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Fe(III)-catalyzed AGET ATRP of styrene using triphenyl phosphine as ligand

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Abstract Activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP) is a new technique for conducting ATRP developed recently. In this work, an iron(III)-mediated AGET ATRP of styrene in bulk was carried out at 110 °C, using benzyl bromide as an initiator, oxidatively stable iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) as a catalyst, triphenyl phosphine as a ligand, and ascorbic acid as a reducing agent. The polymerizations demonstrated the features of "living"/controlled free-radical polymerization, such as the number–average molecular weights increasing linearly with monomer conversion and narrow molecular weight distributions ($M_w/M_n = 1.14$–1.31).

Keywords Iron catalyst · AGET ATRP · Styrene · Triphenyl phosphine · Thermal initiation

Introduction

Atom transfer radical polymerization (ATRP), an especially powerful controlled/"living" free-radical polymerization (LRP) technique, has been reported to produce large arrays of polymeric materials with extraordinary control over topologies, composition, microstructures, and functionalities in the last decade [1–6]. However, normal ATRP has some limitation since a relatively unstable lower oxidation state metal catalyst [e.g., Cu(I) or Fe(II)] complex is used, and therefore a special handling procedure to remove the oxygen or other oxidants should be required [7–10]. Recently, the appearance of an improved ATRP, the activators generated by electron transfer (AGET) ATRP [11–22] provides an excellent way to overcome the

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drawbacks of normal ATRP. In a typical AGET ATRP system, an oxidatively stable Cu(II) complex is used to replace the unstable Cu(I) complex, but the active species Cu(I) complex can be produced by reducing the Cu(II) complex in situ using a reducing agent such as ascorbic acid (VC) or tin(II) 2-ethylhexanoate ($Sn(EH)_2$) [23–25].

Actually, various metal complexes have been successfully employed to mediate ATRP, including Ti [26], Mo [27, 28], Re [29, 30], Ru [31–34], Rh [35, 36] Ni [37–42], Pd [43], Co [44, 45], Os [46],[] Cu [47–55], and Fe [56–65]. Complexes of copper have been found to be the most efficient catalysts in the ATRP of a broad range of monomers in diverse media, and the copper-mediated AGET ATRP systems have been intensively reported [11–22]. However, in view of the known toxicity of copper compounds, a more environmentally friendly iron-mediated AGET ATRP system are more appreciated for the synthesis of materials, especially for biomedical applications. As compared with the copper-mediated AGET ATRP, only fewer works involved the iron catalyst. In our previous work, we reported the iron-mediated AGET ATRPs of methyl methacrylate (MMA) using iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) as the catalyst, iminodiacetic acid [66] or triphenylphosphine (PPh_3) [67] as a ligand and ethyl 2-bromoisobutyrate (EBiB) as an initiator. Luo and Sen [68] also reported an iron-mediated AGET ATRP of styrene and MMA using iron(III) bromide as the catalyst, tributylamine as the ligand, 1-bromoethylbenzene as the initiator, and $Sn(EH)_2$ or D-glucose as the reducing agent. Very recently, we have reported the iron(III)-mediated AGET ATRP of styrene using a commercially available tris(3,6-dioxaheptyl)amine (TDA-1) as the ligand [69, 70] and the iron(III)-mediated surface AGET ATRP of methacrylates [71].

It is well known that, in a ATRP process, ligands play key roles in solubilizing the transition-metal salt in the organic media and in adjusting the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [72]. Building on the known use of ligands, nitrogen-based ligands such as 2,2′-bipyridine (bpy) and phosphorus-based ligands are the most frequently used ones. Triphenylphosphine as a simple and cheap ligand was usually used in the iron-mediated normal or reverse ATRP systems. Ibrahim et al. [73] reported a normal ATRP using $FeCl_2{\cdot}4H_2O$ as the catalyst and PPh_3 as the ligand; and well-defined poly(*n*-butyl methacrylate) (PBMA) homopolymer, or triblock copolymer PMMA-*b*-PEO-*b*-PMMA and PBMA-*b*-PEO-*b*-PBMA [74], were obtained. Hou et al. [75] reported a reverse ATRP of acrylonitrile (AN) using $FeCl_3{\cdot}6H_2O$ as the catalyst, PPh_3 as the ligand and diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) as the initiator. However, to the best of our knowledge, there is no any report involved the iron-mediated AGET ATRP of styrene (St) using the phosphorus-based ligand. In this work, the AGET ATRP of St in bulk was investigated using $FeCl_3{\cdot}6H_2O$ as the catalyst, PPh_3 as the ligand, ascorbic acid as the reducing agent, and benzyl bromide (BB) as the initiator. Well-defined polystyrenes with molecular weights being close to their corresponding theoretical values and narrow molecular weight distributions were obtained by this catalyst system.

Experimental section

Materials

Styrene (>99%), was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). It was washed with an aqueous solution of sodium hydroxide (5 wt%) three times, followed by deionized water until neutralization, and then dried over anhydrous magnesium sulfate, distilled under reduced pressure and stored at −18 °C. $FeCl_3{\cdot}6H_2O$ (>99%), PPh_3 (>99%), VC (>99.7%), and BB (analytical reagent) were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and used as received. Tetrahydrofuran (THF) (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

General procedure for AGET ATRP of St

A typical polymerization procedure for the molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$ was as follows: $FeCl_3{\cdot}6H_2O$ (35.4 mg, 0.131 mmol), PPh_3 (102.9 mg, 0.393 mmol), St (3.0 mL, 26.2 mmol), BB (15.6 μL, 0.131 mmol) and VC (11.6 mg, 0.066 mmol) were added to a dried ampoule under stirring. The ampoule was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen in the heterogeneous mixture. The ampoule was flame-sealed and then transferred into an oil bath held by a thermostat at the desired temperature (110 °C) to polymerize under stirring. After the desired polymerization time, the ampoule was cooled by immersing it into iced water. Afterwards, it was opened and the contents were dissolved in THF (~2 mL), precipitated into a large amount of methanol (~200 mL). The polymer obtained by filtration was dried under vacuum until constant weight at 50 °C. The monomer conversion was determined gravimetrically. The procedures for other molar ratios of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0$ were same as that described above except the different amount of components.

Characterization

The number–average molecular weight ($M_{n,GPC}$) values and molecular weight distribution (M_w/M_n) values of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8 × 300 mm, 5 μm beads' size) columns with molecular weights ranged 10^2–5×10^5 g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min and 30 °C. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with polystyrene standards from Waters. ^1H NMR spectrum was recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature.

Results and discussion

Polymerization of St at different molar ratios of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0$

Figure 1 shows the kinetic plot of $\ln([M]_0/[M])$ via time for the AGET ATRP of St in bulk with a molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$ at 110 °C. A first-order kinetic plot was observed, which indicated that the propagating free-radical concentration was stationary during the polymerization. At the same time, an induction period (4.2 h) was observed in Fig. 1. This phenomenon was also observed in our previous work reported on the iron(III)-mediated AGET ATRP of MMA [67]. Similarly, according to the mechanism of iron(III)-mediated AGET ATRP of MMA, in this work, the active iron(II) complexes were produced by the in situ reduction between the reducing agent VC and the iron(III) complexes, and therefore further produced free-radicals by reversible redox reaction between iron(II) complexes and initiator (BB); subsequently initiate the polymerization of St according to normal ATRP mechanism. In the beginning of polymerization, if no enough Fe(II) complexes were generated duly, the reaction shifted towards left in the presence of a large amount of Fe(III) species, resulting in too low radical concentration to polymerize with the appearance of the induction period [67]. From Fig. 2, the molecular weight ($M_{n,GPC}$) values of the polymers increased linearly with conversion and were close to their corresponding theoretical ones; meanwhile the molecular weight distribution (M_w/M_n) values of the obtained PS remained narrow (less than 1.3).

The reducing agent (i.e., VC) plays an important role in the AGET ATRP process according to the mechanism reported [11, 66, 67]. The effect of VC on the bulk polymerization of St was investigated in this work. The results are listed in Table 1. From the table, it can be seen that even if a low molar ratio of $[Fe(III)]_0/[VC]_0 = 1/0.2$ was used, the polymerization could also be conducted successfully; and that increasing the amount of VC (from a ratio of 1/0.2–1/1.5) the corresponding polymerization rate increased and all the M_w/M_n values kept narrow (~ 1.3), indicating a wide range of the amount of VC can be used. It is noted that the

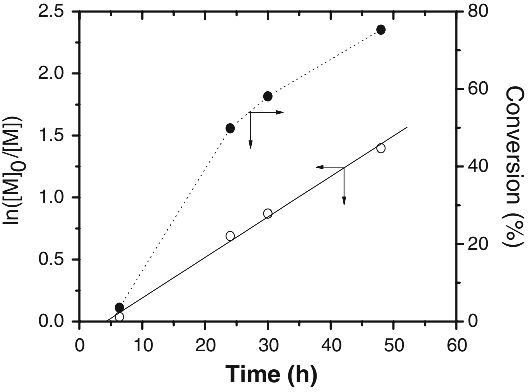

Fig. 1 $\ln([M]_0/[M])$ and conversion as a function of time for AGET ATRP of St in bulk. Polymerization conditions: $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$; St = 3 mL; temperature = 110 °C

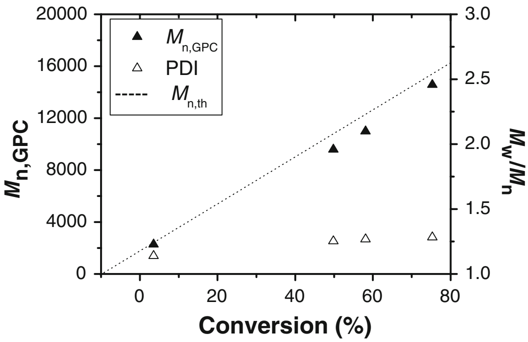

Fig. 2 Average–number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion for the AGET ATRP of St in bulk. Polymerization conditions: $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$; St = 3 mL; temperature = 110 °C

polymerization of St could also be carried out with a controlled way although no VC was used (Entry 1 in Table 1). However, the polymerization rate in that case is much slower than those in the presence of the reducing agent VC (Entries 2–5 in Table 1). For example, only 13.7% of conversion was obtained for 60 h polymerization time in the absence of the reducing agent VC; while 86.3% of conversion was obtained for 52 h polymerization time in the presence of VC ($[Fe(III)]_0/[VC]_0 = 1/0.5$). Figure 3 shows another polymerization kinetics of AGET ATRP of St in bulk with a molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/1$ at 110 °C. A first-order kinetic plot like as that with a molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$ (Fig. 1) indicated the polymerization proceeded with an approximately constant number active species for the duration of the polymerizations up to 89% monomer conversion. In addition, the induction period observed in Fig. 3 shortened to 3.2 h under this polymerization conditions. By calculating the apparent rate constant of polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[P_n{\cdot}][M] = k_p^{app}[M]$), as determined from the kinetic slops, a k_p^{app} of 9.07×10^{-6} s^{-1} for the molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/0.5$ (Fig. 1) and another k_p^{app} of 10.4×10^{-6} s^{-1} for the molar ratio of $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/1$ (Fig. 3) were obtained. As expected, increasing the amount of VC increased the polymerization rate (R_p). This is due to that increasing the amount of VC resulted in a higher concentration of Fe(II) salts produced by the in situ reduction of a iron(III) complex with VC. From Fig. 4, the M_w/M_n values of the obtained PSs still kept narrow (1.14–1.31). $M_{n,GPC}$ values increased linearly with conversion, and were close to the corresponding theoretical values, indicating that the iron(III)-mediated AGET ATRP of St was a controlled/"living" radical polymerization.

It is well known that thermal initiation of styrene polymerization usually happens at high temperature (e.g. above 110 °C) [76–81]. The most widely accepted mechanism for the spontaneous generation of radicals from St was first proposed by Mayo in 1968 [77, 82]. In order to assess the effect of thermal initiation on the AGET ATRP of styrene, reference experiments in the absence of initiator (BB) were carried out. The results are shown in Figs. 5 and 6. A first-order kinetic plot was also observed (Fig. 5); and the molecular weights increased with the monomer conversion while the molecular weight distributions kept narrow (less than 1.30), indicating a controlled polymerization fashion in that case as expected by similarly

Table 1 Effect of the amount of reducing agent on AGET ATRP of St in bulk at 110 °C

Entry	R	Time (h)	Conversion (%)	$M^{a}_{n,th}$	$M_{n,GPC}$	M_w/M_n
1	200/1/1/3/0	60.0	13.7	2,850	4,280	1.30
2	200/1/1/3/0.2	66.7	81.6	16,980	13,730	1.37
3	200/1/1/3/0.5	52	86.3	17,940	13,140	1.34
4	200/1/1/3/1.0	44.7	73.4	15,260	11,780	1.31
5	200/1/1/3/1.5	44.2	74.0	15,400	13,020	1.29

R = $[St]_0/[BB]_0/[Fe(III)]_0/[PPh_3]_0/[VC]_0$

$^{\alpha}$ $M_{n,th} = ([St]_0/[BB]_0) \times M_{w,St} \times$ conversion%

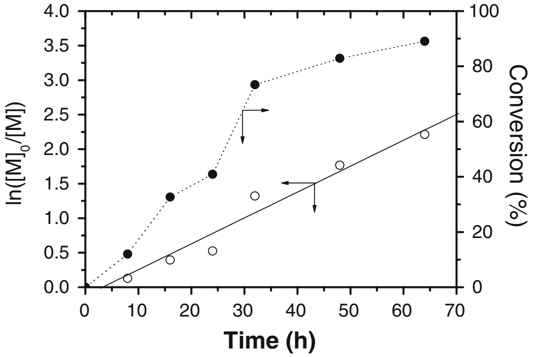

Fig. 3 ln($[M]_0/[M]$) and conversion as a function of time for AGET ATRP of St in bulk. Polymerization conditions: $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0$ = 200/1/1/3/1; St = 3 mL; temperature = 110 °C

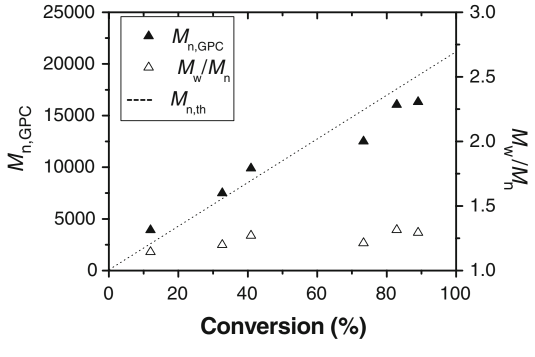

Fig. 4 Average–number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion for the AGET ATRP of St in bulk. Polymerization conditions: $[St]_0/[BB]_0/[FeCl_3{\cdot}6H_2O]_0/[PPh_3]_0/[VC]_0$ = 200/1/1/3/1; St = 3 mL; temperature = 110 °C

previous work [77]. At the same time, by comparison with the results shown in the Fig. 1, it can be seen that the polymerization rate of the thermal initiation of styrene (in the absence of initiator BB) was slower than that in the presence of initiator BB. For example, a 23.8% of conversion was obtained for the former while a 75.3% of conversion was obtained for the latter after 48 h polymerization time. Thus, thermal initiation of styrene polymerization played a non-negligible role during the AGET ATRP of styrene in that case.

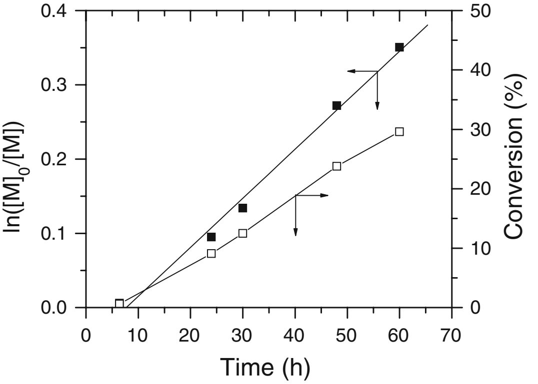

Fig. 5 $\ln([M]_0/[M])$ and conversion as a function of time for AGET ATRP of St in the absence of initiator (BB) in bulk. Polymerization conditions: $[St]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/3/1$; St = 3 mL; temperature = 110 °C

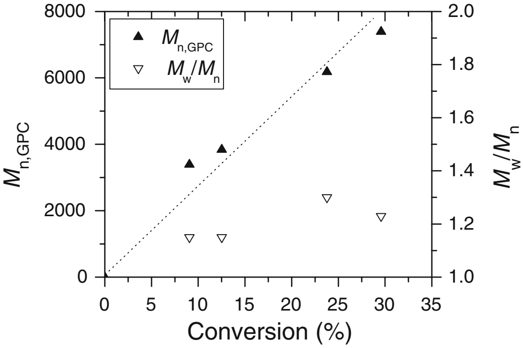

Fig. 6 Average–number molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus the conversion for the AGET ATRP of St in the absence of initiator (BB) in bulk. Polymerization conditions: $[St]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[VC]_0 = 200/1/1/3/1$; St = 3 mL; temperature = 110 °C

Effect of the amount of $FeCl_3 \cdot 6H_2O$ on polymerization of St

In order to further investigate the effect of Fe(III) concentration on the AGET ATRP of St, 5–100 mol% catalyst relative to the initiator was used. The results are listed in Table 2. From Table 2, it can be seen that when more than 10% catalyst was used, the M_w/M_n values of the obtained PSs kept narrow (less than 1.35); however, when less than 50 mol% catalyst was used, the molecular weights of the obtained PSs deviated from the corresponding theoretical values, which indicated the decrease of controllability over the polymerization of the catalyst system. In addition, when the amount of catalyst was decreased to 5 mol% of the initiator, the M_w/M_n of the obtained PS was 1.6, indicating an uncontrolled polymerization. At the same time, these results showed that the catalyst system was not a very highly active catalyst system. Thus, in order to obtain well-defined PSs, more than 50 mol% catalyst relative to the initiator should be used.

Analysis of chain end

The chain end of the PS was analyzed by ^{1}H NMR spectroscopy, as shown in Fig. 7. The chemical shifts at $\delta = 6.37$–7.08 ppm (a in Fig. 7) were attributed to the aromatic protons of the BB initiator moieties and PS chains. The chemical shifts at

Table 2 Effect of the amount of catalyst on the AGET ATRP of St in bulk at 110 °C

Entry	R	Time (h)	Conversion (%)	$M^{a}_{n,th}$	$M_{n,GPC}$	M_w/M_n
1	200/1/1/3/1	46	76.4	15,890	14,650	1.28
2	200/1/0.5/1.5/1	46	70.8	14,720	16,370	1.23
3	200/1/0.2/1/1	46	56.6	11,770	18,180	1.27
4	200/1/0.1/1/1	46	53.5	11,130	21,380	1.35
5	200/1/0.05/1/1	46	68.2	14,180	38,160	1.60

R = $[St]_0/[BB]_0/[Fe(III)]_0/[PPh_3]_0/[VC]_0$

[α] $M_{n,th} = ([St]_0/[BB]_0) \times M_{w,St} \times$ conversion%

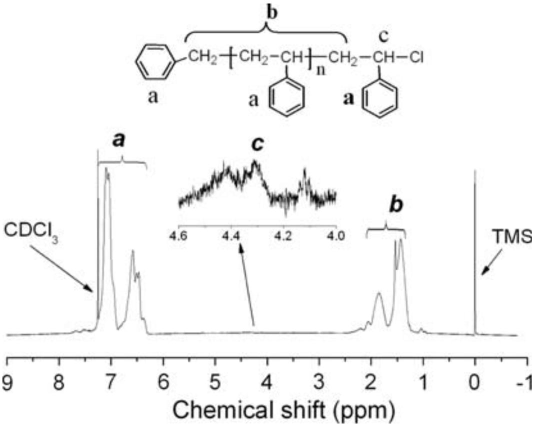

Fig. 7 ^{1}H NMR spectrum of the polymer obtained from AGET ATRP of St in bulk at 110 °C. Sample: $M_{n,GPC}$ = 12,500 g/mol, PDI = 1.21

1.42–2.06 ppm (b in Fig. 7) were assigned to the methylene and methyne protons in the PS main chains. The chemical shifts at 4.2–4.5 ppm (c in Fig. 7) were assigned to the methyne protons in the chain ends of PSs because of the electron-attracting function of ω-Cl atom [83], indicating that a ω-Cl atom from catalyst is obtained from $[BB]_0/[FeCl_3 \cdot 6H_2O]_0/[PPh_3]_0/[VC]_0$ initiating system.

Conclusions

A novel method for conducting AGET ATRP of St in bulk mediated by iron(III)/PPh_3 complexes, using VC as the reducing agent and BB as the initiator, was developed, and it demonstrated the "living"/controlled features. Well-defined polystyrenes with molecular weights being close to their corresponding theoretical values and narrow molecular weight distributions could be obtained when 50–100 mol% catalyst relative to the initiator was used.

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References

1. Coessens V, Pintauer T, Matyjaszewski K (2001) Functional polymers by atom transfer radical polymerization. Prog Polym Sci 26:337–377
2. Pyun J, Matyjaszewski K (2001) Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living" radical polymerization. Chem Mater 13:3436–3448
3. Davis KA, Matyjaszewski K (2002) Statistical, gradient, block, and graft copolymers by controlled/living radical polymerizations. Adv Polym Sci 159:1–13
4. Matyjaszewski K (2005) Macromolecular engineering: from rational design through precise macromolecular synthesis and processing to targeted macroscopic material properties. Prog Polym Sci 30:858–875
5. Kamigaito M, Ando T, Sawamoto M (2001) Metal-catalyzed living radical polymerization. Chem Rev 101:3689–3745
6. Tsarevsky NV, Matyjaszewski K (2007) "Green" atom transfer radical polymerization: from process design to preparation of well-defined environmentally friendly polymeric materials. Chem Rev 107:2270–2299
7. Zhu S, Yan D (2000) Atom transfer radical polymerization of methyl methacrylate catalyzed by iron(II) chloride/isophthalic acid system. Macromolecules 34:8233–8238
8. Hong SC, Matyjaszewski K (2002) Fundamentals of supported catalysts for atom transfer radical polymerization (ATRP) and application of an immobilized/soluble hybrid catalyst system to ATRP. Macromolecules 35:7592–7605
9. Shen Y, Tang H, Ding S (2004) Catalyst separation in atom transfer radical polymerization. Prog Polym Sci 29:1053–1078
10. Kubisa P (2004) Application of ionic liquids as solvents for polymerization processes. Prog Polym Sci 29:3–12
11. Jakubowski W, Matyjaszewski K (2005) Activator generated by electron transfer for atom transfer radical polymerization. Macromolecules 38:4139–4146
12. Min K, Gao HF, Matyjaszewski K (2005) Preparation of homopolymers and block copolymers in miniemulsion by ATRP using activators generated by electron transfer (AGET). J Am Chem Soc 127:3825–3830
13. Min K, Gao HF, Matyjaszewski K (2006) Development of an ab initio emulsion atom transfer radical polymerization: from microemulsion to emulsion. J Am Chem Soc 128:10521–10526
14. Min K, Matyjaszewski K (2005) Atom transfer radical polymerization in microemulsion. Macromolecules 38:8131–8134
15. Oh JK, Perineau F, Matyjaszewski K (2006) Preparation of nanoparticles of well-controlled water-soluble homopolymers and block copolymers using an inverse miniemulsion ATRP. Macromolecules 39:8003–8010
16. Wu DX, Yang YF, Cheng XH, Liu L, Tian J, Zhao HY (2006) Mixed molecular brushes with PLLA and PS side chains prepared by AGET ATRP and ring-opening polymerization. Macromolecules 39:7513–7519
17. Kwiatkowski P, Jurczak J, Pietrasik J, Jakubowski W, Mueller L, Matyjaszewski K (2008) High molecular weight polymethacrylates by AGET ATRP under high pressure. Macromolecules 41:1067–1069
18. Stoffelbach F, Belardi B, Santos JMRCA, Tessier L, Matyjaszewski K, Charleux B (2007) Use of an amphiphilic block copolymer as a stabilizer and a macroinitiator in miniemulsion polymerization under AGET ATRP conditions. Macromolecules 40:8813–8816
19. Oh JK, Dong H, Zhang R, Matyjaszewski K, Schlaad H (2007) Preparation of nanoparticles of double-hydrophilic PEO-PHEMA block copolymers by AGET ATRP in inverse miniemulsion. J Polym Sci Part A Polym Chem 45:4764–4772
20. Min K, Yu S, Lee H, Mueller L, Sheiko SS, Matyjaszewski K (2007) High yield synthesis of molecular brushes via ATRP in miniemulsion. Macromolecules 40:6557–6563
21. Esteves ACC, Bombalski L, Trindade T, Matyjaszewski K, Barros-Timmons A (2007) Polymer grafting from CdS quantum dots via AGET ATRP in miniemulsion. Small 3:1230–1236

22. Li W, Min K, Matyjaszewski K, Stoffelbach F, Charleux B (2008) PEO-based block copolymers and homopolymers as reactive surfactants for AGET ATRP of butyl acrylate in miniemulsion. Macromolecules 41:6387–6392
23. Pietrasik J, Dong H, Matyjaszewski K (2006) Synthesis of high molecular weight poly(styrene-*co*-acrylonitrile) copolymers with controlled architecture. Macromolecules 39:6384–6390
24. Matyjaszewski K, Tsarevsky NV, Braunecker WA, Dong H, Huang J, Jakubowski W, Kwak Y, Nicolay R, Tang W, Yoon JA (2007) Role of Cu^0 in controlled/"living" radical polymerization. Macromolecules 40:7795–7806
25. Yamamura Y, Matyjaszewski K (2007) Methylaluminoxane as a reducing agent for activators generated by electron transfer ATRP. J Macromol Sci Part A Pure Appl Chem 44:1035–1039
26. Kabachii YA, Kochev SY, Bronstein LM, Blagodatskikh IB, Valetsky PM (2003) Atom transfer radical polymerization with Ti(III) halides and alkoxides. Polym Bull 50:271–278
27. Le Grognec E, Claverie J, Poli R (2001) Radical polymerization of styrene controlled by half-sandwich Mo(III)/Mo(IV) couples: all basic mechanisms are possible. J Am Chem Soc 123:9513–9524
28. Stoffelbach F, Haddleton DM, Poli R (2003) Controlled radical polymerization of alkyl acrylates and styrene using a half-sandwich molybdenum(III) complex containing diazadiene ligands. Eur Polym J 39:2099–2105
29. Kotani Y, Kamigaito M, Sawamoto M (1999) Re(V)-mediated living radical polymerization of styrene: $ReO_2I(PPh_3)_2/R{-}I$ initiating systems. Macromolecules 32:2420–2424
30. Kotani Y, Kamigaito M, Sawamoto M (2000) Living radical polymerization of para-substituted styrenes and synthesis of styrene-based copolymers with rhenium and iron complex catalysts. Macromolecules 33:6746–6751
31. Percec V, Barboiu B, Neumann A, Ronda JC, Zhao M (1996) Metal-catalyzed "living" radical polymerization of styrene initiated with arenesulfonyl chlorides. From heterogeneous to homogeneous catalysis. Macromolecules 29:3665–3668
32. Simal F, Demonceau A, Noels AF (1999) Highly efficient ruthenium-based catalytic systems for the controlled free-radical polymerization of vinyl monomers. Angew Chem Int Ed 38:538–540
33. Opstal T, Verpoort F (2003) Synthesis of highly active ruthenium indenylidene complexes for atom-transfer radical polymerization and ring-opening-metathesis polymerization. Angew Chem Int Ed 42:2876–2879
34. Zhao X, Luo X, Li B, Song H, Xu S, Wang B (2008) A new ruthenium complex with benz[*f*]indenyl ligand for living radical polymerization. Eur Polym J 44:3264–3270
35. Moineau G, Granel C, Dubois P, Jerome R, Teyssie P (1998) Controlled radical polymerization of methyl methacrylate initiated by an alkyl halide in the presence of the Wilkinson catalyst. Macromolecules 31:542–544
36. Mecerreyes D, Moineau G, Dubois P, Jerome R, Hedrick JL, Hawker CJ, Malmstrom EE, Trollsas M (1998) Simultaneous dual living polymerizations: a novel one-step approach to block and graft copolymers. Angew Chem Int Ed 37:1274–1276
37. Granel C, Dubois P, Jerome R, Teyssie P (1996) Controlled radical polymerization of methacrylic monomers in the presence of a bis(ortho-chelated) arylnickel(II) complex and different activated alkyl halides. Macromolecules 29:8576–8582
38. Uegaki H, Kotani Y, Kamigaito M, Sawamoto M (1997) Nickel-mediated living radical polymerization of methyl methacrylate. Macromolecules 30:2249–2253
39. Carrot G, Hilborn J, Hedrick JL, Trollsas M (1999) Novel initiators for atom transfer radical and ring-opening polymerization: a new general method for the preparation of thiol-functional polymers. Macromolecules 32:5171–5173
40. Gao C, Muthukrishnan S, Li W, Yuan J, Xu Y, Muller AHE (2007) Linear and hyperbranched glycopolymer-functionalized carbon nanotubes: synthesis, kinetics, and characterization. Macromolecules 40:1803–1815
41. Shao Q, Sun H, Pang X, Shen Q (2004) A neutral Ni(II) acetylide-mediated radical polymerization of methyl methacrylate using the atom transfer radical polymerization method. Eur Polym J 40:97–102
42. Duquesne E, Degée PH, Habiman J, Dubois PH (2004) Supported nickel bromide catalyst for Atom Transfer Radical Polymerization (ATRP) of methyl methacrylate. Chem Commun 640–641
43. Lecomte P, Drapier I, Dubois P, Teyssie P, Jerome R (1997) Controlled radical polymerization of methyl methacrylate in the presence of palladium acetate, triphenylphosphine, and carbon tetrachloride. Macromolecules 30:7631–7633

44. Wang B, Zhang Y, Luo X, Xu S, Zhou X (2003) Controlled/“living” radical polymerization of MMA catalyzed by cobaltocene. Macromolecules 36:9684–9686
45. Luo X, Zhuang Y, Zhao X, Zhang M, Xu S, Wang B (2008) Controlled/living radical polymerization of styrene catalyzed by cobaltocene. Polymer 49:3457–3461
46. Braunecker WA, Itami Y, Matyjaszewski K (2005) Osmium-mediated radical polymerization. Macromolecules 38:9402–9404
47. Wang JS, Matyjaszewski K (1995) Controlled/“living” radical polymerization. Halogen atom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process. Macromolecules 28:7901–7910
48. Percec V, Barboiu B (1995) “Living” radical polymerization of styrene initiated by arenesulfonyl chlorides and CuI(bpy)$_n$Cl. Macromolecules 28:7970–7972
49. Xia J, Matyjaszewski K (1997) Controlled/“living” radical polymerization. Atom transfer radical polymerization using multidentate amine ligands. Macromolecules 30:7697–7700
50. Haddleton DM, Jasieczek CB, Hannon MJ, Shooter AJ (1997) Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper(I) complexes. Macromolecules 30:2190–2193
51. Haddleton DM, Crossman MC, Dana BH, Duncalf DJ, Heming AM, Kukulj D, Shooter AJ (1999) Atom transfer polymerization of methyl methacrylate mediated by alkylpyridylmethanimine type ligands, copper(I) bromide, and alkyl halides in hydrocarbon solution. Macromolecules 32:2110–2119
52. Xiong M, Zhang K, Chen Y (2008) ATRP of 3-(triethoxysilyl)propyl methacrylate and preparation of “stable” gelable block copolymers. Eur Polym J 44:3835–3841
53. Tong L, Shen Z, Zhang S, Li Y, Lu G, Huang X (2008) Synthesis and characterization of perfluorocyclobutyl aryl ether-based amphiphilic diblock copolymer. Polymer 49:4534–4540
54. Gong H, Huang W, Zhang D, Gong F, Liu C, Yang Y, Chen J, Jiang B (2008) Studies on the development of branching in ATRP of styrene and acrylonitrile in the presence of divinylbenzene. Polymer 49:4101–4108
55. Jiang J, Lu X, Lu Y (2008) Stereospecific preparation of polyacrylamide with low polydispersity by ATRP in the presence of Lewis acid. Polymer 49:1770–1776
56. Ando T, Kamigaito M, Sawamoto M (1997) Iron(II) chloride complex for living radical polymerization of methyl methacrylate. Macromolecules 30:4507–4510
57. Matyjaszewski K, Wei M, Xia J, McDermot NE (1997) Controlled/“living” radical polymerization of styrene and methyl methacrylate catalyzed by iron complexes. Macromolecules 30:8161–8164
58. Moineau G, Dubois P, Jerome R, Senninger T, Teyssie P (1998) Alternative atom transfer radical polymerization for MMA using FeCl3 and AIBN in the presence of triphenylphosphine: an easy way to well-controlled PMMA. Macromolecules 31:545–547
59. Wang G, Zhu XL, Zhu J, Cheng ZP (2006) Iron-mediated atom transfer radical polymerization of styrene with tris(3,6-dioxaheptyl) amine as a ligand. J Polym Sci Part A Polym Sci 44:483–489
60. Zhu S, Yan D, Zhang G, Li M (2000) Controlled/living radical polymerization of styrene catalyzed by FeCl$_2$/succinic acid. Macromol Chem Phys 201:2666–2669
61. Gibson VC, O’Reilly RK, Reed W, Wass DF, White AJP, Williams DJ (2002) Four-coordinate iron complexes bearing α-diimine ligands: efficient catalysts for Atom Transfer Radical Polymerisation (ATRP). Chem Commun 1850–1851
62. Gibson VC, O’Reilly RK, Wass DF, White AJP, Williams DJ (2003) Polymerization of methyl methacrylate using four-coordinate (α-diimine)iron catalysts: atom transfer radical polymerization vs catalytic chain transfer. Macromolecules 36:2591–2593
63. Xue Z, Lee BW, Noh SK, Lyoo WS (2007) Pyridylphosphine ligands for iron-based atom transfer radical polymerization of methyl methacrylate and styrene. Polymer 48:4704–4714
64. Gong R, Maclaughlin S, Zhu S (2008) Surface modification of active metals through atom transfer radical polymerization grafting of acrylics. Appl Surf Sci 254:6802–6809
65. Hou C, Qu R, Sun C, Ji C, Wang C, Ying L, Jiang N, Xiu F, Chen L (2008) Novel ionic liquids as reaction medium for ATRP of acrylonitrile in the absence of any ligand. 49:3424–3427
66. Zhang LF, Cheng ZP, Shi SP, Li QH, Zhu XL (2008) AGET ATRP of methyl methacrylate catalyzed by FeCl$_3$/iminodiacetic acid in the presence of air. Polymer 49:3054–3059
67. Zhang LF, Cheng ZP, Tang F, Li Q, Zhu XL (2008) Iron(III)-mediated ATRP of methyl methacrylate using activators generated by electron transfer. Macromol Chem Phys 209:1705–1713

68. Luo R, Sen A (2008) Electron-transfer-induced iron-based atom transfer radical polymerization of styrene derivatives and copolymerization of styrene and methyl methacrylate. Macromolecules 41:4514–4518
69. Zhang LF, Cheng ZP, Lü YT, Zhu XL (2009) A highly active iron-based catalyst system for the AGET ATRP of styrene. Macromol Rapid Commun 30:543–547
70. Bai LJ, Zhang LF, Zhu J, Cheng ZP, Zhu XL (2009) Iron(III)-mediated AGET ATRP of styrene using tris(3,6-dioxaheptyl)amine as a ligand. J Polym Sci Part A Polym Chem 47:2002–2008
71. Tang F, Zhang LF, Zhu J, Cheng ZP, Zhu XL (2009) Surface functionalization of chitosan nanospheres via surface-initiated AGET ATRP mediated by iron catalyst in the presence of limited amounts of air. Ind Eng Chem Res 48:6216–6223
72. Matyjaszewski K, Xia J (2001) Atom transfer radical polymerization. Chem Rev 101:2921–2990
73. Ibrahim K, Starck P, Löfgren B, Seppälä J (2003) Towards more controlled poly(*n*-butyl methacrylate) by atom transfer radical polymerization. Eur Polym J 39:939–944
74. Ibrahim K, Starck P, Löfgren B, Seppälä J (2005) Synthesis and characterization of amphiphilic triblock copolymers by iron-mediated atom transfer radical polymerization. J Polym Sci Part A Polym Chem 43:5049–5061
75. Hou C, Qu RJ, Ji CN, Wang CH, Wang CG (2006) Synthesis of polyacrylonitrile via reverse atom transfer radial polymerization (ATRP) initiated by diethyl 2,3-dicyano-2,3-diphenylsuccinate, $FeCl_3$, and triphenylphosphine. Polym Int 55:326–329
76. Moad G, Solomon DH (1995) The chemistry of free radical polymerization. Pergamon, Oxford, p 92
77. Cheng ZP, Zhu XL, Zhou NC, Lu JM (2003) Living/controlled radical autopolymerization of styrene in the presence of $CuCl_2$ and 2,2'-bipyridine. J Appl Polym Sci 90:1532–1538
78. Fukuda T, Terauchi T, Goto A, Ohno K, Tsujii Y, Miyamoyo T, Kobatake S, Yamada B (1996) Mechanisms and kinetics of nitroxide-controlled free radical polymerization. Macromolecules 29:6393–6398
79. Kothe T, Fischer H (2001) Formation rate constants of the Mayo dimer in the autopolymerization of styrene. J Polym Sci Part A Polym Chem 39:4009–4013
80. Lutz JF, Matyjaszewski K (2002) Kinetic modeling of the chain-end functionality in atom transfer radical polymerization. Macromol Chem Phys 203:1385–1395
81. Nabifara A, McManusa NT, Vivaldo-Limab E, Lonac LMF, Penlidisa A (2009) Thermal polymerization of styrene in the presence of TEMPO. Chem Eng Sci 64:304–312
82. Mayo FR (1968) The dimerization of styrene. J Am Chem Soc 90:1289–1295
83. Cheng ZP, Zhu XL, Zhou NC, Zhu J, Zhang ZB (2005) Atom transfer radical polymerization of styrene under pulsed microwave irradiation. Radiat Phys Chem 72:695–701