

Atom transfer radical polymerization of styrene initiated by 2-(4-chloromethyl-phenyl)-benzoxazole with high activity and fluorescent property

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Received 8 December 2004; received in revised form 27 June 2005; accepted 5 July 2005

Available online 10 August 2005

Abstract

Functionalized polystyrene (PSt) was synthesized utilizing atom transfer radical polymerization (ATRP), which was conducted by using 2-(4-chloromethyl-phenyl)-benzoxazole (CMPB) as initiator, CuCl/PMDETA as catalyst, and cyclohexanone as solvent. The mechanism of ATRP was proved by characterizing the structure of PSt via ¹H NMR and preparing of PSt-*b*-PMMA block copolymer. The polymerization showed first order with respect to monomer concentration and relatively narrow polydispersity (M_w/M_n range from 1.30 to 1.50). Factors such as different reaction temperatures, mole ratio of monomer to initiator and so on, which can affect the ATRP system, were discussed in the paper. Moreover, CMPB showed high activity and could initiate styrene polymerization even at ambient temperature. The optical property of initiator was well preserved in the obtained PSt, and the end-functionalized PSt exhibited strong fluorescent emission at 351 nm. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Ambient temperature polymerization; Fluorescent property

1. Introduction

Synthesis of polymers with well-controlled architecture and predictable molecular weight is currently of great academic and industrial interests [1–4], while atom transfer radical polymerization (ATRP) is one of the relatively new and versatile methods for controlled polymerizations [5–9]. Initiator is of prime importance for an ATRP. The reason is twofold. One is that the main role of the initiator is to determine α -end-function of polymers [10–15]. Various functionalized polymers with large conjugated function at α -end can be obtained using different initiators. For example, pyrene, anthracene end functionalized macromonomers were obtained using initiators containing pyrene, anthracene groups [16,17], which could be used as photoresist materials, and fluorescent probes. Fullerene

(C₆₀) terminal can be introduced to the α -end of polymer [18,19], and C₆₀-containing polymers have special electro- and optical properties. Hydroxyl spirooxazine end functionalized PSt can be used as photochromic material [20]. The other is that different initiating systems have different initiation activities which directly affect the polymerization rate and temperature [8,9]. Although the monomers of methacrylate can be polymerized in many ATRP systems even at ambient temperature [8,9,21–24], it is still uncommon for polymerization of styrene to be reached at such room temperature [8,9].

Recently, much attention has been paid to benzoxazole derivatives [25–29] because of their optical applications such as photoluminescents [30], whitening agents [31], and dye laser [32]. Herein, we introduce 2-(4-chloromethyl-phenyl)-benzoxazole (CMPB) as initiator to prepare α -end-functionalized polystyrene (PSt) via ATRP. Due to the good fluorescent property of CMPB and the fine film forming property of PSt, inducing CMPB to PSt's terminal would be a very inspiring application aiming at preparing optical apparatus.

In this paper, an ATRP of styrene using CMPB as initiator, CuCl/PMDETA (PMDETA = *N,N,N',N''*-pentamethyldiethylenetriamine) as catalyst system is studied.

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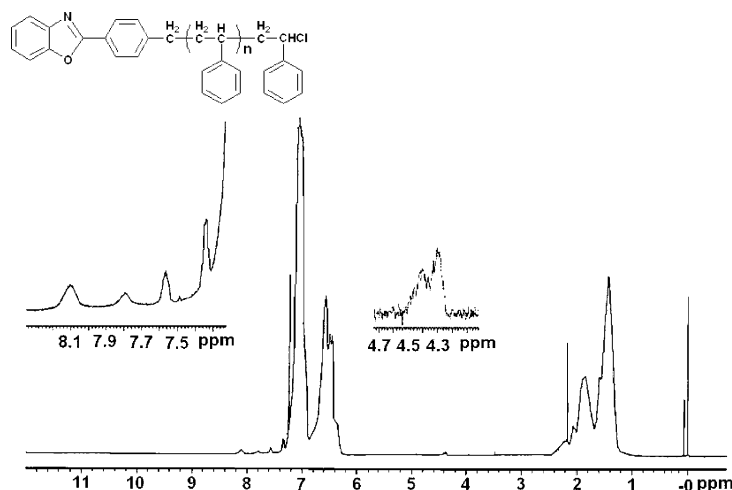


Fig. 1. ^1H NMR spectrum of PSt with CDCl_3 as solvent.

The results show that the polymerization is well controlled and CMPB has high activity, which can induce the polymerization even at ambient temperature. Moreover, the α -end functionalized PSt has good fluorescent property.

2. Experimental

2.1. Materials

2-(4-Chloromethyl-phenyl)-benzoxazole (98%, Liaonyungang Based Chemical Co. Ltd) was recrystallized with ethanol. Styrene (CP, Shanghai Chemical Reagent Co. Ltd) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and drying with magnesium sulfate anhydrous overnight, and finally distilled in vacuum. Copper(I) chloride (CuCl) (AR, Shanghai Zhenxing Chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried in vacuum. PMDETA (98%, Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4-Å molecular sieve and distilled in vacuum. Cyclohexanone (AR) was dried with magnesium sulfate overnight and distilled in vacuum. Other agents were analytic pure and used without further purification.

2.2. Polymerization

All ATRP reactions were carried out following the similar experimental procedure. CuCl , 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. The polymerization was processed at a pre-determined temperature under N_2 . Samples for conversion and molecular weight analysis

were taken at regular intervals, dissolved in THF and precipitated into a large amount of methanol/ HCl (100/0.5, v/v). The precipitation was filtrated and dried under vacuum.

2.3. Characterizations

The IR spectra were recorded on a Perkin–Elmer577 FT-IR spectrometer (KBr pellet, $4000\text{--}400\text{ cm}^{-1}$). ^1H NMR spectra were measured by INOVA 400 MHz NMR spectrometer, CDCl_3 as solvent. Element analyses were obtained by Carlo Erba-MOD1106 instrument. Purity of initiator was analyzed by Waters515 HPLC. Conversions for monomer were determined by gravimetry. Molecular weights and the polydispersity relative to polystyrene were measured using Waters1515 GPC with THF as a mobile phase and with column temperature of $30\text{ }^\circ\text{C}$. UV–vis spectra were recorded on a Perkin–Elmer λ -17 UV–vis instrument. Room temperature emission and excitation spectra were carried out using Edinburgh-920 fluorescence spectra photometer.

2.4. Determination of fluorescence quantum yield (Φ)

The Φ values were determined using quinine sulfate in 0.1 M sulfuric acid ($\Phi_{\text{Q}}=0.55$ with excitation of 366 nm) as a standard [33]. Using the following equation [34].

$$\Phi_{\text{S}} = \Phi_{\text{Q}} \left(\frac{F_{\text{S}}}{F_{\text{Q}}} \right) \left(\frac{A_{\text{Q}}}{A_{\text{S}}} \right) \left(\frac{n_{\text{S}}}{n_{\text{Q}}} \right)^2 \quad (1)$$

Where F is the area under the fluorescence spectra, A is the absorbance, n is the refractive index of the solvent, and the subscripts Q and S represent quinine sulfate and sample, respectively.

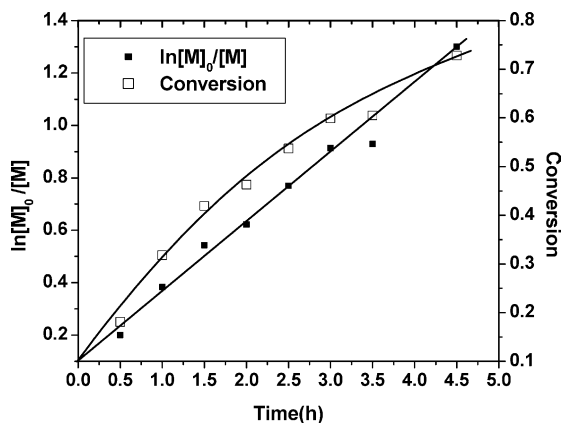


Fig. 2. Kinetic plot for the polymerization of styrene in cyclohexanone solution (50% v/v) at 100 °C ([styrene]/[CMPB]/[CuCl]/[PMDETA]=200:1:1:1).

3. Results and discussion

3.1. Polymerization and characterization of polymers

The polymerization of styrene was processed by use of CMPB as initiator, CuCl/PMDETA as catalyst system. The mechanism of ATRP can be characterized by ^1H NMR spectrum, kinetic plot, polydispersity and block copolymerization, etc.

According to the mechanism of ATRP, initiator group is incorporated at α -end of the polymer chain, while ω -end remains a terminal halide. It can be verified by ^1H NMR spectrum (Fig. 1). Signals at 4.30–4.54 ppm are attributed to the terminal protons next to the halogen atoms, and signals at 8.11, 7.80, 7.76 and 7.35 ppm are assigned to the protons of CMPB, respectively.

The kinetic plot of polymerization at 100 °C is presented in Fig. 2. The linearity of the semilogarithmic plot of $\ln[M]_0/[M]$ vs time indicates that the polymerization is first-order with respect to monomer and the concentration of the growing radicals remains constant. The number average

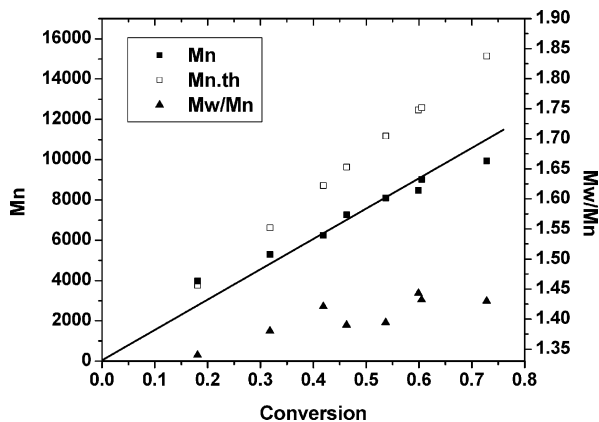


Fig. 3. Evolution of M_n and M_w/M_n with conversion for the polymerization of styrene in cyclohexanone solution (50% v/v) at 100 °C ([styrene]/[CMPB]/[CuCl]/[PMDETA]=200:1:1:1).

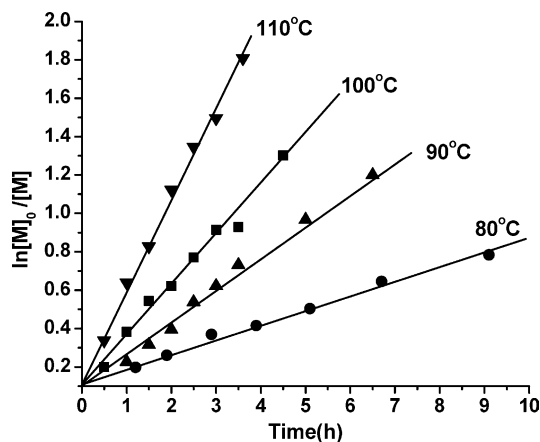


Fig. 4. Kinetic plot for the polymerization of styrene with CMPB and CuCl/PMDETA, in cyclohexanone solution (50% v/v) at different temperature.

molecular weights (M_n) increase linearly with conversion, and the polydispersity is relatively narrow ($M_w/M_n=1.3$ –1.45) (Fig. 3). All of the results suggest a ‘living’ polymerization process.

The obtained PSt with chlorine atom at ω -end can be further used as a macroinitiator for block copolymerization, which is one of the most important applications and characters of ATRP [35–38]. The polymerization was carried out in cyclohexanone at 90 °C, with MMA as second monomer and the ratio of [MMA]/[macroinitiator]/[CuCl]/[PMDETA]=200:2:1:1. After 4 h reaction, the number average molecular weight increased from 6268 to 11,338 with the conversion of MMA reaching to 90.8%, but the polydispersity index changed from 1.37 to 1.63. The GPC traces also showed that the polymerization of second monomer (MMA) was initiated quantitatively by the macroinitiator. The block copolymer was further verified by FT-IR, ^1H NMR spectra. ^1H NMR spectrum of PSt-*b*-PMMA exhibits characteristic signals at 0.81–1.02 ppm ($-\text{CH}_3$), 1.21–2.06 ppm ($-\text{CH}_2$ and $-\text{CH}$), 3.60 ppm ($-\text{OCH}_3$), 6.41–7.20 ppm (phenyl protons). Signals at 4.30–4.50 ppm assigned to $-\text{CH}(\text{Ph})-\text{Cl}$ (in Fig. 1) disappear while signal at 3.78 ppm derived from the methyl ester group adjacent to the terminal halide appears. FT-IR spectrum of PSt-*b*-PMMA shows that characteristic peak at 1732 cm^{-1} corresponds to the absorption of ester carbonyl of PMMA, and peaks at 3025 , 1601 , 752 , 698 cm^{-1} indicate the existence of benzene ring in the block copolymer.

3.2. Influence of reaction conditions on polymerization

The parameters including temperature, solvent, initiator concentration, ligand, and catalyst concentration are discussed.

The effect of temperature in the polymerization was investigated firstly. Fig. 4 shows a good linear relationship between $\ln[M]_0/[M]$ and the polymerization time. The slope of lines represents the apparent rate constant of

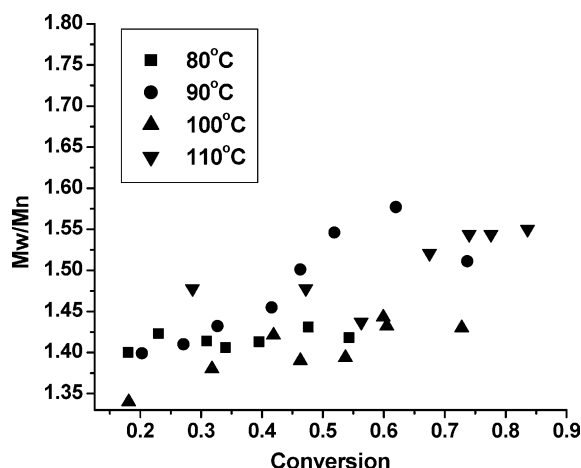


Fig. 5. Dependence of M_w/M_n on conversion for the polymerization of styrene with CMPB and CuCl/PMDETA, in cyclohexanone solution (50% v/v) at different temperature.

polymerization (K_p^{app}) at different temperature. The rate of polymerization accelerates with temperature increasing. Such a result conforms to the following Eq. (2) [9] and Eq. (3) (Arrhenius equation). The conversion of styrene reached 51% after 4 h at 80 °C, while longer time or higher temperature in many other ATRP systems were required [4–6,8,9,39,40]. This shows that the initiating system is high active.

$$R_p = K_p[P^*][M] = K_p^{app}[M] \quad (2)$$

$$\ln K_p = \ln A_p - \frac{E_p}{RT} \quad (3)$$

At different temperature, relationships of polydispersity and conversion are shown in Fig. 5. According to Fig. 5, the M_w/M_n fluctuates around 1.45, and temperature has little effect on the polydispersity.

It should be noted that the initiator efficiency (f) is larger than 1.00 almost at any period during the polymerization (Fig. 3), even polymerization temperature was dropped to 30 °C. In order to better understand the problem, we substituted cyclohexanone (dielectric constant is 18.3 at 20 °C) with other ketone solvents, such as acetone and hypnone. The polymerizations were both in good control but at lower polymerization rate, and their initiator efficiencies were still larger than 1.00 (Table 1). Whereas,

Table 1

Influence of solvents on polymerization of styrene with CMPB and CuCl/PMDETA, [styrene]=4.35 M; [CMPB]=0.0217 M; [CuCl]=0.0217 M; [PMDETA]=0.0217 M

Solvent	Temperature (°C)	Time (h)	Conversion (%)	$M_{n,GPC}$	M_{nth}^a	M_w/M_n	f
Cyclohexanone	90	4	55.2	7476	11,481	1.41	1.54
Acetone	60	24	41.3	5997	8590	1.48	1.43
Hypnone	100	4	40.8	6963	8486	1.31	1.22
Anisole	120	8	49.4	12,530	10,275	1.30	0.82

^a Calculated M_n by using $M_{nth} = [M]_0/[I]_0 \times (M_{w,St}) \times \text{conversion}$, where $M_{w,St}$ is the molecular weight of styrene monomer (104.15).

when polymerization was conducted with anisole as solvent at 120 °C for 8 h, the initiator efficiency decreased to 0.82 with $M_w/M_n = 1.31$. This indicates that the polymerization process is strongly solvent-dependent, and may exist intricate solvent effect with ketones as solvents in such an ATRP system. The solvent effect in the polymerization probably induce the initiator efficiency exceeds 1.00.

The effects on conversion, molecular weights and the polydispersity with different mole ratio of monomer to CMPB are also discussed (Table 2). With increasing mole ratio of monomer to initiator (the concentration of Cu/PMDETA is constant), calculated number average molecular weights increased, but number average molecular weights measured by GPC did not increase as fast as calculated counterpart. Thus, initiator efficiency was enhanced and the polydispersity of PSt was widened accordingly. It might be attributed to the solvent effect in cyclohexanone as we mentioned above. It seems that the polymerization is under poor control when concentration of initiator is low.

CuCl/bpy (2,2'-bipyridine) was primarily employed as the catalyst system for polymerization. It is found that polymerization is in bad control and the polydispersity of polymer is wide ($M_w/M_n = 1.76$). Subsequently, CuCl/PMDETA was used as the catalyst system. Table 3 shows the effects of different mole ratio of PMDETA to CuCl in the polymerization. It is found that conversions and number average molecular weights have little change with increasing mole ratio of PMDETA to CuCl, but the polydispersity become wider. So we conclude an optimal condition with the ratio of PMDETA to CuCl is 1:1.

The influence of concentration of catalyst is further investigated and the results are shown in Table 4. According to Table 4, conversions and number average molecular weights have little change as the concentration of catalyst changing, but polydispersity increase gradually. Three systems probably have almost the same concentration of radical, and the optimal condition is [styrene]/[CMPB]/[CuCl]/[PMDETA] = 200:1:1:1.

3.3. Ambient temperature polymerization

Sawamoto and coworkers once reported that an iodide initiator induced efficient living radical polymerizations of styrene at 30 °C, and the reaction reached 83% conversion

Table 2

Influence of concentration of CMPB on polymerization of styrene with CuCl/PMDETA, in cyclohexanone solution (50% v/v) at 90 °C, [styrene]=4.35 M; [CuCl]=0.0217 M; [PMDETA]=0.0217 M

$n(\text{styrene}):$ $n(\text{CMPB})$	Time (h)	Conversion (%)	$M_{n\text{GPC}}$	M_{nth}	M_w/M_n	f
100:1	4	68.3	5039	7103	1.31	1.41
150:1	4	59.6	6268	9298	1.38	1.48
200:1	4	55.2	7476	11,481	1.41	1.54
300:1	4	56.7	10,109	17,690	1.53	1.75
400:1	4	54.8	12,665	22,797	1.51	1.80

Table 3

Influence of concentration of PMDETA on polymerization of styrene with CMPB and CuCl/PMDETA, in cyclohexanone solution (50% v/v) at 90 °C, [styrene]=4.35 M; [CMPB]=0.0217 M; [CuCl]=0.0217 M

$n(\text{CuCl}):$ $n(\text{PMDETA})$	Time (h)	Conversion (%)	$M_{n\text{GPC}}$	M_{nth}	M_w/M_n	f
1:1	4	55.2	7476	11,481	1.41	1.54
1:2	4	49.0	8003	10,192	1.43	1.27
1:3	4	48.1	8678	10,005	1.46	1.15

in 27 days with $M_w/M_n=1.26$ [41]. To our surprise, polymerization induced by CMPB can also be proceeded even at ambient temperature. Polymerizations are well controlled with a linear increase of molecular weights with conversion and relatively low polydispersity, and its conversion could reach about 76% after 85 h. Because the polymerization took so long time in such lower temperature, we considered whether the initiator could form an initiating radical species via homolytic cleavage of labile carbon–halogen bond. ^1H NMR spectrum helped us to prove that CMPB did initiate styrene polymerization at 30 °C. The result is the same as that in Fig. 1 (the ^1H NMR spectrum of PSt polymerized at 100 °C). It can be concluded that CMPB is a highly active initiator, and its carbon–halogen bond can easily generate radical species through electronic and steric effects of their substituents [42]. In addition, polydispersity at 30 °C becomes a bit lower than those at higher temperatures, which might be caused by low radical concentration at lower temperature.

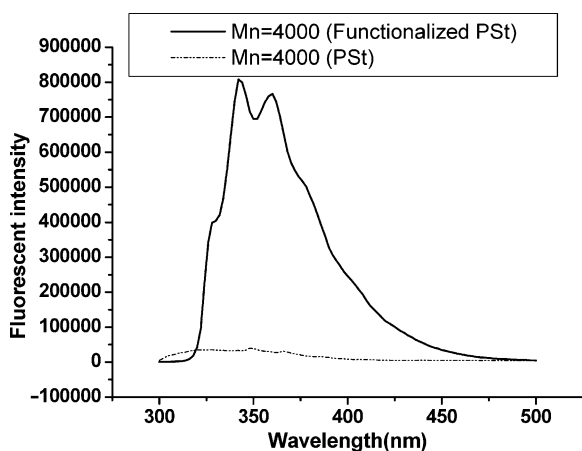


Fig. 6. The fluorescent intensity of the same molecular weight of functionalized PSt and PSt with $\lambda_{\text{ex}}=278$ nm.

3.4. Fluorescent property

PSt initiated by chloromethyl benzene emits relatively weak fluorescence (Fig. 6), while PSt initiated by CMPB with the same molecular weight and concentration in DMF solution (10^{-4} M) could emit strong fluorescence at about $\lambda_{\text{em}}=351$ nm with $\lambda_{\text{ex}}=278$ nm. It indicates that CMPB may act an important role in fluorescent property.

The UV–vis absorption maxima of functionalized PSt and initiator CMPB are shown in Table 5. Their UV–vis absorption region are similar, because both of them have 2-benzyl benzoxazole group which occurred $\pi-\pi^*$ transition.

Fluorescence emission spectra for CMPB in DMF solution shows the emission band is at about $\lambda_{\text{em}}=392$ nm with $\lambda_{\text{ex}}=345$ nm, and emission band of functionalized PSt has an blue shift about 41–52 nm. Table 5 shows that the fluorescence quantum yield of functionalized PSt is almost equal to that of CMPB. The introduction of 2-benzyl benzoxazole group though ATRP successfully enhances the fluorescent intensity of PSt.

4. Conclusion

The polymerization of styrene using CMPB as initiator, CuCl as catalyst, PMDETA as ligand and cyclohexanone as solvent matched well to atom transfer radical polymerization. The polymerization is under good control with [styrene]/[CMPB]/[CuCl]/[PMDETA]=200:1:1:1. The factors influencing the ATRP system are discussed. As one of the most important factors, initiator CMPB is studied because of its high activity and possible functionality. The result also shows that polymerization of styrene can be conducted successfully even at ambient temperature. Moreover, PSt functionalized by CMPB can emits strong

Table 4

Influence of concentration of catalyst on polymerization of styrene with CMPB and CuCl/PMDETA, in cyclohexanone solution (50% v/v) at 90 °C, [styrene]=4.35 M; [CMPB]=0.0217 M

$n(\text{styrene}):$ $n(\text{CMPB}):$ $n(\text{CuCl}):$ $n(\text{PMDETA})$	Time (h)	Conversion (%)	$M_{n\text{GPC}}$	M_{nth}	M_w/M_n	f
200:1:1:1	4	55.2	7476	11,481	1.41	1.54
200:1:0.5:0.5	4	52.9	7840	11,003	1.55	1.40
200:1:0.2:0.2	4	51.0	7144	10,608	1.62	1.48

Table 5

UV–vis absorption and fluorescence emission data of polymer and CMPB in DMF solution at room temperature 25 °C

	UV–vis λ_{max}^a (nm)	Fluorescence λ_{em}^a (nm) emission	Fluorescence quantum yield ^b
Functionalized PSt	299	351	0.58
CMPB	299	392	0.54

^a 10^{-4} M in DMF.

^b Relative to 10^{-4} M quinine sulfate in 0.1 M H_2SO_4 .

fluorescence at $\lambda_{\text{em}}=351$ nm with $\lambda_{\text{ex}}=278$ nm, and the fluorescence quantum yield of functionalized PSt is almost equal to CMPB with the solutions at the same solution concentration. The further research about polymer's fluorescent property is under way.

Acknowledgements

Authors gratefully thank Chinese Natural Science Foundation No. 20476066 for financial support in this work.

References

- [1] Hadjichristidis N, Pitsikalis M, Pispas S, Iatrou H. *Chem Rev* 2001; 101:3747–92.
- [2] Hawker CJ, Bosman AW, Harth E. *Chem Rev* 2001;101:3661–88.
- [3] Perrier S, Takolpuckdee P, Mars CR. *Macromolecules* 2005;38: 2033–6.
- [4] Coessens V, Pintauer T, Matyjaszewski K. *Prog Polym Sci* 2001;26: 337–77.
- [5] Wang JS, Matyjaszewski K. *J Am Chem Soc* 1995;117:5614–5.
- [6] Percec V, Barboiu B. *Macromolecules* 1995;28:7970–2.
- [7] Kato M, Kamigaito M, Sawamoto M, Higashimura T. *Macromolecules* 1995;28:1721–3.
- [8] Kamigaito M, Ando T, Sawamoto M. *Chem Rev* 2001;101:3689–745.
- [9] Matyjaszewski K, Xia JX. *Chem Rev* 2001;101:2921–90.
- [10] Haddleton DM, Waterson C. *Macromolecules* 1999;32:8732–9.
- [11] Mecerreyes D, Atthoff B, Boduch KA, Trollsås M, Hedrick JL. *Macromolecules* 1999;32:5175–82.
- [12] Reining B, Keul H, Höcker H. *Polymer* 1999;40:3555–63.
- [13] Zhang X, Xia J, Matyjaszewski K. *Macromolecules* 2000;33:2340–5.
- [14] Wang XS, Armes SP. *Macromolecules* 2000;33:6640–7.
- [15] Lu JM, Li H, Xia XW, Yao SC, Zhu XL. *Polym Bull* 2004;51:327–32.
- [16] Korn MR, Gagne MR. *Chem Commun* 2000;1711–2.
- [17] Zhang H, Klumperman B, van der Linde R. *Macromolecules* 2002;35: 2261–7.
- [18] Zhou P, Chen GQ, Li CZ, Du FS, Li ZC, Li FM. *Chem Commun* 2000;797–8.
- [19] Hua J, Yang WH, Zhu YJ, Guo ZX, Yang HQ, Xu L, et al. *Mater Lett* 2005;59:644–7.
- [20] Georgina KS, Richard AE, Thomas PD. *Macromolecules* 2004;37: 9664–6.
- [21] Chatterjee DP, Chatterjee U, Mandal BM. *J Polym Sci, Part A: Polym Chem* 2004;42:4132–42.
- [22] Munirasu S, Dhamodharan R. *J Polym Sci, Part A: Polym Chem* 2004; 42:1053–7.
- [23] Krishnan R, Srinivasan KSV. *Macromolecules* 2004;37:3614–22.
- [24] Save M, Weaver JVM, Armes SP, McKenna P. *Macromolecules* 2002;35:1152–9.
- [25] Tarek AF, Safaa EDHE, Hayam MK. *J Photochem Photobiol A: Chem* 2005;170:97–103.
- [26] Marcelo GH, Leandra FC, Adriano B, Valter S. *J Photochem Photobiol A: Chem* 2002;149:217–25.
- [27] Kiyoshi T, Tsutomu K, Hiroko A, Makoto D, Satoru I. *J Org Chem* 2001;66:7328–33.
- [28] Emiko K, Gang Y, Kazuhisa H. *Tetrahedron Lett* 2000;41:8111–6.
- [29] Maged MH, Christoph JF. *J Phys Chem A* 2002;106:5210–20.
- [30] Claussen U, Harnisch H. *Eur Pat Appl* 1981;25:136.
- [31] Stendby S. *Surfactant Sci Ser* 1981;5:729.
- [32] Reiser A, Leyshon LJ, Saunders D, Mijovic MV, Bright A, Bogie J. *J Am Chem Soc* 1972;94:2414–21.
- [33] Demas JN, Crosby GA. *J Phys Chem* 1971;75:991–1024.
- [34] Arimori S, Bell ML, Oh CS, Frimat KA, James TD. *J Chem Soc Perkin Trans 1* 2002;803–8.
- [35] Reining B, Keul H, Höcker H. *Polymer* 2002;43:3139–45.
- [36] Reining B, Keul H, Höcker H. *Polymer* 2002;43:7145–54.
- [37] Tao T, Luan B, Pan CY. *Polymer* 2003;44:1013–20.
- [38] Kurjataa J, Chojnowskia J, Yeohb CT, Rossib NAA, Holder SJ. *Polymer* 2004;45:6111–21.
- [39] Kotani Y, Kamigaito M, Sawamoto M. *Macromolecules* 2000;33: 3543–9.
- [40] Watanabe Y, Ando T, Kamigaito M, Sawamoto M. *Macromolecules* 2001;34:4370–4.
- [41] Kotani Y, Kamigaito M, Sawamoto M. *Macromolecules* 1999;32: 2420–4.
- [42] Gillies MB, Matyjaszewski K, Norrby PO, Pintauer T, Poli R, Richard P. *Macromolecules* 2003;36:8551–9.