EPR Study of Atom Transfer Radical Polymerization (ATRP) of Styrene

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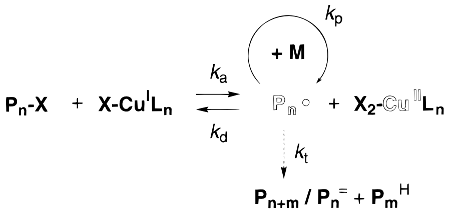
Controlled/“living” polymerization methods offer the best way to prepare well-defined (co)polymers (controlled molecular weight, polydispersities, terminal functionalities, chain architecture composition) in systems where the contribution of side reactions is small.[1−3]

Extension of atom transfer radical addition (ATRA)[4,5] to atom transfer radical polymerization (ATRP) provides a new and efficient way to conduct controlled/“living” radical polymerization.[6] With a variety of alkyl halides, R−X (X = Cl or Br), as the initiator and a transition metal species complexed by suitable ligand(s), CuX/2,2′-bipyridine, as the catalyst, ATRP of vinyl monomers such as styrene and (meth)acrylates proceeds in a controlled/“living” fashion.[7] The resulting polymers have degrees of polymerization predetermined by Δ[M]/[I]$_0$ up to $M_n \sim 10^5$ and low polydispersities, $1.05 < M_w/M_n < 1.5$. For example when 1-phenylethyl chloride[8a] or arenesulfonyl chloride[8b] is used as an initiator and CuCl/4,4′-diheptyl-2,2′-bipyridine or 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbipy) complex is used as the catalyst, styrene is polymerized by repetitive atom transfer radical additions to yield a well-defined polymer with a narrow molecular weight distribution ($M_w/M_n = 1.05$).

According to kinetic and mechanistic studies of styrene ATRP, it was proposed that the polymerization proceeds by monomer addition to free radicals which are reversibly generated by an atom transfer process from dormant polymer chains with halide end groups.[9] In these reactions, a small amount of Cu^{II} species serve as a deactivator which moderates rates and is responsible for maintaining low polydispersities. The Cu^{II} species can be separately added to the system or can be formed spontaneously as a result of the so-called persistent radical effect.[10] A rough estimate of the amount of formed CuBr$_2$/dNbipy species from kinetic studies was ~5%, based on the CuBr/dNbipy catalyst.[9]

Electron pramagnetic resonance (EPR) spectroscopy is a very useful tool to investigate paramagnetic species.[11] Structures, concentrations, and dynamics of paramagnetic compounds can be obtained from EPR measurements in the study of radical polymerizations.[12,13] EPR has been used to determine concentrations of free TEMPO in nitroxide-mediated polymerization of styrene.[14,15] Furthermore, EPR spectroscopy can be used to investigate the chemistry of paramagnetic metal complexes. EPR can potentially yield information on the local structure, coordination structure, symmetry, concentration, and aggregated structure of paramagnetic copper(II) species.[16] This communication reports the direct determination by EPR of copper(II) species in styrene ATRP.[17]

Scheme 1. Reaction Scheme of ATRP



X = halogen atom
M = styrene, MMA, acrylonitrile, and MA

A typical scheme for an ATRP system is shown in Scheme 1. A halogenated initiator reacts with a diamagnetic copper(I) complex with the rate constant of activation (k_a) to form an initiating radical and a paramagnetic copper(II) species. The organic radical then initiates a radical polymerization which is controlled by the reversible deactivation of the propagating radical with paramagnetic copper(II) species with the rate constant k_d. Polymeric radicals propagate with the rate constant k_p, and irreversibly terminate with the rate constant k_t via coupling (product P$_{n+m}$) and/or disproportionation (products $P^{=}{}_n$ and $P^{H}{}_m$). Every act of termination is accompanied by the irreversible formation of excess deactivator (copper(II)). In the investigation of this reaction by EPR spectroscopy, initiating and propagating radicals, as well as copper(II) species are paramagnetic and EPR active. In principle, all of these species could be observed by EPR spectroscopy; however, unfortunately (or fortunately) only the paramagnetic copper(II) species can be observed due to its high concentration relative to the organic radicals. Initiating radicals usually have short lifetimes; they are present in extremely low concentrations and react easily with monomer to form propagating radicals which are also present in low concentrations. The concentration of organic radicals in these systems is usually in the range of 10^{-8} to 10^{-7} mol/L.[12,13] The concentrations of copper(II) species in this system are above 10^{-3} mol/L (vide infra) which is 10^4 or 10^5 times higher than the initiating and propagating radicals according to persistent radical effect.[10] Thus, the copper(II) species is the predominant species observed by EPR in ATRP systems.

Time-dependent EPR signals of copper species in the ATRP of styrene are shown in Figure 1. The signal feature present after 20 min heating is considered to be a typical axial symmetric copper(II) signal.[16] The preliminary studies of the structure of copper(II) species in the presence of copper(I) indicate some interactions between them, possibly via halogen bridging. The concentration of copper(II) species was estimated by double integration of these signals. The time dependence of copper(II) concentrations in the ATRP of styrene, in toluene, initiated by 1-phenylethyl bromide and benzyl bromide is shown in Figure 2 along with the result of bulk polymerization of styrene initiated by 1-phenylethyl bromide.

In the case of the solution polymerization initiated by 1-phenylethyl bromide, the concentration of copper(II) initially increased very rapidly and nearly reached a steady-state concentration. This concentration may be regulated not only by the ATRP equilibria but additionally by slow generation of radicals resulting from the thermal self-initiating process. The “steady-state” concentration was about 2.5−2.8 mmol/L. In the case of the benzyl bromide initiated system, the con-

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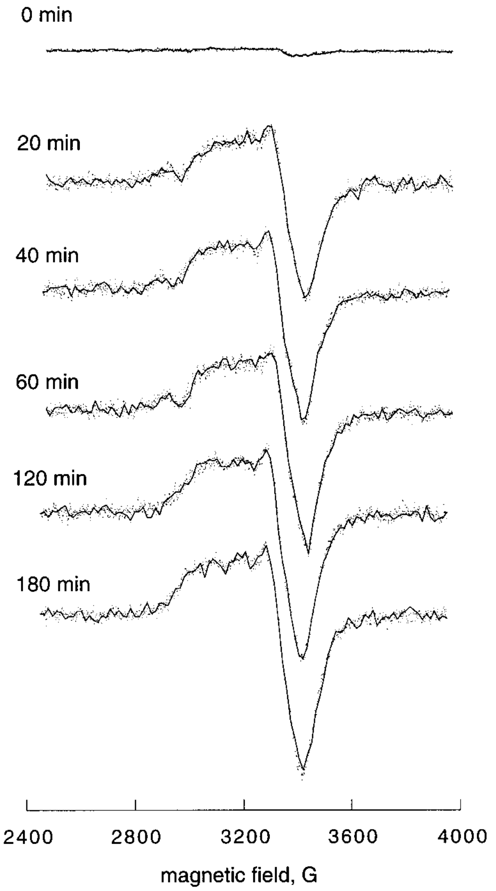

Figure 1. EPR spectra of the polymerization mixture measured at 25 °C after 0, 20, 40, 60, 120, and 180 min at 110 °C. Styrene/1-phenylethyl bromide/CuBr/dNbipy (=100/1/1/2) in toluene (50 vol %).

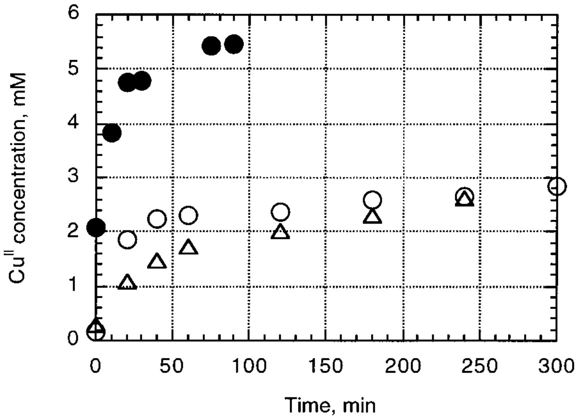

Figure 2. Time-dependent concentrations of copper(II) species for ATRP initiated by 1-phenylethyl bromide (○) and benzyl bromide (△) in toluene solution and bulk polymerization initiated by 1-phenylethyl bromide (●).

centration of copper(II) increased gradually reaching a "steady state" only after 4−5 h. The EPR results support the kinetic results of these polymerizations which showed that benzyl bromide is a slow initiator. The higher concentration of copper(II) species in bulk is due to higher initial concentrations of both initiator and copper(I), since in all experiments the same $[M]_0$:$[RX]_0$:$[Cu(I)]_0$ ratios were used.

The percentage of Cu^{II} formed from Cu^{I} was calculated, and the results are shown in Figure 3. In all of the cases of the ATRP of styrene, approximately 4−6% of the copper(I) formed copper(II) species in the polymerization system with 94−96% of copper(I) species still remaining in the monovalent state.

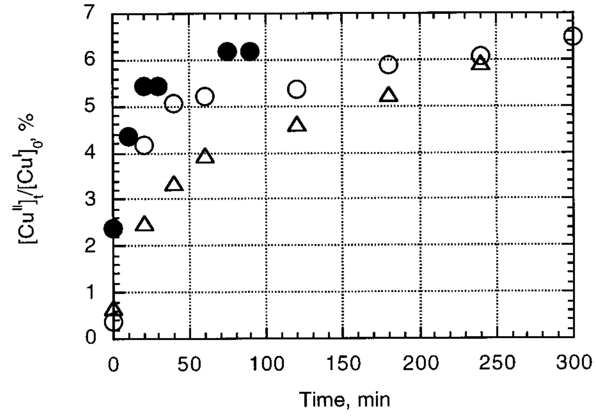

Figure 3. Time-dependent proportion of copper(II) species formed from copper(I) species by ATRP initiated by 1-phenylethyl bromide (○) and benzyl bromide (△) in toluene solution and bulk polymerization initiated by 1-phenylethyl bromide (●).

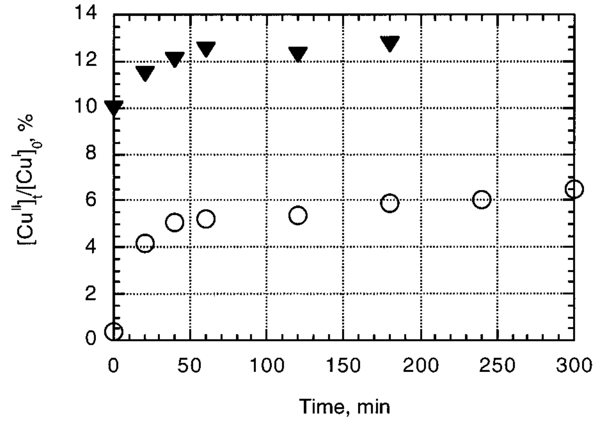

Figure 4. Time-dependent proportion of copper(II) species for ATRP initiated by 1-phenylethyl bromide (○) and the same system containing initially 0.01 M of $CuBr_2$/dNbipy (▼) in toluene solution.

A system with copper(II) added before polymerization (10 mol % $CuBr_2$ relative to CuBr) was examined. The time dependence of copper(II) concentrations, along with the results of the same system without copper(II) species at the beginning, are shown in Figure 4. When $CuBr_2$ was added independently, the copper(II) concentration stabilized at a steady-state concentration of 12.5%, which is consistent with the slower polymerization rate.[9] Apparently, some initial radical coupling could occurr despite excess copper(II) present.

In summary, we observed EPR signal of copper(II) species in the ATRP system. The steady state concentration of copper(II) species is approximately 4−6% of the original copper(I) species. These results are consistent with our previous kinetic data.[9]

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References and Notes

(1) Webster, O. W. *Science* **1991**, *251*, 887.

(2) Matyjaszewski, K. *J. Phys. Org. Chem.* **1995**, *8*, 197.

(3) Matyjaszewski, K. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 769.

(4) Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827.

(5) (a) Curran, D. P. *Synthesis* **1988**, 417. (b) Curran, D. P. *Synthesis* **1988**, 489.

(6) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(7) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.

(8) (a) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866. (b) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.

(9) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(10) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925.

(11) Bolton, J. A.; Wertz, J. R.; Weil, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; John Wiley & Sons: New York, 1994.

(12) Kamachi, M.; Kajiwara, A. *Macromolecules* **1996**, *29*, 2378.

(13) Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y. *Macromolecules* **1993**, *26*, 7369.

(14) (a) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346. (b) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 4161.

(15) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393.

(16) (a) Hathaway, B.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143. (b) Hathaway, B.; Duggan, M.; Murph, A.; Mullane, J.; Power, C.; Walsh, A.; Walsh, B. *Coord. Chem. Rev.* **1981**, *36*, 267.

(17) EPR spectra were recorded on a Bruker ESP-300 X-band EPR spectrometer. A 0.2 mL samples of the polymerization mixtures were taken from the polymerization systems and put into an EPR tube (o.d. 4 mm) under argon. The mixture was degassed three times by freeze−pump−thaw cycles and sealed under vacuum. Spectra were recorded at room temperature after polymerization at controlled temperature for a given time. It is recognized that concentration of growing radicals is much higher at polymerization temperature ($[P^\bullet] \sim 10^{-7}$ M at 110 °C) than at room temperature ($[P^\bullet] \ll 10^{-8}$ M). However, this does not effect concentration of Cu^{II} species which can change by less than 0.01%, since $[Cu^{II}] > 10^{-3}$ M. Concentrations of copper(II) species were estimated by double integration of spectra. Spectra of copper(II) trifluoroacetylacetonate in the same media at the same temperature were used as standards. Typical polymerization system is styrene/initiator/CuBr/dNbipy (=100/1/1/2) with 50% of toluene or bulk. Polymerization temperature was 110 °C for styrene.

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