

Synthesis, Characterization, and Property of End-functionalized Telechelic PSt via ATRP

Jian-Mei Lu, Xue-Wei Xia, Xiang Guo, Qing-Feng Xu, Feng Yan, Li-Hua Wang

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, China

Received 1 August 2007; accepted 15 November 2007

DOI 10.1002/app.27804

Published online 6 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polystyrene incorporating carboxylate group as α -end was synthesized by using initiator 4-chloromethyl benzoic acid via atom transfer radical polymerization. Its ω -chlorine end-group was transformed by cumic acid, diethyl malonate, and thiol, respectively, to form end-functionalized telechelic polystyrenes. These PSts with different functionalized ω -end group (PSt1, PSt2, and PSt3) were obtained and characterized by H NMR and TGA. This type of end-functionalized telechelic polymers can further act as polymeric ligands to form poly-

meric metal complexes. In this study, PSt1 with carboxylate group at each end was allowed to react with $\text{Eu}(\text{DBM})_2\text{Cl}\cdot 2\text{H}_2\text{O}$ to afford a new polymeric complex PSt1-Eu(III) showing significant red-light emission. Moreover, the film of PSt1-Eu shows similar emission pattern with its DMF solution. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3430–3434, 2008

Key words: atom transfer radical polymerization (ATRP); end-functionalized telechelic polystyrene; fluorescence

INTRODUCTION

Atom Transfer Radical Polymerization (ATRP) has been successfully used to prepare well designed polymer with controlled molecular weight and narrow molecular weight distribution. The α -end functionalized polymers via ATRP can be synthesized by selecting various initiators that contain specified functional groups, while its ω -end generally remains a terminal halide.^{1–9} Because the terminal C-X bond is always active, the halogen can be transformed into other functional groups by some organic procedures such as nucleophilic displacement groups by nucleophilic displacement reaction. For example, Matyjaszewski has reported that the halogen end group of polymer was successfully substituted by azide,¹⁰ hydroxyl,¹¹ phosphonium,¹² and so on. László

Garamszegi has reported a new method to convert terminal halogen into thiol¹³ and Dong Yang has reported that C_{60} end-capped polymer had been successfully synthesized.¹⁴

Our research plan is focused on obtaining double-end functionalized telechelic polymers which can act as polymeric ligands with identified coordination location and numbers. Furthermore, this kind of ligand has good film-forming ability and will provide a novel method to obtain organic/inorganic film materials. If functional inorganic complexes are coordinated with the above ligand, the novel polymeric complex is possible to exhibit both of their properties and become a new functional material. Our previous research has concentrated on the nonlinear optical or fluorescent properties of polymer and polymeric complexes.^{15–17} Therefore, we utilize the initiator, 4-(chloromethyl)benzoic acid to initiate the ATRP of styrene to obtain PSt containing carboxylate group at α -end. The ω -end of this PSt was substituted by cumic acid, diethyl malonate, and thiol groups, respectively, by organic substitution reaction. The double end-capped telechelic PSt was characterized by HNMR and thermal analysis. The PSt1 (polystyrene) containing double carboxylate end groups was further coordinated with fluorescent complex $\text{Eu}(\text{DBM})_2\text{Cl}\cdot 2\text{H}_2\text{O}$, and the polymeric Eu(III) complex shows obvious strong red emission which attributed to the typical excitation of Eu(III) ions. It's worthy of noting that the film of PSt1-Eu(III) keeps the fluorescent property well.

This article contains supplementary material available via the Internet at <http://www.interscience.wiley.com/pages/0021-8995/suppmat>.

Correspondence to: J.-M. Lu (lujm@suda.edu.cn).

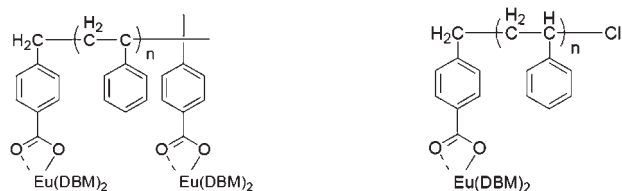
Contract grant sponsor: Chinese Natural Science Foundation; contract grant numbers: 20476066, 20571054.

Contract grant sponsor: Jiangsu Province Natural Science Foundation; contract grant number: BK 2005031.

Contract grant sponsor: High technology project in Jiangsu Province; contract grant number: BG 2005021.

Contract grant sponsor: "Science and Technology Plan" Project in Suzhou; contract grant number: SG0718.

Journal of Applied Polymer Science, Vol. 108, 3430–3434 (2008)
© 2008 Wiley Periodicals, Inc.



Scheme 1 Speculated structures of PSt1-Eu (left) and PSt4-Eu (right).

EXPERIMENTAL

Materials

Cumic acid (Chemical pure, Shanghai Reagent Co. of China) used without purification. Malonic acid diethyl ester (Chemical pure Shanghai Reagent Co. of China) was distilled. 4-(chloromethyl) benzoic acid (HPLC, 99.6%) was recrystaled by ethanol. Styrene (CP, Shanghai Chemical Reagent, Shanghai, China) was purified by extracting with a 5% sodium hydroxide aqueous solution, followed by washing with deionized water, dried overnight with magnesium sulfate anhydrous and finally distilled in vacuum. Copper(I) chloride (CuCl, AR, Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried in vacuum. Cyclohexanone (AR, Shanghai Chemical Reagent) dried overnight with magnesium sulfate and distilled in vacuum. All others reagents and solvents were used without purification.

Preparation of polystyrene via ATRP

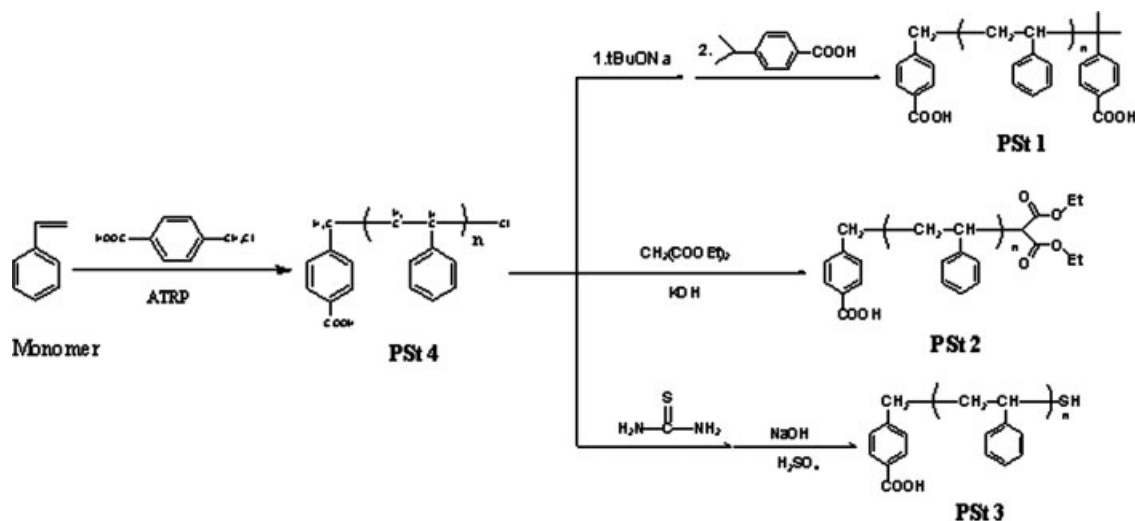
CuCl, 2,2'-bipyridyl, cyclohexanone, initiator, and styrene were added to a tube. The tube was sealed and

cycled between vacuum and high-purity nitrogen for four times. Then the tube was sealed under N₂ and placed in a thermostatically controlled oil bath. Samples were taken periodically for conversion and molecular weight analysis. The samples was dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.5, V/V), then filtrated and dried under vacuum.

Preparation of PSt with ω-end functionalized by cumic acid (PSt1), diethyl malonate (Pst2) and thiol (Pst3)

PSt with cumic acid ω-end group (PSt1) was obtained as following procedures: the mixture of excessive *tert*-butyl alcohol and sodium was added into a 100 mL round-bottom flask and refluxed at 92°C till sodium disappears, then the excessive *tert*-butyl alcohol was evaporated. 1,4-dioxane solution of PSt obtained (in the previous section) was added in and refluxed at 104°C for 2 days. Product was precipitated into a large amount of methanol, washed by 100 mL water, and dried under vacuum at 40°C until its constant weight. It was added into a 100 mL round-bottom flask with excessive cumic acid. Then the mixture was heated to 300°C under nitrogen atmosphere for 6 h. The excess cumic acid was solved with methanol. The residue was solved with THF, precipitated into a large amount of methanol, and dried under vacuum at 40°C until its constant weight.

PSt with diethyl malonate end group (PSt2) was obtained from reaction of PSt (1 g) in cyclohexanone (10 mL), tetraethyl ammonium bromide (0.4 g), diethyl malonate (3 g), and KOH (6 g) in H₂O (6 mL). The mixture was refluxed in a 100 mL round-bottom flask at 150°C for 5 days. Then polymer was precipitated into a large amount of methanol and



Scheme 2 Synthesis of PSt1-4.

dried under vacuum at 40°C until its weight was constant.

The polymer with thiol end-group (PSt3) was synthesized following the literature.¹³ All PSt were characterized by ¹H NMR and thermal behavior.

Preparation of polymeric Eu(III) complexes

Excessive amount of $\text{Eu}(\text{DBM})_2\text{Cl} \cdot 2\text{H}_2\text{O}$ ^{18,19} was dissolved in hot ethanol and added dropwise into a THF solution of PSt [a series of PSt contains PSt without any functional end group (PSt), PSt with only benzoic acid at α -end (PSt-Cl) and PSt with cumic acid ω -end group (PSt1)]. The mixture was stirred under reflux for 2 h, NaOH (2M) aqueous solution was added to adjust the pH value to 10. After refluxed for another 10 h, polymer was precipitated in a large amount of methanol. The obtained polymeric complex was collected by filtration, washed by methanol under reflux for 10 h and by deionized water for five times to remove the excessive inorganic compounds. The obtained polymeric complexes (PSt1-Eu, PSt-Cl-Eu, PSt-Eu) were finally dried at 50°C under vacuum for another 10 h. ICP results: the content of Eu(III) ion is about 11% for PSt1-Eu (Mn of PSt1 is 2797), 6% PSt-Cl-Eu (Mn of PSt-Cl is 2700), 4% for PSt-Eu (Mn of PSt is 3047), respectively.

The speculated structures of PSt1-Eu and PSt-Cl-Eu are shown in Scheme 1.

Characterization

Conversion for monomer is determined by gravimetry. Molecular weights and molecular weight distributions relative to polystyrene were measured using a Waters 1515GPC (Waters Corporation, Milford, MA) with THF as a mobile phase and with a column temperature of 30°C. ¹H NMR spectrum was measured by an INOVA 400 MHz NMR instrument (Varian Company, San Francisco, CA), with CDCl_3 as a solvent, and tetramethylsilane as internal reference. Thermal gravimetric (TG) analysis was conducted on a Universal V3.7A TA instrument in flowing N_2 with a heating rate of 10°C/min⁻¹.

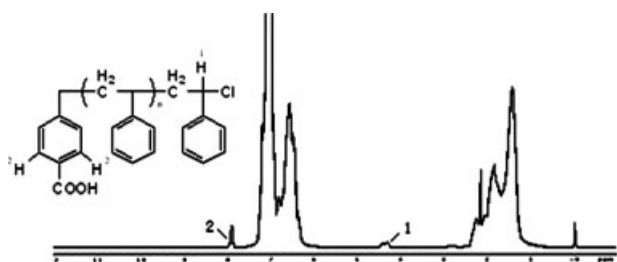


Figure 1 ¹H NMR spectrum of PSt-Cl.

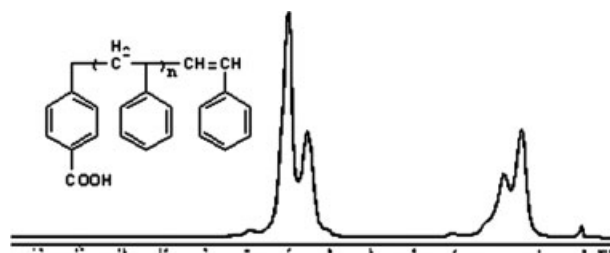


Figure 2 ¹H NMR spectrum of PSt without ω -chlorine at the chain end (PSt).

Fluorescence spectrums were performed on an Edinburgh-920 fluorescence spectra photometer.

RESULTS AND DISCUSSION

Confirmation of the living/controllable polymerization

Preparation of PSt1–PSt3 is illustrated in Scheme 2. The ATRP of styrene is prepared according to the previous reports. The H NMR, the first-order semi logarithmic kinetic plot, relationship of the molecular weights with conversion and narrow polydispersities are all verified the free radical polymerization. The detailed description was provided in supplemental information.

Confirmation of PSt with double end functional groups

The H NMR of PSt obtained via above ATRP was shown in Figure 1. According to the Figure 1, singles at 4.30 ppm assign to the methine proton of $-\text{CH}_2\text{C}(\text{Ph})\text{H}-\text{Cl}$ at ω -end. It is different from other methine, due to the effect of electron withdrawing from Cl atom. To better verify the removal of the ω -chlorine of PSt, the PSt without ω -chlorine was also prepared for comparison, and no peak at 4.30 ppm shows in ¹H NMR spectrum (Fig. 2).

The ¹H NMR spectrum (Fig. 3) of PSt1 which ω -chlorine was replaced by cumic acid shows a new peak at 1.26 ppm assigned to the proton (H_1) of the methyl group of cumic acid, the peak at 7.91 ppm indicative of aromatic protons (H_2) from the initiator and the peak at 8.02 ppm assigned to the aromatic proton (H_3) from cumic acid. Compared with Figure 3, obvious decrease of the peak at 4.3 ppm

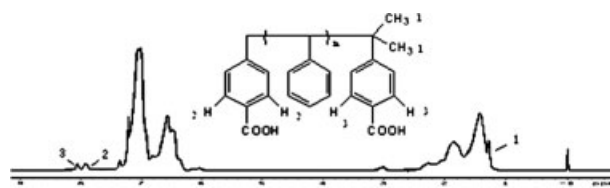


Figure 3 ¹H NMR spectrum of PSt1.

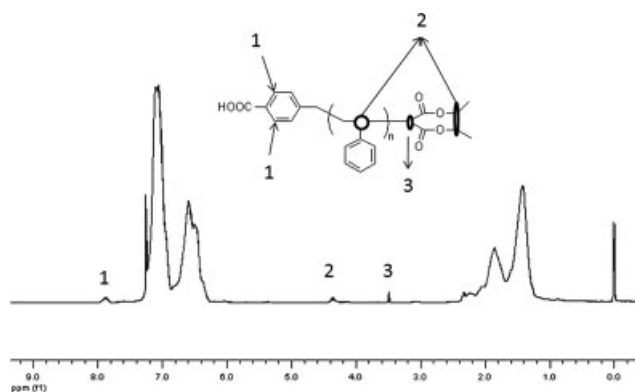


Figure 4 ^1H NMR spectrum of PSt2.

confirmed that the chlorine has been substituted by cumic acid successfully. The conversion of substitution reaction is about 80% according to the ratio of proton of the initiator (at 7.91 ppm) and cumic acid (at 8.02).

Figure 4 shows the ^1H NMR spectrum of PSt2 which ω -chlorine was substituted by diethyl malonate. The peaks at 1.26 ppm is assigned to the proton (H_1 , H_2) of the methyl group from diethyl malonate, peaks at 3.42 and 4.38 ppm are assigned to the proton of the methine group and those of the methane group, respectively. Figure 5 shows the ^1H NMR spectrum of PSt3 which ω -chlorine was substituted by thiol group. Because the methine proton close to the chloride chain end has a chemical shift of 4.30 ppm in Figure 1, the peak shifts quantitatively to 3.0–3.3 ppm, which is indicative of thiol formation.¹³

The thermal stability of different end-functionalized polymer

Table I shows the thermal stability of these telechelic PSt1-3. When the end group of polystyrene was replaced by cumic acid or diethyl malonate, their thermal stability was improved because the instable C–Cl bond at the end of the polymer chain was replaced by more stable C–C bond. On the contrary, after the instable C–Cl bond at the end of the polymer chain was substituted by the more instable C–S bond, the thermal stability of PSt3 was weak-

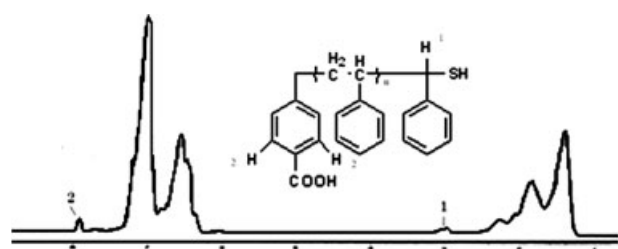


Figure 5 ^1H NMR spectrum of PSt3.

TABLE I
The Thermal Stability of Different End-Functionalized Telechelic Polymers

Polymer	Mn	PDI	Bond at the chain end	T_{onset} ($^{\circ}\text{C}$)
PSt-Cl	2700	1.27	C–Cl bond	368.9
PSt1	2797	1.30	C–C bond	379.6
PSt2	2850	1.29	C–C bond	374.6
PSt3	2733	1.27	C–S bond	336.4

ened remarkably. The results are also testified the formation of new telechelic PSt.

Application of the functional polymer

These telechelic PSts can act as polymeric ligand to form PMC with inorganic metal compounds. In this study we choose PSt1 as ligand and $\text{Eu}(\text{DBM})_2 \text{Cl} \cdot 2\text{H}_2\text{O}$ as metal center. The obtained PSt1-Eu(II) complex shows significant red fluorescence at 615 nm which is assigned to characteristic bands of Eu(III) complex (ascribe to the excitation of $^5\text{D}_0 \rightarrow ^7\text{F}_2$, Fig. 6).²⁰ However, it's well known that the structures of PMCs are always difficult to be characterized. To confirm the obtained PMC is our aim product, i.e., the metal is coordinated with two end groups of PSt1. For better comparison, a series of corresponding PSts with similar Mn are utilized: PSt without any functional end group (PSt), PSt with only benzoic acid at α -end (PSt4) and PSt1. Their Eu(III) complexes (PSt-Cl-Eu, and PSt1-Eu) and the mixture of PSt-Eu are obtained under the same reaction, respectively. Probably, due to the simple mixture of PSt and Eu(III) complex in PSt-Eu, the emission spectrum of the mixture shows that the emission is weak and shows different pattern from those of PSt-Cl-Eu and PSt1-Eu. In pattern of

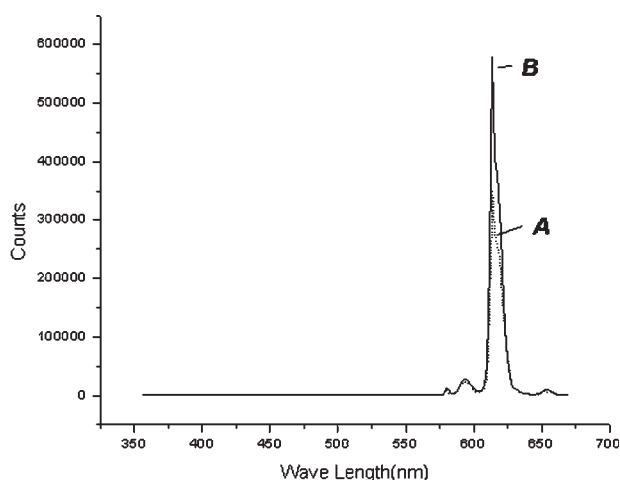


Figure 6 Fluorescent emission of PSt-Cl-Eu (A) and PSt1-Eu (B) in DMF solution ($\lambda_{\text{ex}} = 336$ nm, Mn (PSt1) = 2797; PDI:1.30; Mn (PSt-Cl) = 2700; PDI : 1.27, concentration: 1 g/mL).

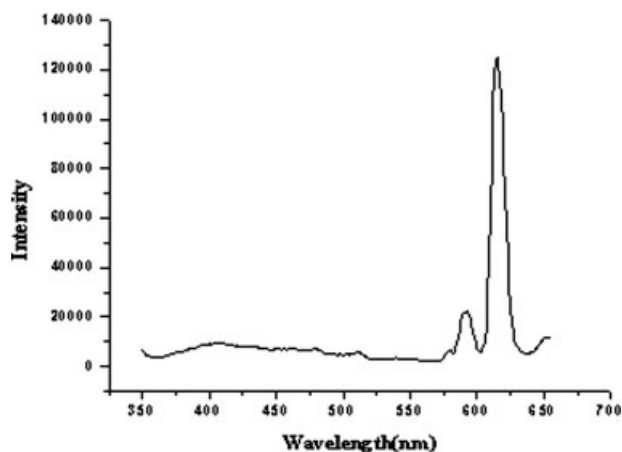


Figure 7 Emission spectrum of PSt1-Eu complex film ($\lambda_{\text{ex}} = 336$ nm, M_n (PSt1) = 2797; PDI:1.30).

complex PSt-Eu, the emission band of PSt is preserved and the characteristic bands of Eu(III) ion at about 615 nm is relatively weak, whereas in the spectra of complexes PSt-Cl-Eu and PSt1-Eu, the characteristic bands of Eu(III) ion are acutely increased and the emission band of PSt is negligible. It's also indicative that Eu(III) is linked with PSt1 (or PSt-Cl) by coordination interaction. Figure 6 shows emission spectra of complexes PSt-Cl-Eu (curve A) and PSt1-Eu (curve B). According to Figure 6, the complex PSt1-Eu shows obviously stronger emission intensity than PSt-Cl-Eu, which may be ascribed that two coordination sites (carboxylate groups) in PSt1 coordinate more Eu(III) ions accordingly and result in stronger emission. In addition, emission of the film of PSt1-Eu shows similar pattern with that of complex PSt1-Eu in DMF solution (Fig. 7) and the red fluorescence is strong enough to be observed under ultraviolet radiation directly. Therefore, the Eu(III) complexes using functionalized telechelic PSt ligand will not only perverse good ability of film forming of PSt but also good fluorescence of Eu(III) ions, which may provide a novel method to produce organic/inorganic fluorescent film materials.

CONCLUSIONS

Polystyrene (PSt-Cl) with benzoic acid at α -end was synthesized by using initiator 4-chloromethyl benzoic acid via atom transfer radical polymerization

(ATRP). Its ω -chlorine end-group was substituted by cumic acid, diethyl malonate and thiol, respectively, and therefore, telechelic PSt1, PSt2, and PSt3 with different functionalized ω -end group were obtained and characterized by IR, H NMR and thermal behavior. PSt1 with carboxylate group at the double ends was further reacted with $\text{Eu}(\text{DBM})_2\text{Cl} \cdot 2\text{H}_2\text{O}$ to afford a novel polymeric complex PSt1-Eu(III). This complex shows significant red fluorescence, which is stronger than PSt-Cl-Eu(III). However, this type of end-functionalized telechelic polymers can coordinate with various functional metal complexes to form functional polymeric metal complexes. Together with the good film forming of PSt, such PMCs can become a new series of organic/inorganic film materials, and this job is ongoing in our lab.

References

- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Matyjaszewski, K. *Macromolecules* 1998, 31, 4710.
- Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* 1996, 29, 8576.
- Haddleton, D. M.; Jasieczek, C. B.; Hannon, N. J.; Shooter, A. J. *Macromolecules* 1997, 30, 2190.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Percec, V.; Barboiu, B.; Kim, H. J. *J Am Chem Soc* 1998, 120, 305.
- Haddleton, D. M.; Waterson, C.; P. Derrick, J.; Jasieczek, C. B.; Shooter, A. J. *Chem Commun* 1997, 7, 683.
- Carrot, G.; Hilborn, J.; Hedrick, J. L.; Trollsas, M. *Macromolecules* 1999, 32, 5171.
- Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog Polym Sci* 2001, 26, 337.
- Matyjaszewski, K.; Nakagawa, Y.; Gaynor, S. G. *Macromol Rapid Commun* 1997, 18, 1057.
- Coessens, V.; Matyjaszewski, K. *Macromol Rapid Commun* 1999, 20, 127.
- Coessens, V.; Matyjaszewski, K. *J Macromol Sci Pure Appl Chem* 1999, 36, 653.
- Garamszegi, L.; Donzel, C.; Carrot, G.; Nguyen, T. Q.; Hilborn, J. *React Funct Polym* 2003, 55, 179.
- Yang, D.; Li, L.; Wang, C. *Mater Chem Phys* 2004, 87, 114.
- Yang, Z.; Lu, J. M.; Wang, L. H. *Polym Bull* 2005, 53, 249.
- Xia, X. W.; Lu, J. M.; Li, H.; Yao, S. C.; Wang, L. H. *Opt Mater* 2005, 27, 1350.
- Li, N. J.; Lu, J. M.; Yao, S. C. *Macromol Chem Phys* 2005, 206, 559.
- Taylor, M. D.; Carter, C. P. *J Inorg Nucl Chem* 1962, 24, 387.
- Lian, X. S.; Sheng, H. *Spectrosc Spectral Anal* 1999, 19, 562.
- Xu, Q. F.; Dai, J.; Zhang, D.; Zhou, Q. H. *J Rare Earth* 2002, 20, 93.