Atom Transfer Radical Polymerization of Styrene Using a Copper Catalyst with a Pseudohalogen Anion

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ABSTRACT: Atom transfer radical polymerization has been a very useful method in the recent advances in controlled radical polymerization. It needs an activated alkyl halide as an initiator and a copper halide as a catalyst. This investigation reports the successful application of copper thiocyanate, a catalyst with a pseudohalide anion, in the presence of different ligands such as $N,N,N=,N'',N''',N'''$-hexamethyltriethylenetetramine (HMTETA), pentyl-2-pyridylmethaneimine, and substituted bipyridine in the atom transfer radical polymerization of styrene. Among the three ligands used, HMTETA was found to be very efficient. The polymers were characterized with ^{13}C-NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, and gel permeation chromatography analysis. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1418–1426, 2005

Key words: atom transfer radical polymerization (ATRP); living radical polymerization; pseudohalogens

INTRODUCTION

Living polymerization techniques are unique methods to produce well-defined homopolymers, block copolymers, gradient copolymers, and polymers with well-defined topology.[1–4] Free-radical polymerization is a powerful synthetic tool because of its robust character, and it can be applied to a variety of monomers over a wide range of temperatures.[5] Conventional free-radical polymerization does not allow accurate control over the molecular weight and molecular weight distribution. Until 1990, controlled radical polymerization was limited to the iniferter concept[6,7] but with limited success. Free-radical polymerizations can never be truly living because these processes are always accompanied by bimolecular termination and chain-transfer reactions.[4,5] Controlled radical polymerization can be achieved by a dynamic equilibrium being maintained between the transient (propagating) radicals and the dormant species via reversible deac-

tivation.[4,5] This process can be achieved by several recent techniques, including stable free-radical processes[8–10] (e.g., nitroxide-mediated), various organometallic derivatives,[11] transition-metal-catalyzed atom transfer radical polymerization (ATRP),[4,12–16] and thiocarbonylthio-compound-mediated reversible addition–fragmentation chain transfer (RAFT).[17,18] ATRP usually requires an alkyl halide (R—X) as an initiator and a transition-metal complex [e.g., Cu(I)-based] as a catalyst or activator. ATRP involves a fast initiation by the initiator, catalyzed by the Cu(I) complex, followed by propagation and frequent reversible deactivation of a propagating chain radical by repetitive transfer of halogen or pseudohalogen atoms from and to the transition-metal catalyst[4] (Scheme 1).

Styrene is a widely used monomer, and advances in the different methods for the polymerization of styrene were reviewed by Priddy.[7] The controlled radical polymerization of styrene has been reported with stable free-radical mediated polymerization,[4,8–10] RAFT,[17,18] and ATRP.[4,13,14,19–22] In ATRP, transition-metal complexes based on transition-metal halides such as Cu, Fe, Ni, and Ru in their lower oxidation state have been used for the polymerization of styrene. The goal of this article is to report the successful application of a copper catalyst with a pseudohalide anion (—SCN) as an ATRP catalyst for the polymerization of styrene. Polymers end-capped with —SCN groups may have interesting applications, as —SCN is a versatile functionality susceptible to several chemi-

$$R—X \; + \; Cu(I)L_2Y \;\; \rightleftarrows \;\; R^{\cdot} \;\; + \;\; Cu(II)L_2XY$$

$$k_p$$
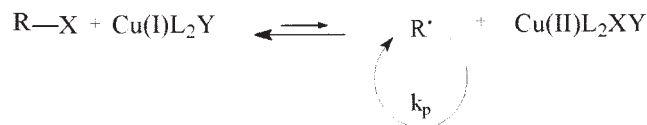
Scheme 1

cal transformations. Recently, we successfully carried out the ATRP of methyl methacrylate (MMA), using copper thiocyanate (CuSCN) as the catalyst.[23]

EXPERIMENTAL

Materials

Styrene (Aldrich) was passed through an inhibitor removal (Aldrich) column to remove the inhibitor (4-*tert*-butylcatechol) and then was purified via vacuum distillation. The initiator, 1-phenyl-ethylbromide (PEBr), from Aldrich was used as received. *N*-*n*-Pentyl-2-pyridylmethaneimine (NPPI) was prepared by the condensation of *n*-pentylamine with 2-pyridine carboxaldehyde (Aldrich).[23] *N*,*N*,*N'*,*N''*,*N'''*,*N'''*-Hexamethyltriethylenetetramine (HMTETA; Aldrich) and 4,4'-dinonyl-2,2'-bipyridine (dNbpy; Aldrich) were used as received. The catalyst CuSCN (99%), obtained from Aldrich, was used as received.

Polymerization

Styrene (10.0 g), *p*-xylene (10.0 g), butyl acetate (0.40 g; used as an internal standard for gas chromatography), the required amount of ligands (i.e., NPPI and HMTETA), and PEBr were added to a 100-mL, three-necked, round-bottom flask. The flask was equipped with a condenser in one neck and a silicon septum in the other. The mixture was purged with argon for 15 min. After the addition of the calculated amount of the catalyst CuSCN, the flask was kept *in vacuo* and back-filled with argon by three freeze–pump–thaw cycles. Polymerization was carried out at 110°C.

Characterization

The monomer conversion was determined from the concentration of the residual styrene monomer with a Hewlett–Packard HP 5890 gas chromatograph. The gas chromatograph was equipped with an AT-Wax capillary column (30 m × 0.53 mm, i.d. = 10 μm).

The molecular weight distributions of polystyrene (PS) were measured with size exclusion chromatography (SEC). SEC was performed in tetrahydrofuran (THF) at the ambient temperature at a flow rate of 1.0 mL/min. The Waters gel permeation chromatography (GPC) instrument was equipped with a Waters model 510 pump, a model 410 refractive-index detector, and

a model 486 UV detector. A set of two linear columns (mixed-C, Polymer Laboratories) was used for the SEC analysis of the PS samples. Calibration was carried out with narrow-polydispersity PS standards. Data acquisition and processing were performed with Waters Millennium 32 software.

^{13}C-NMR was recorded in the solvent CDCl$_3$ with a Varian 400-MHZ NMR machine. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis was carried out in a Voyager DE-PRO (Perceptive Biosystems, MA). Solutions of 40 mg of dithranol/mL, 5 mg of silver trifluoroacetate/mL, and 1 mg of polymer/mL in THF were prepared. The respective solutions were mixed in a 5:1:5 ratio on a volume basis. Enough of the mixture was applied to the sample position to cover the 2.5-mm-diameter sample position (typically 0.3 μL). The spot was allowed to air-dry without any assistance.

RESULTS AND DISCUSSION

Thiocyanate was used as the pseudohalogen anion for the copper catalyst for the ATRP of styrene. Styrene was polymerized at 110°C with PEBr as an initiator in conjunction with CuSCN as a catalyst. NPPI was used as a ligand for CuSCN. The complexation of CuSCN with NPPI was observed to result in a deep brown solution, which indicated the presence of the Cu(I) complex. Figure 1 shows a linear increase in the logarithmic conversion with the polymerization time. There was some induction period in the polymerization. The reason for the induction period is not fully understood. However, CuSCN took some time to dissolve completely in styrene. An approximately 60% conversion was obtained in 6 h.

Figure 2 shows that the molecular weight of PS increased linearly with the monomer conversion. The number-average molecular weight (M_n) of PS obtained from GPC was slightly higher than the theoretical number-average molecular weight [$M_{n,\mathrm{th}}$; [defined as $M_{n,\mathrm{th}} = (\Delta[\text{styrene}]/[\text{PEBr}]_0) \times$ molecular weight of styrene]. The polydispersity indices (PDIs) were around 1.6, and this could suggest that the exchange between the active and dormant species was relatively slow. On the basis of the general mechanism of ATRP, ATRP of styrene using the PEBr/Cu-catalyst system is represented in Scheme 2.

Because of the soft–hard acid–base principle, Cu(I) will tend to form a bond with the sulfur atom of the —SCN group,[24] as S is the weak base site in —SCN. According to the spectrochemical series,[25] the strength of the ligand —SCN is higher than that of —Br. Therefore, the rate of deactivation (k_{deact}) of CuBr$_2$ (if CuBr is used instead of CuSCN in Scheme 2) is higher than k_{deact} of Cu(Br)(SCN). In the case of the CuBr system, a relatively narrow polydispersity polymer is ob-
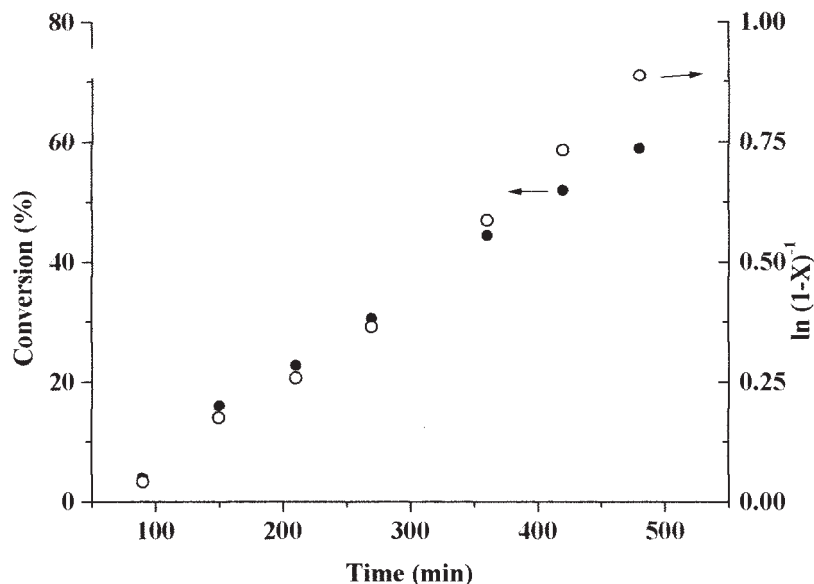
Figure 1 (●) Plots of the conversion versus the time and (○) a semilogarithmic kinetic plot for the solution ATRP of styrene in p-xylene at 110°C with PEBr as an initiator and NPPI as a ligand ([styrene]$_0$ = 5.37M, [NPPI] = 0.107M, [PEBr] = 0.043M, [CuSCN)] = 0.043M).

tained.[22] In a CuSCN catalyzed system, it is likely that more monomers are added per activation–deactivation cycle because of slower deactivation. Especially at low chain lengths, this will lead to a broadening of the molar mass distribution.

Ligands play an important role in ATRP.[4(a)] They influence the solubility, electronic environment, and redox potential of the catalysts. Multidentate aliphatic tertiary amines are useful ligands for ATRP cata-

lysts.[22] They are easily available and do not yield strongly colored polymer solutions because they do not have a conjugated skeleton (e.g., bipyridines or imines). Styrene was polymerized with CuSCN as a catalyst and HMTETA as a ligand. PEBr was used as an initiator. In this case, the polymerization of styrene was fast in comparison with the CuSCN/NPPI system, and the kinetic plot of ln([M]$_0$/[M]) versus time (where [M]$_0$ is the initial monomer concentration and
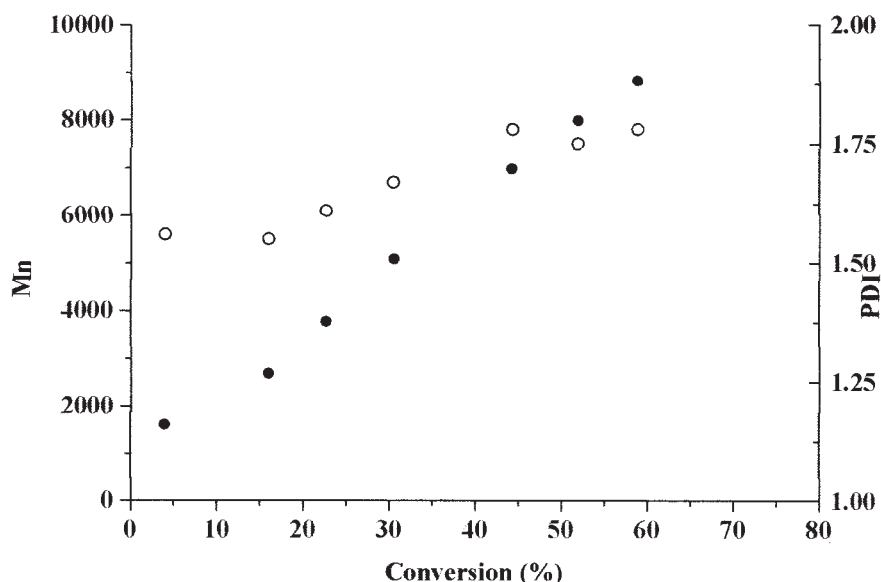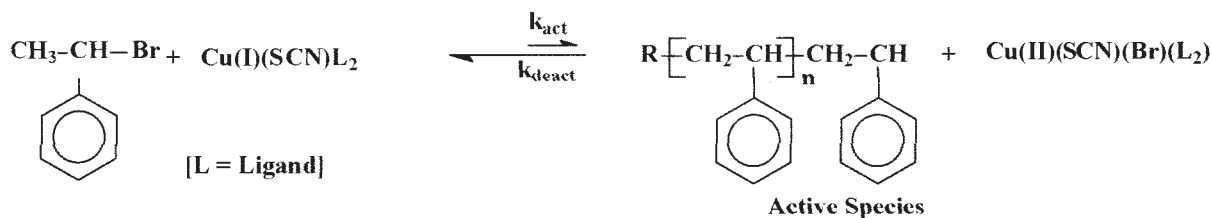

Figure 2 Dependence of (●) the molecular weights and (○) the polydispersities of PS on the monomer conversion for the solution ATRP of styrene in p-xylene at 110°C with PEBr as an initiator and NPPI as a ligand ([styrene]$_0$ = 5.37M, [NPPI] = 0.107M, [PEBR] = 0.043M, [CuSCN] = 0.043M).

Scheme 2

[M] is the monomer concentration) showed a pseudo-first-order behavior, indicating an approximately constant number of active species during the reaction (Fig. 3). A linear increase in M_n versus the monomer conversion was observed during the polymerization. The observed molecular weights ($M_{n,SEC}$) were almost equal to the $M_{n,th}$ values, and the polydispersity was relatively low (Fig. 4). This indicates that the polymerization process shows fast initiation, good initiation efficiency, and a negligible amount of chain transfer. Figure 5 shows that there was gradual increase in the molecular weight with the polymerization time. Initially, the molecular weight distribution was high, and later, it led to a relatively low PDI. dNbpy, a substituted bipyridine, was also used as a ligand for CuSCN in the ATRP of styrene. The polymerization was slow in comparison with CuSCN/HMTETA (Fig. 3). The gradual increase in M_n with the conversion (Fig. 4) and the relatively narrow molecular weight distribution indicate that there is very little termination during the ATRP of styrene with the CuSCN/dNbpy system. The results obtained with the CuSCN/HMTETA and

CuSCN/dNbpy systems are better than those obtained with the CuSCN/NPPI system in terms of the control over the molecular weight and PDI. Copper–imine complexes have been successfully used for the ATRP of acrylate monomers[15] without much report on styrene.

Table I shows that polymerization with the CuSCN/HMTETA system is faster than that with the CuSCN/dNbpy or CuSCN/NPPI system. This can be explained by the lower redox potential of the HMTETA–Cu system compared with that of the Cu–bipyridine or Cu–imine systems.[4(a)] Xia and Matyjas-zeswski[22] also observed slower polymerization of MMA with the CuBr/dNbpy system in comparison with the CuBr/HMTETA system. Polymerizations of styrene using CuBr/HMTETA and CuBr/dNbpy have been reported to have lower PDIs (~1.20).[22] The broadening of the molecular weight distribution in our CuSCN/HMTETA and CuSCN/dNbpy systems may be due to slow activation of the dormant macromolecular chains having a —SCN end group. Being an ambidentate functional group, —SCN can bind
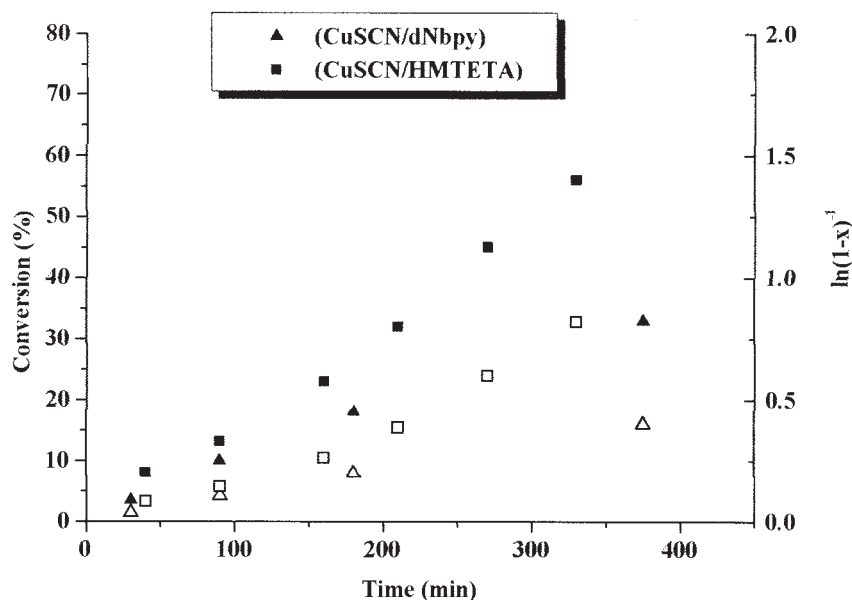

Figure 3 (■,▲) Plots of the conversion versus the time and (□,△) a semilogarithmic kinetic plot for the solution ATRP of styrene in *p*-xylene at 110°C with PEBr as an initiator and HMTETA as a ligand ([styrene]$_0$ = 5.37M, [dNbpy] = 0.087M, [PEBr] = 0.043M, [CuSCN] = 0.043M, [styrene]$_0$ = 5.37M, [HMTETA] = 0.05M, [PEBr] = 0.043M, [CuSCN] = 0.043M).
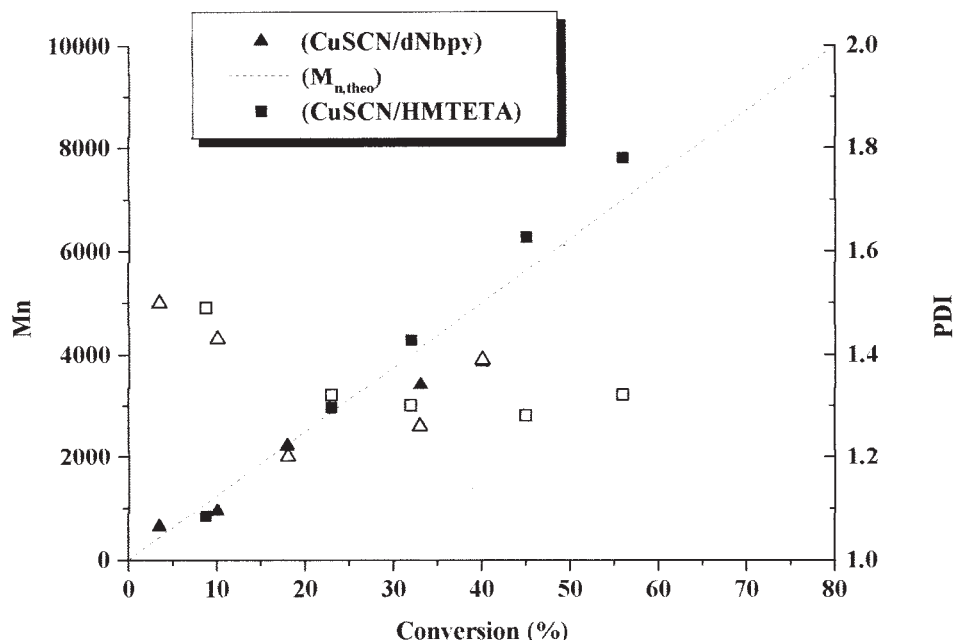
Figure 4 Dependence of (■,▲) the molecular weights and (□,△) the polydispersities of PS on the monomer conversion for the solution ATRP of styrene in p-xylene at 110°C with PEBr as an initiator and HMTETA as a ligand ($[styrene]_0 = 5.37M$, $[dNbpy] = 0.087M$, $[PEBr] = 0.043M$, $[CuSCN] = 0.043M$, $[styrene]_0 = 5.37M$, $[HMTETA] = 0.05M$, $[PEBr] = 0.043M$, $[CuSCN] = 0.043M$).

through a sulfur atom or nitrogen atom to form thio-cyanate and isothiocyanate end groups, respectively. However, binding through nitrogen instead of sulfur may lead to inactive chain ends (when benzyl isothio-cyanate was used as the initiator and CuSCN was used as the catalyst in ATRP, there was no polymer-ization).[26] Because the bond strength of C—Br is weaker than that of C—SCN, the former system shows faster activation. Davis and coworkers[27,28] reported ATRP of styrene and methyl acrylate with benzyl thiocyanate (BzSCN) as an initiator and CuBr as the catalyst. They found slow initiation and very broad
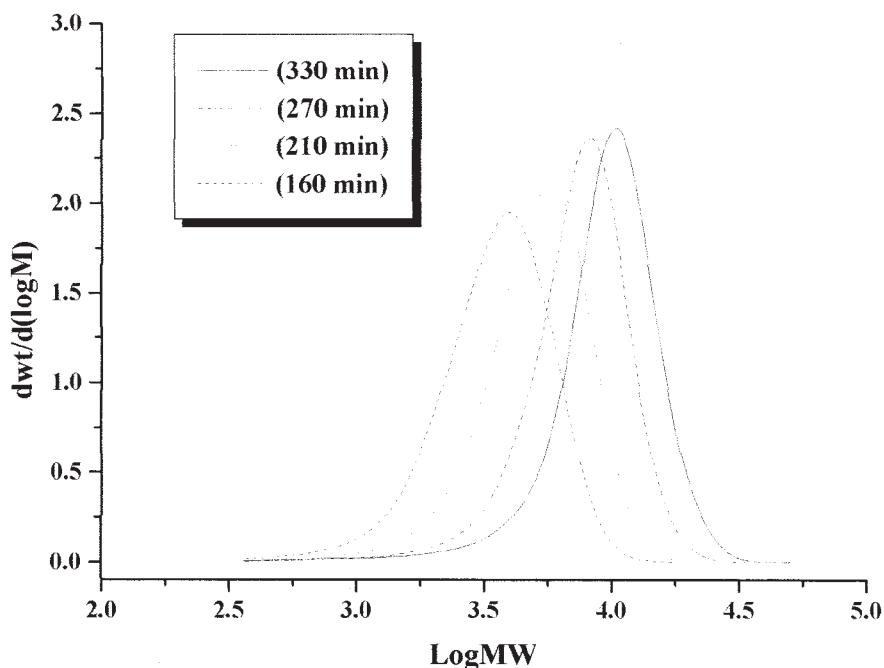

Figure 5 GPC traces of PS (CuSCN/HMTETA) obtained at different polymerization times (MW = molecular weight).

TABLE I
ATRP of Styrene with PEBr as the Initiator, CuSCN as the Catalyst, and Different Ligands

No.	Ligand	Time (min)	Conversion (%)	$M_{n,\text{SEC}}$	$M_{n,\text{th}}$	PDI
1	HMTETA	330	56	7800	7000	1.32
2	dNbpy	1230	40	3900	5000	1.39
3	NPPI	480	58	8800	7250	1.75

Solvent = *p*-xylene; $[\text{Styrene}]_0 = 5.37M$; $[\text{PEBr}] = 0.043M$; $[\text{CuSCN})] = 0.043M$; $[\text{HMTETA}] = 0.05M$; $[\text{dNbpy}] = 0.87M$; $[\text{NPPI}] = 0.107M$; temperature = 110°C.

polydispersity. When they used the CuSCN/BzSCN system, the polymerization of styrene was not controlled, and the polydispersity was very broad. When they used an unsymmetrical system (i.e., a conventional halide initiator and CuSCN as a catalyst), the polymerization was controlled and the polydispersity was lower. They also found that —SCN was not an effective mediator in ATRP of styrene and led to relatively broad polydispersity in comparison with a conventional halide system. In all cases, they used only dNbpy as the ligand. Interestingly, we found
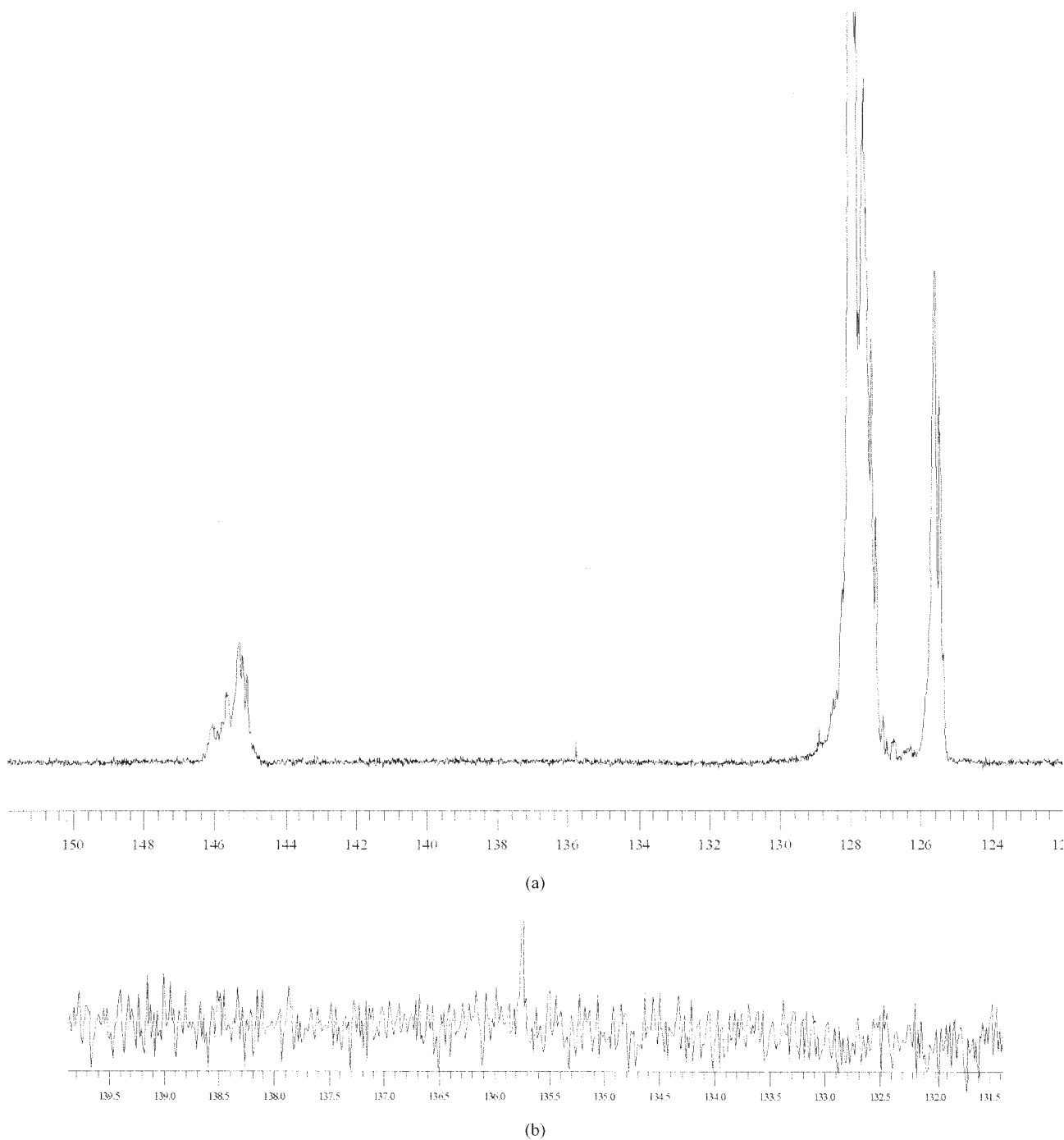

Figure 6 (a) ^{13}C-NMR spectrum of PS prepared with CuSCN/HMTETA and (b) an amplified region at $\delta = 135$ ppm.
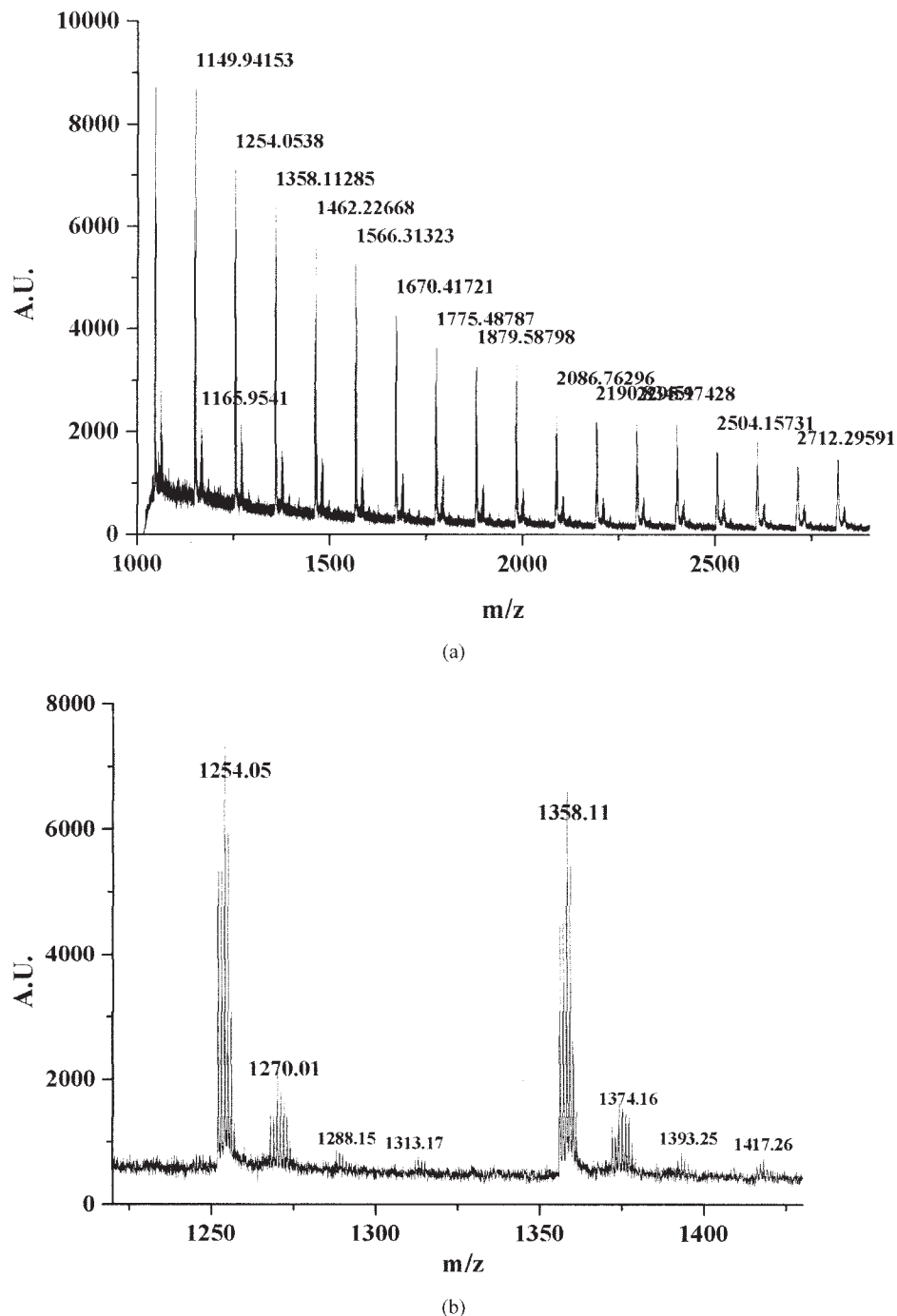
(a)

(b)

Figure 7   MALDI-TOF MS of PS prepared with the CuSCN/HMTETA system.

faster polymerization with HMTETA as the ligand. The broad PDI with the anion ligand, —SCN, can also be explained by the role of the copper catalyst. The copper catalyst with the —SCN ligand [e.g., Cu(Br)(SCN) in Scheme 2] is an inefficient deactivator in the reversible deactivation process in ATRP (Scheme 2). This is because of the greater ligand strength of —SCN in comparison with —Br, as explained earlier. Bromide (—Br) has been reported to have better deactivation efficiency in comparison with other ligands.[29]

PS obtained by CuSCN/HMTETA-mediated ATRP was characterized by ^{13}C-NMR and MALDI-TOF MS to find the nature of the end group. ^{13}C-NMR shows a peak at δ = 135.6 ppm that is characteristic of the carbon of the —SCN group[30] [Fig. 6(a,b)]. The peaks at δ values of 145, 128, and 125 ppm are due to the different aromatic carbons in the phenyl group.[30] The MALDI-TOF mass spectrum of PS with a silver salt for cationization is shown in Figure 7(a). The amplification of a part of Figure 7(a) ($m/z = 1220$–1430) is

shown in Figure 7(b). It shows an envelope of species each separated by 104, which is characteristic of PS. The high intensity peak at 1254 is due to H—[(CH$_2$—CH(Ph))]$_{11}$Ag$^+$. It is due to de-(pseudo)halogenation of the end group of PS, which is well known during MALDI-TOF MS of PS with a Ag salt. The peaks at 1270 and 1288 cannot be assigned to either the —Br or —SCN end group. They may be due to unwanted fragmentation of PS. Dourges et al.[31] also observed several fragmentations while carrying out the MALDI-TOF MS analysis of PS prepared by controlled radical polymerization with 2,2,6,6 tetramethyl 1-piperidinyloxy. The small peak at 1313 is due to PS having —SCN as the end group H—[(CH$_2$—CH(Ph))]$_{11}$—SCN Ag$^+$. The loss of thiocyanate may not be complete during MALDI-TOF MS, and this is in accordance with the bond strength argument (i.e., C—SCN > C—Br).[32]

Recently, we reported MALDI-TOF MS of poly(methyl methacrylate) samples prepared by ATRP with the CuSCN catalyst.[33] It showed the presence of the —SCN group as the end group, but it could not detect the —Br group.

CONCLUSIONS

The results reported here demonstrate the successful application of a copper catalyst having a pseudohalide anion (—SCN) as an ATRP catalyst for styrene. Imine, HMTETA, and substituted bipyridine can be used as ligands for CuSCN. HMTETA seems to be the most efficient of the three ligands used. ^{13}C-NMR and MALDI-TOF MS analysis show the presence of —SCN as the end group. Thiocyanate (—SCN) is a very versatile functional group that can undergo several chemical reactions[34] and thus can make PS end-capped with —SCN an interesting material for potential applications.

References

1. (a) Szwarc, M.; Levy, M.; Milkovich, R. J Am Chem Soc 1956, 78, 2657; (b) Szwarc, M. Nature 1956, 178, 1168.
2. (a) Webster, O. W. Science 1991, 251, 887; (b) Cationic Polymerizations: Mechanisms, Synthesis and Application; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996.
3. (a) Szwarc, M.; Van Beylen, M. Ionic Polymerization and Living Polymers; Chapman & Hall: London, 1993; (b) Hsieh, H. L.; Quirk, R. P. Anionic Polymerization: Principles and Practical Applications; Marcel Dekker: New York, 1996.
4. (a) Matyjaszewski, K. ACS Symp Ser 1997, 685, 2; (b) Matyjaszewski, K. ACS Symp Ser 2000, 768, 2; (c) Matyjaszewski, K.; Jia, J. Chem Rev 2001, 101, 2921; (d) Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689.
5. Moad, G.; Solomon, D. H. The Chemistry of Free Radical Polymerization; Pergamon: Oxford, 1995.
6. (a) Nair, C. P.; Clouet, G. J Macromol Sci Rev Macromol Chem Phys 1991, 31, 311; (b) Otsu, T.; Yoshick, M.; Tazaki, T. Macromol Rapid Commun 1992, 3, 127; (c) Otsu, T.; Yoshick, M.; Tazaki, T. Macromol Rapid Commun 1992, 3, 133; (d) Endo, K.; Murata, K.; Otsu, T. Macromolecules 1992, 25, 5554; (e) Turner, S. R.; Blevins, W. R. Macromolecules 1990, 23, 1856; (f) Kroeze, E.; Brinke, G.; Hadziioannou, G. Macromolecules 1995, 28, 6650.
7. Priddy, D. B. Adv Polym Sci 1994, 67, 111.
8. (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Pat. 4,581,429 (1985); (b) Rizzardo, E. Chem Aust 1987, 54, 32; (c) Moad, G.; Rizzardo, E.; Solomon, D. H. In Comprehensive Polymer Science; Eastmond, G. C.; Ledwith, A.; Russo, S.; Sigwalt, P., Eds.; Pergamon: Oxford, 1989; Chapter 3, p 141; (d) Moad, G.; Rizzardo, E. Macromolecules 1995, 28, 8722.
9. (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987; (b) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 5316; (c) Hawker, C. J. J Am Chem Soc 1994, 116, 11185; (d) Hawker, C. J.; Hedrick, J. L. Macromolecules 1995, 28, 2993; (e) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. J Am Chem Soc 1995, 117, 10763; (f) Bon, S.; Klumperman, B.; German, A. L. Macromolecules 1997, 30, 324.
10. (a) Colombani, D.; Steenbock, M.; Klapper, M.; Mullen, K. Macromol Rapid Commun 1997, 18, 243; (b) Grande, D.; Gnanou, Y.; Guerrero, R. Polym Prepr 1997, 38(1), 666.
11. (a) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. J Am Chem Soc 1994, 116, 7943; (b) Mardare, D.; Matayjaszewski, K. Macromolecules 1994, 27, 645; (c) Arvanitopoulos, L. D.; Greuel, M. P.; Harwood, H. J. Polym Prepr (Am Chem Soc Div Polym Chem) 1994, 35(2), 549.
12. Kato, M.; Kamigato, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721.
13. (a) Wang, J. S.; Matayjaszewski, K. J Am Chem Soc 1995, 117, 5614; (b) Wang, J. S.; Matayjaszewski, K. Macromolecules 1995, 28, 7901; (c) Matyjasewski, K.; Patten, T. E.; Xia, J. J Am Chem Soc 1997, 119, 674.
14. (a) Percec, V.; Borboiu, B. Macromolecules 1995, 28, 7970; (b) Percec, V.; Borboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. Macromolecules 1996, 29, 3665.
15. (a) Haddleton, D. M.; Jasieczeck, C. B.; Hannon, J. M.; Shooter, A. J. Macromolecules 1998, 30, 2016; (b) Haddleton, D. M.; Heming, A. M.; Kukulj, D.; Duncalf, D. J.; Shooter, A. J. Macromolecules 1998, 31, 2016; (c) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. Macromolecules 1999, 32, 2110; (d) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. Macromolecules 1997, 30, 2190; (e) Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Crossman, M. C.; Jackson, S. G.; Bon, S. A. F.; Clark, A. J.; Shooter, A. J. Eur J Inorg Chem 1998, 11, 1799.
16. (a) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. Macromolecules 1996, 29, 8573; (b) Moineu, G.; Minet, M.; Dubois, P.; Teyssie, P.; Senninger, T.; Jerome, R. Macromolecules 1999, 32, 27.
17. Le, T. P. T.; Moad, G.; Rizardo, E.; Thang, S. H. PCT Int. Pat. Appl. WO 9801478 A1 980115 (1998).
18. Chiefari, J.; Chong, Y. K.; Erede, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.
19. Wang, J.; Matyjaszewski, K. Macromolecules 1995, 28, 7572.
20. Krishnan, R.; Srinivasan, K. S. V. Macromolecules 2003, 36, 1643.
21. Jewrajk, S. K.; Mondal, B. M. Macromolecules 2003, 36, 311.
22. Xia, J.; Matyjaszewski, K. Macromolecules 1997, 30, 7697.

23. Singha, N. K.; Klumperman, B. Macromol Rapid Commun 2000, 21, 1116.

24. King, R. B. Encyclopedia of Inorganic Chemistry; Wiley: 1994; Vol. 6, p 3084.

25. Huheey, J. E. Inorganic Chemistry: Principles of Structure and Reactivity; Harper & Row: New York, 1972; p 307.

26. Jenkins, C. L.; Kochi, J. K. I. J Org Chem 1971, 36, 3095.

27. Davis, K.; O'Malley, J.; Paik, H. J.; Matyjasewski, K. Polym Prepr 1997, 38, 687.

28. Davis, K. A.; Matyjaszewski, K. J Macromol Sci Pure Appl Chem 2004, 41, 449.

29. Grimaud, T.; Matyjasewski, K. Macromolecules 1997, 30, 2216.

30. Spectroscopic Methods in Organic Chemistry; Hesse, M.; Meier, H., Eds.; Thieme: Stuttgart, 1997; p 158.

31. Dourges, M.; Charleux, B.; Vairon, J. P.; Blais, J. C.; Bolbach, G.; Tabet, J. C. Macromolecules 1999, 32, 2495.

32. (a) Kerr, J. A. Chem Rev 1966, 66, 465; (b) Lovering, E. G.; Laidler, K. J. Can J Chem 1968, 38, 2367.

33. Singha, N. K.; Rimmer, S.; Klumperman, B. Eur Polym J 2004, 40, 159.

34. (a) Guy, R. G. In The Chemistry of Cyanates and Their Thio Derivatives; Patai, S., Ed.; Wiley: New York, 1977; Part 2, Chapter 18, p 871; (b) Riemschneider, R. J Am Chem Soc 1956, 78, 844.