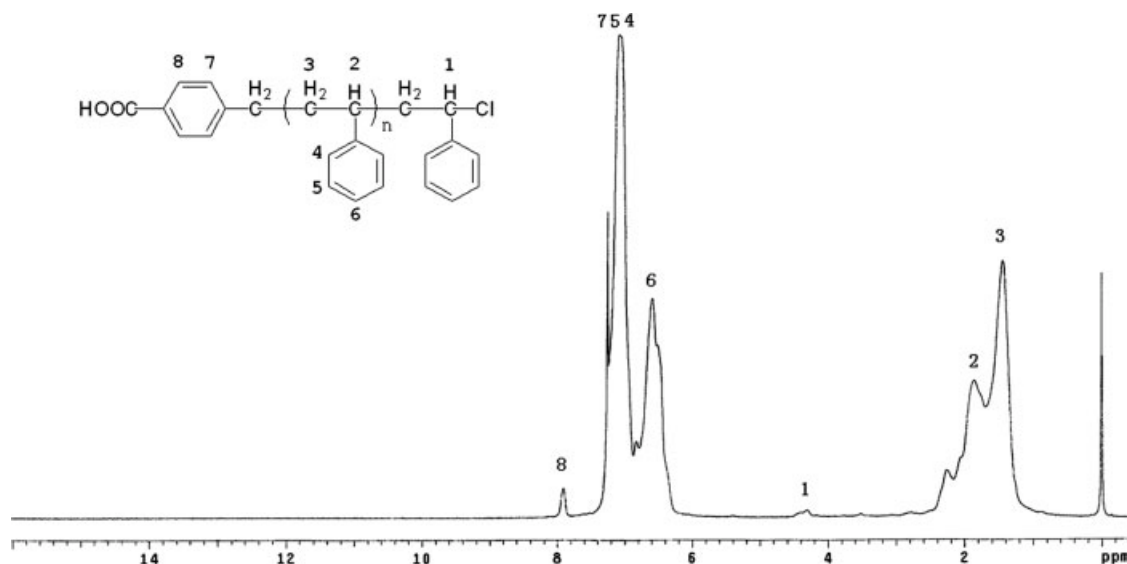


Figure 1 $^1\text{H-NMR}$ of the polymer Pst1.

controlled polymerization of styrene can be achieved by using ethyl 4-(chloromethyl)benzenecarboxylate as initiator than by using 4-(chloromethyl)benzoic acid, in CuCl/PMDETA catalyst system.

EXPERIMENTAL

Materials and instruments

Styrene (CP grade, Shanghai chemical Reagent), copper(I) chloride (CuCl) (AR grade, Shanghai Zhenxin Chemical Reagent Factory), and cyclohexanone (AR grade) were purified before using. *N,N,N',N',N''*-pentamethyldiethyltriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuum. 4-(Chloromethyl)benzoic acid (HPLC, 99.6%), ethyl 4-(chloromethyl) benzenecarboxylate (92.03%), and 2,2-bipyridine (BPY) (AR grade) were used without further purification.

IR spectrum was measured by PerkinElmer 577 FTIR instrument (KBr pellet). $^1\text{H-NMR}$ was measured by INOVA 400 MHz NMR instrument, using CDCl_3 as solvent. Elemental analysis was obtained by Carlo Erba-MOD1106 instrument. Purity of initiator was analyzed by Waters 515 HPLC. Conversion of monomer was determined by gravimetry. Weights and the molecular weight distributions relative to polystyrene were measured using Waters 1515 GPC, with THF as a mobile phase and with column temperature of 30°C. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer in DMF solution.

Synthesis of ethyl 4-(chloromethyl) benzenecarboxylate

ECBC (0.1 mol, 17.04 g), ethanol (2 mol, 92 g), and 4-methyl benzenesulfonic acid were refluxed for 48 h.

Ethanol was distilled and 100 mL 10% NaHCO_3 cold solution was poured into the flask. The mixture was kept stirring for 2–3 h and extracted with acetic ether. The extract was dried with MgSO_4 , filtered, and solvent was removed under vacuum. The residue was distilled and gathered at 128–130°C/4 mmHg (140–150°C/15 mmHg¹⁵). A colorless liquid product was obtained. Yield: 61.96%; purity: 92.03% (GC).

Polymerization of styrene

All atom-transfer radical polymerization (ATRP) reactions were carried out following the similar experimental procedure: CuCl, BPY or PMDETA, cyclohexanone, initiator, and styrene were mixed in a round-bottomed flask. The flask was sealed and cycled between vacuum and N_2 for four times. Then, the flask was sealed under N_2 and placed in a preheated oil bath at a desired temperature. Samples were taken at regular intervals for conversion and molecular weight analysis. The samples were dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.5, V/V). The precipitation was filtered and dried under vacuum.

Coordination of the PSt1 with EuCl_3

PSt1 (0.5 g) was dissolved in 50 mL DMF and adjusted to the pH value of 7–8 with ammonia. Then, the solution was dropped into 20 mL EuCl_3 (0.5 g) DMF solution. The mixture was stirred for 12 h and precipitated with excess ethanol, and the polymeric complex was filtered, washed with 50 mL methanol, and dried in vacuum. The obtained polymeric Eu(III) complexes were purified by dissolving in DMF, precipitated with ethanol for at least five times to remove excessive

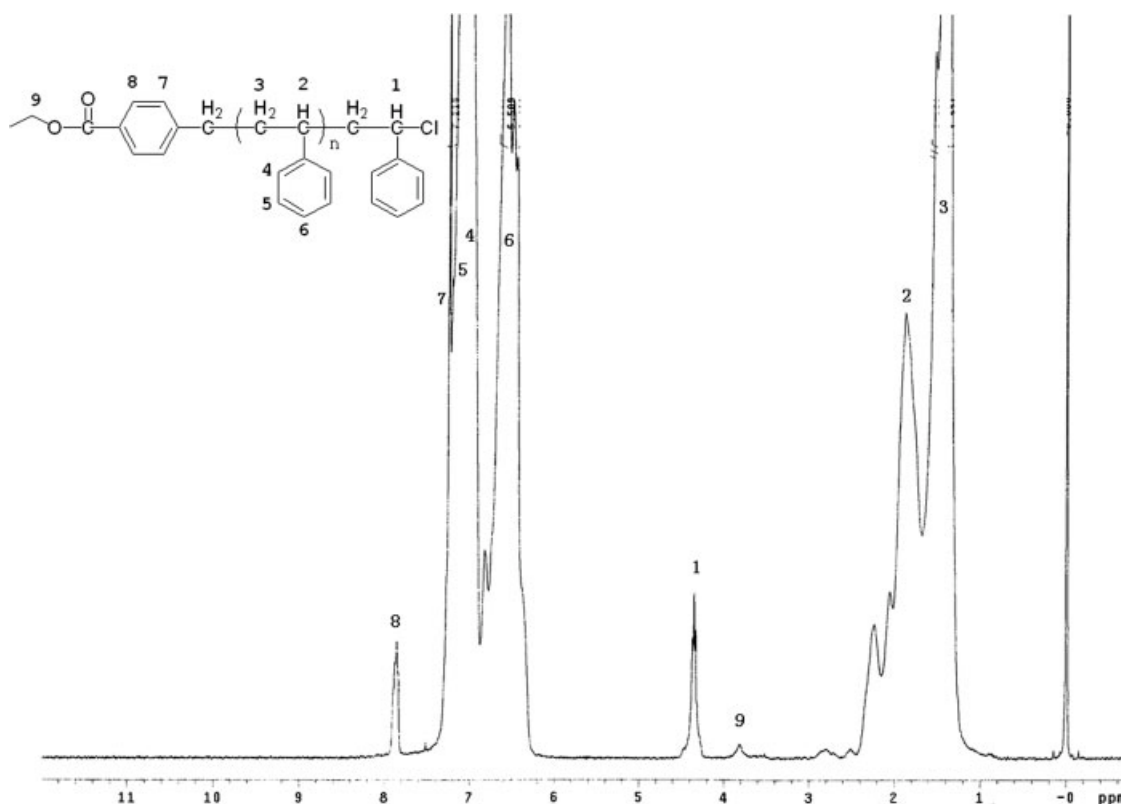


Figure 2 $^1\text{H-NMR}$ of the polymer Pst2.

EuCl_3 compounds. Elemental analysis of PSt1-Eu(III): C, 61.49 H, 5.57%; ICP: Eu, 18.4% (content).

RESULTS AND DISCUSSION

Characterization of ATRP

According to the mechanism of an ATRP, initiator group should be incorporated at α -end of the polymer chain, while ω -end remains a terminal halide. It was verified by FTIR and $^1\text{H-NMR}$. IR spectrum of PSt with CMBA as end group shows strong absorption at 1690 cm^{-1} (C=O), which attributes to the existence of carboxylic acid in the polymer while similar absorption in PSt with ECBC end group at 1715.51 cm^{-1} (C=O), which attributes to the existence of ester group.

$^1\text{H-NMR}$ spectra of PSt with CMBA (PSt1) and ECBC (PSt2) end group are shown in Figures 1 and 2 respectively. The peak at 7.9 ppm shown in Figure 1 (7.85 ppm in Fig. 2) corresponds to protons of benzene in initiator CMBA (ECBC) while the peak at 4.317 ppm in Figure 1 (4.35 ppm in Fig. 2) corresponds to the protons of methine, which is at ω -end of polystyrene. In addition, the peak at 3.81 ppm corresponds to the protons of methene in the initiator ECBC. Obviously, both FTIR and $^1\text{H-NMR}$ spectra testified that the initiator was labeled at the end of polystyrene.

The kinetic plot of $\ln([M]_0/[M])$ for the ATRP of styrene using different initiators (CMBA and ECBC) is

shown in Figure 3. In each case, as can be seen that $\ln([M]_0/[M])$ increases linearly with the polymerization time, indicating the polymerization is first-order kinetics and the concentration of growing radical is a constant. Such results suggest the "living" polymerization processes. Two different catalytic systems CuCl/BPY and $\text{CuCl}/\text{PMDETA}$ are adopted, to better

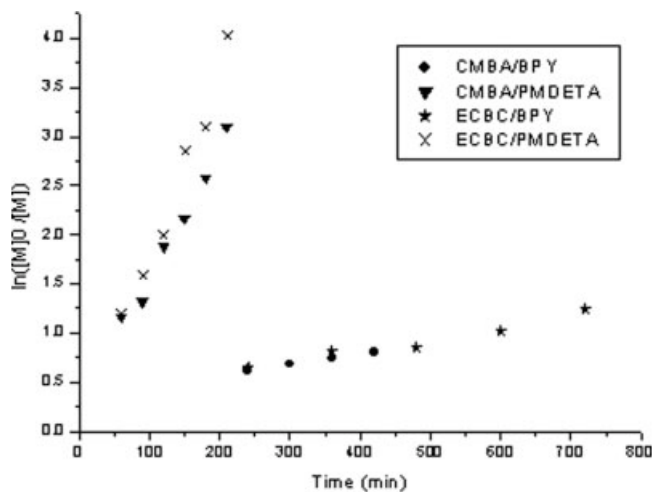


Figure 3 Kinetic plots for the ATRP of styrene initiated by CMBA and ECBC. Polymerization conditions: V (styrene): V (cyclohexanone) = 1 : 1; for BPY, $[\text{styrene}]_0$: $[\text{initiator}]_0$: $[\text{CuCl}]$: $[\text{BPY}]_0$ = 200 : 3 : 3 : 9, at 130°C ; for PMDETA, $[\text{styrene}]_0$: $[\text{initiator}]_0$: $[\text{CuCl}]$: $[\text{PMDETA}]_0$ = 200 : 3 : 3 : 4, at 120°C .

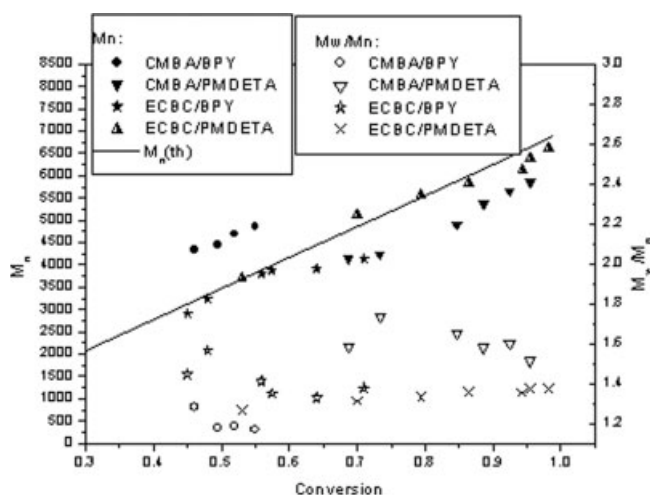
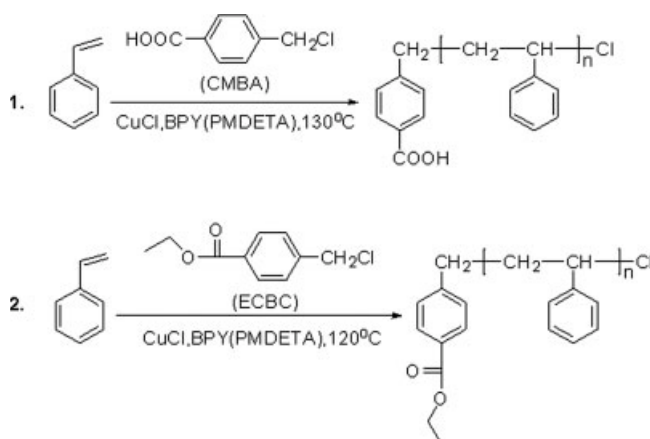


Figure 4 Evolution of molecular weights and polydispersity index with conversion for the ATRP of styrene initiated by CMBA and ECBC. The polymerization conditions are given in Figure 3.

understand the kinetics of polymerizations of styrene. Polymerizations using CuCl/PMDETA catalyst system proceeds obviously faster than those using CuCl/BPY catalyst, which is reasonable that the complex of copper and PMDETA had lower redox potential than that of the Cu/BPY complex.¹⁶ When using PMDETA as ligand, the polymerization initiated by CMBA has the lower rate than that initiated by ECBC. By contrast, using BPY as ligand, the polymerization initiated by CMBA proceeds faster than that of ECBC.

Evolution of molecular weight and polydispersity index with monomer conversion initiated by CMBA and ECBC are depicted in Figure 4. The M_n values increased linearly with conversion with low polydispersities throughout the polymerization. When using CMBA as initiator, the polydispersity index of PSt in CuCl/PMDETA catalyst system (mostly above 1.5) is obviously higher than that in CuCl/BPY catalyst system (Scheme 1). It may infer that polymerization using



Scheme 1 Syntheses of PSt by ATRP using CMBA (1) and ECBC (2) initiator, respectively.

CuCl/BPY catalyst system is easier to be controlled. However, when using ECBC as initiator, the M_n s measured by GPC are in better agreement with the theoretical values in CuCl/PMDETA catalyst system than those in CuCl/BPY catalyst system, while the controllability of these two systems are nearly the same.

Hereto, it is concluded that different ligand is suitable for different initiator. For CMBA, the polymerization has a faster rate (than ECBC/BPY) and narrower polydispersity indices (than CMBA/PMDETA) using BPY as ligand, while lose of control using PMDETA as ligand. For ECBC, the optimum ligand should be PMDETA.

Influence of temperature, initiator, and catalyst on polymerization

The effect of temperature in the polymerization is also investigated. Table I lists the yield, molecular weight, and polydispersity index of the polymerization of St initiated by CMBA and ECBC at different temperature. It indicates that the rate of polymerization apparently increases with an increasing polymerization temperature. As shown in Table I, the optimum polymerization temperature is 130°C for CMBA as initiator and 120°C for ECBC as initiator.

Table II shows the effects of monomer to initiator mole ratio on conversion, molecular weight initiation rate, and polydispersity index of synthesized PSt. In each case, with the increase of mole ratio of monomer to initiator, the initiation efficiency decreases, which may be due to the increasing occurrence of radical coupling. The polymerization with CMBA as the initiator shows the best controllability at the molar ratio of 200 : 3, and that with ECBC the initiator shows the best controllability at the molar ratio of 200 : 4.

Synthesis of the polymeric Eu(III) complexes and their fluorescence

The polymers PSt1 and PSt2 as unprotected and protected end groups, respectively, are coordinated with

TABLE I
Effects of Temperature on Yield, Molecular Weight, and Polydispersity Index of the Synthesized Pst Initiated by CMBA and ECBC

Initiator	Temperature (°C)	Yield (%)	$M_{n,GPC}$	M_w/M_n	$M_{n,th}$	I_{eff}
CMBA	140	65	4774	1.193	4528	0.95
	130	52	4696	1.185	3623	0.77
	120	46	4050	1.316	3205	0.79
	110	36.18	3779	1.546	2508	0.66
ECBC	140	67	4237	1.219	4668	1.10
	130	55	3614	1.426	3832	1.06
	120	48	3394	1.334	3344	0.99
	110	43	3223	1.364	2996	0.93

Conditions: [styrene]₀ : [initiator]₀ : [CuCl] : [BPY]₀ = 200 : 3 : 3 : 9, V(styrene) : V(cyclohexanone) = 1 : 1, for 6 h.

TABLE II
Effect of Monomer to Initiator Mole Ratio on Yield, Molecular Weight, and Polydispersity Index of PSt1 Initiated by CMBA and ECBC

Initiator	[St] ₀ : [initiator] ₀	Yield (%)	<i>M_n</i> ,th	<i>M_n</i> ,GPC	<i>M_w</i> / <i>M_n</i>	<i>I_{eff}</i>
CMBA	200 : 1	44.19	9235	7657	1.395	1.21
	200 : 2	48.23	5040	4773	1.36	1.06
	200 : 3	49.5	3448	4447	1.179	0.78
	200 : 4	50.73	2651	3688	1.281	0.72
	200 : 5	54.9	2295	2602	1.365	0.88
ECBC	200 : 1	64	13376	7582	1.418	1.76
	200 : 2	52	5434	4160	1.431	1.31
	200 : 3	55	3832	3614	1.426	1.06
	200 : 4	50	2613	2742	1.299	0.95
	200 : 5	45	1881	2313	1.350	0.81

Conditions: [styrene]₀ : [CuCl] : [BPY]₀ = 200 : 3 : 9, *V*(styrene) : *V*(cyclohexanone) = 1 : 1, at 130°C.

EuCl₃, respectively, and the obtained compounds were characterized by IR, thermal analysis, ICP, and Fluorescence.

Figure 5 shows IR spectra of PSt with CMBA end group (PSt1) and its Eu(III) complex. The carboxyl (C=O) absorption wavelength at 1690 cm⁻¹ in PSt1 is obviously red-shifted after the coordination. However, IR spectra of PSt with ECBC end group (PSt2) and its Eu(III) complex have no obvious difference, which is probably due to the weaker interaction between Eu(III) and the ester group and the interaction of EuCl₃ and the PSt2 might be the simple mixture. To better testify the coordination between Eu(III) ion and PSt1, we choose PSt1 with low molecular weight (*M_n* = 1000, detected by ¹H-NMR and GPC) as ligand. The thermal analysis shows that the first step of weight loss is assigned to loss of coordinated water molecules, which does not appear in decomposition of PSt1. The polymer PSt1 decomposes completely from 390 to 471°C, whereas decomposition of the PSt1-Eu complex is advanced to 337°C. The final residue (19.84%, calcd.14.36%) is assigned to Eu₂O₃, in which a small amount of uncoordinated EuCl₃ exists in the

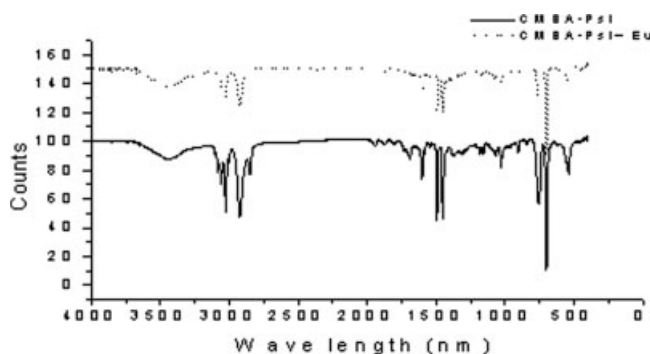


Figure 5 IR spectra of PSt1 and PSt1-Eu.

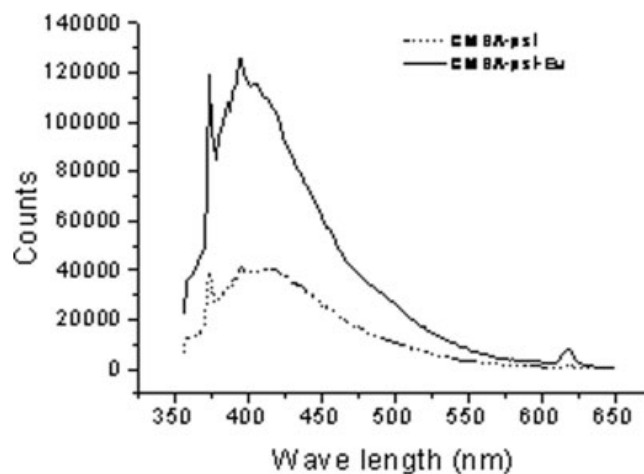


Figure 6 Emission spectra of Pst1 and Pst1-Eu(III) complex.

polymeric complex. According to the results of thermal analysis and ICP, possible component of PSt1-Eu complex is speculated as PSt-CH₂C₆H₅COO-EuCl₂·3H₂O or PSt-CH₂C₆H₅COOH-EuCl₃·3H₂O, i.e., only one polymeric chain coordinated with EuCl₃.

The fluorescence spectra of the above-mentioned polymers and their complexes are interesting and the coordination of Eu(III) and PSt1 may be further testified. Figure 6 shows the emission spectra of PSt1 and its Eu(III) complex. According to Figure 6, the broad emission band at about 415 nm belongs to the emission of PSt1, while the sharper side band at 616 nm is the emission band of Eu(III) ion. With the formation of the complex, the intensity of emission band of complex is much stronger than that of PSt1. More importantly, the characterized emission (⁵D₀→⁷F₂) of Eu(III) ion at 616 nm as a small side band is observed, which may verify the coordination of Eu(III) and polymer to some degree. Figure 7 shows the emission spectra of PSt2 and its mixture with EuCl₃, which is similar but

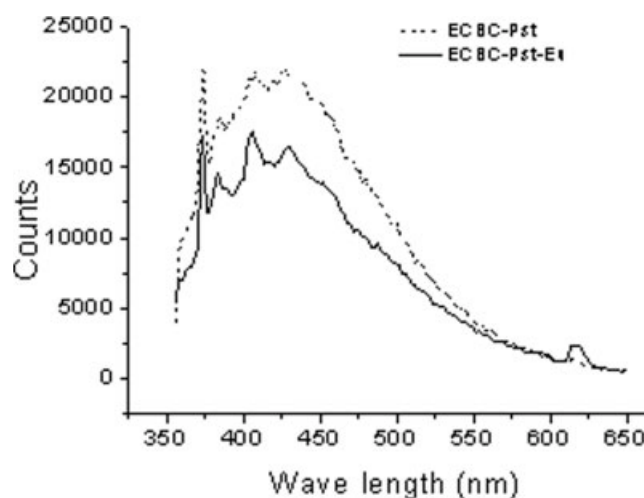


Figure 7 Emission spectra of Pst1 and Pst2-Eu(III) complex.

much weaker than those of PSt1 and its Eu(III) complex. The simple mixture of Eu(III) and PSt2 may cause the decrease of fluorescent intensity of PSt. However, a tiny side band at 616 nm is indicative of the existence of EuCl_3 .

CONCLUSIONS

The carboxylic acid group or ester group can be introduced into the end of polymer by choosing initiator bearing carboxylic acid group or ester group via ATRP. ATRP of styrene can be processed by using 4-(chloromethyl)benzoic acid or ethyl 4-(chloromethyl)benzenecarboxylate as initiators. Different substituting groups in initiator will cause the different controllability of ATRP in different catalyst system. Better controlled polymerization of styrene can be achieved by using ethyl 4-(chloromethyl)benzenecarboxylate as initiator than by using 4-(chloromethyl)benzoic acid as initiator with $\text{CuCl}/\text{PMDETA}$ as catalyst.

The PSt with carboxylic acid group at α -end can be a polymeric ligand to coordinate metal ions forming polymeric metal complexes. In this study, Eu(III) complex and its fluorescent property were discussed, which owns good solubility and shows both emissions

of polymer and Eu(III) ion. A further study of their fluorescence and film-forming capability is on-going.

References

1. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
2. Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970.
3. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
4. Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
5. Matyjaszewski, K.; Xia, J. X. *Chem Rev* 2001, 101, 2921.
6. Haddleton, D. M.; Waterson, C. *Macromolecules* 1999, 32, 8732.
7. Mecerreyes, D.; Atthoff, B.; Boduch, K. A.; Trollsås, M.; Hedrick, J. L. *Macromolecules* 1999, 32, 5175.
8. Reining, B.; Keul, H.; Höcker, H. *Polymer* 1999, 40, 3555.
9. Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* 2000, 33, 2340.
10. Wang, X. S.; Armes, S. P. *Macromolecules* 2000, 33, 6640.
11. Yuan, X.; Lu, J. M.; Xu, Q. F.; Wang, L. H. *Polymer* 2005, 46, 9186.
12. Korn, M. R.; Gagne, M. R. *Chem Commun* 2000, 1711.
13. Zhang, H.; Klumperman, B.; van der Linde, R. *Macromolecules* 2002, 35, 2261.
14. Lu, J. M.; Li, H.; Xia, X. W.; Yao, S. C.; Zhu, X. L. *Polym Bull* 2004, 51, 327.
15. Xia, J. H.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7697.
16. Blicke, B. F. F.; Lilibfeld, W. M. *J Am Chem Soc* 1943, 65, 2281.