

Simultaneous EPR and Kinetic Study of Styrene Atom Transfer Radical Polymerization (ATRP)

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ABSTRACT: To investigate the mechanism of the controlled/"living" radical polymerization system, electron paramagnetic resonance (EPR) spectroscopy was applied to the atom transfer radical polymerization (ATRP) of styrene. Although only copper(I) species was added to the system initially, EPR signals of a copper(II) species were clearly observed in the polymerization of styrene initiated by 1-phenylethyl bromide, 1-phenylethyl chloride, and benzyl bromide in toluene solution or in bulk. As the polymerization proceeded, the concentration of copper(II) increased gradually until a steady state was reached. Correlation between the time dependence of the concentration of copper(II) species and the kinetics of the polymerization is also discussed for various ATRP systems. Our results indicate that 4–6% of the initial copper(I) species is converted to copper(II) species in polymerization of styrene at 110 °C. Investigation of the ATRP systems which contain an excess amount of copper(0) powder with a given amount of copper(II) species was also performed by EPR spectroscopy. Concentration of copper(II) species was progressively reduced by a reaction with copper(0), but the reaction was slow enough not to interfere with the control of radical polymerization.

Introduction

Radical polymerization is the most utilized industrial method of polymer formation from vinyl monomers. Accordingly, radical polymerization has been extensively studied and reviewed.^{1,2} Various attempts to control radical polymerization have been earlier approached.^{3–5} However, these methods for controlling radical polymerizations are much more difficult than in ionic polymerization because of unavoidable bimolecular termination between growing chain ends in radical process. Controlled/"living" polymerization methods based on the exchange between dormant and active species offer a convenient way to prepare well-defined (co)polymers (controlled molecular weight, polydispersities, terminal functionalities, chain architecture, and composition) in ionic and also in radical systems in which the contribution of side reactions is relatively small.^{6–8}

Extension of atom transfer radical addition (ATRA)^{9,10} to atom transfer radical polymerization (ATRP) provides a new and efficient way to conduct controlled/"living" radical polymerization.¹¹ 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, the ATRP of vinyl monomers such as styrene and (meth)acrylates proceeds in a controlled/"living" fashion.¹² The resulting polymers have degrees of polymerization predetermined by $\Delta[M]/[I]_0$ up to $M_n \sim 10^5$ and low polydispersities, $1.05 < M_w/M_n < 1.5$. For example, when 1-phenylethyl chloride^{13a} or arenesulfonyl chloride^{13b} 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 ($M_w/M_n = 1.05$).

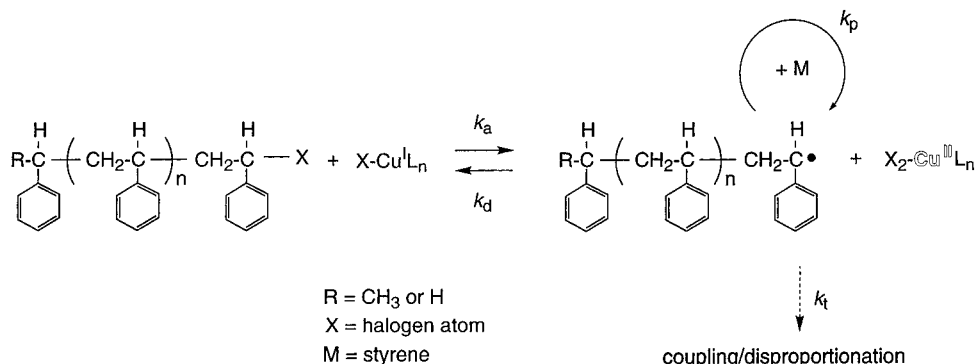
According to kinetic and mechanistic studies of styrene ATRP, it was proposed that the polymerization proceeds by monomer addition to free radicals which are reversibly generated by an atom transfer process from dormant polymer chains with halide end groups.¹⁴ In these reactions, a small amount of Cu^{II} species are considered to serve as a deactivator which moderates reaction rates and are responsible for maintaining low polydispersities. The Cu^{II} species can be separately added to the system or can be formed spontaneously by the so-called persistent radical effect.¹⁵ A rough estimate of the amount of CuBr₂/dNbipy species formed from kinetic studies was ~5%, based on the CuBr/dNbipy catalyst.¹⁴

Electron paramagnetic resonance (EPR) spectroscopy is a very useful tool for the investigation of paramagnetic species.¹⁶ Structures, concentrations, and dynamics of paramagnetic compounds may be obtained from EPR measurements in the study of radical polymerizations.^{17,18} EPR has been previously used to determine concentrations of free TEMPO in the nitroxide-mediated polymerization of styrene.^{19,20} Furthermore, EPR spectroscopy can be used to investigate the nature of paramagnetic metal complexes. EPR can potentially yield information on the local structure, coordination structure, aggregated structure, symmetry, and concentration of paramagnetic copper(II) species.²¹

Recently, we have reported preliminary results of direct measurements of copper(II) concentration in styrene ATRP systems initiated with 1-phenylethyl bromide and benzyl bromide.²² Estimated concentrations of copper(II) species in both cases were in the range of 4–6% relative to the initial amount of copper-

Table 1. Description of the Studied Styrene ATRP Systems at 110 °C

system no.	initiator	CuX	$[M]_0/[RX]_0/[CuX]_0/[dNbpy]_0/[CuX_2]_0$	solvent
system 1	1-phenylethyl bromide	CuBr	100/1/1/2	toluene (50%)
system 2	benzyl bromide	CuBr	100/1/1/2	toluene (50%)
system 3	1-phenylethyl chloride	CuCl	100/1/1/2	toluene (50%)
system 4	1-phenylethyl bromide	CuBr	100/1/1/2	bulk
system 5	1-phenylethyl bromide	CuBr/CuBr ₂	100/1/1/2/(0.2)	toluene (50%)

Scheme 1. Reaction Scheme of Styrene ATRP

(I) complex. Because copper(II) species play an important role in the process of activation/deactivation for control of propagation, it is interesting to correlate the time dependency of concentrations of copper(II) species with kinetic results of actual ATRP systems.

This article reports the direct determination, by EPR, of the time dependence of concentrations of copper(II) species in styrene ATRP under various conditions and correlation of the copper(II) concentration with kinetics of several ATRP systems. In addition, an EPR study of the catalytic system containing copper(0) species is presented.

Experimental Section

EPR Measurements. EPR spectra were recorded on a Bruker ESP-300 X-band EPR spectrometer. A 0.2 mL sample of the polymerization mixtures was taken from the polymerization systems and put into an EPR tube (o.d. 4 mm) under argon.²³ The mixture was degassed three times by freeze-pump-thaw cycles and sealed under vacuum. Spectra were recorded at room temperature after polymerization at a controlled temperature for a given time. It is recognized that the concentration of growing radicals is much higher at the polymerization temperature ($[P^*] \sim 10^{-7}$ M at 110 °C) than at room temperature ($[P^*] \ll 10^{-8}$ 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.

EPR spectra at 110 °C were recorded on a JEOL JES RE-2X spectrometer operating in the X-band, utilizing a 100 kHz field modulation, and a microwave power of 0.2 mW. A TE₀₁₁ mode cavity was used. Temperature was controlled by JEOL DVT2 variable-temperature accessory.

Concentrations of copper(II) species were estimated by the double integration of spectra with the relative error $\pm 10\%$. Spectra of Cu^{II}(trifluoroacetylacetonate) in the same media under the same condition were employed as standards.

Materials. Styrene from Aldrich was distilled over CaH₂ under reduced pressure just before use. The ligand, 4,4'-di(5-nonyl)-2,2'-dipyridyl (dNbpy) was prepared according to the reported procedure.¹⁴ CuBr was washed with glacial acetic acid to remove residual CuBr₂.²⁴ CuBr₂ was purified by recrystallization from water. Initiators, (1-bromoethyl)benzene (1-phenylethyl bromide), 1-phenylethyl chloride, and benzyl bromide, were obtained from Aldrich and used without any further purification. Toluene was purified by distillation over CaH₂.

Polymerization. A dry round-bottomed flask was charged with CuBr and dNbpy. The flask was sealed with a rubber

septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed monomer was added using a degassed syringe. After the CuBr and dNbpy were dissolved completely, a mixture of initiator and toluene was added via a degassed syringe.²³ After a part of the solution was removed for EPR measurements, the flask was immersed in an oil bath held by a thermostat at 110 °C. At timed intervals, samples were withdrawn from the flask using a degassed syringe and added to THF. A typical polymerization system is styrene/initiator/CuX (X = Cl or Br)/dNbpy (=100/1/1/2) with 50% of toluene or in bulk. Polymerization systems used in this study are shown in Table 1.

Model Reaction of Cu(0) with Cu^{II}. A given amount (5 mM) of Cu^{II}Br₂ or Cu^{II}(OTf)₂, 2 equiv of dNbpy, and toluene (50%) were put into an EPR tube with a five times excess amount of Cu(0) powder (Aldrich, copper for organic synthesis). The sample solution was degassed in the same manner as described above. The sample was then heated to 110 °C and the EPR spectrum was recorded at various times at 25 °C to observe the time dependence of the concentration of copper(II) species in the mixture.

Characterization. Monomer conversion was determined from the concentration of residual monomer, with THF as an internal standard, using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatopac. Polymer molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard; linear; 1000 and 100 Å. Polystyrene standards were used to calibrate the columns.

Results and Discussion

Concentrations and Structures of Copper(II) Species. A typical scheme of the styrene ATRP system is shown in Scheme 1. A halogenated initiator reacts with a diamagnetic copper(I) complex 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. In the investigation of this reaction by EPR spectroscopy, initiating radical, propagating radical, and 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

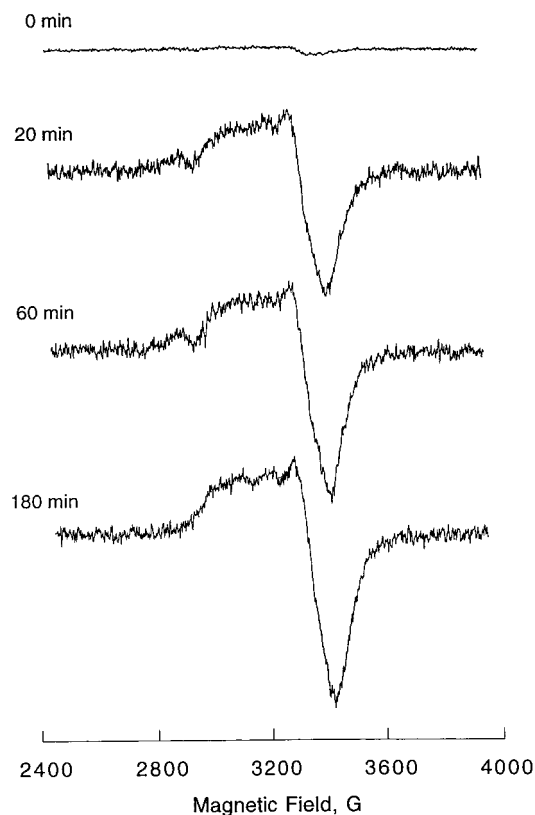


Figure 1. EPR spectra of the polymerization mixture measured at 25 °C after 0, 20, 40, 60, 120, and 180 min at 110 °C, for styrene/1-phenylethyl bromide/CuBr/dNbipy (molar ratios =100/1/1/2) in toluene (50 vol %).

organic radicals. Initiating radicals usually have short lifetimes; they are present in extremely low concentrations and react readily 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} – 10^{-7} mol/L. The concentrations of copper(II) species in this system are above 10^{-3} mol/L²¹ which is 10^4 – 10^5 times higher than the initiating and propagating radicals according to persistent radical effect.¹⁵ Thus, the copper(II) species is the predominant species observed by EPR in the styrene ATRP system.

The results of the time dependence of EPR signals of copper species in the ATRP of styrene is shown in Figure 1. The signal feature which was observed after 20 min of heating is considered to be a typical axial symmetric copper(II) signal and can correspond to either trigonal bipyramidal or square pyramidal structures.²⁵

EPR signals of the polymerization systems 1, 2, 3, and 4 after heating for 2 h are shown in Figure 2. The anisotropic pattern in systems 1, 2, and 4 are very similar. The different signal feature in system 3 is considered to be a result of a different structure of the copper(II) with bound Cl atom.

The concentration of copper(II) species was estimated by the double integration of the spectra. The time dependence of copper(II) concentrations in the ATRP systems 1–5 are shown in Figure 3a. In system 1, the concentration of copper(II) increased very rapidly until a steady state was reached. The steady-state concentration was about 2.5–2.8 mmol/L. The percentage of Cu(II) formed from Cu(I) was calculated and the results are given in Figure 3b. In the case of system 1, approximately 5–6% of the copper(I) was converted to copper(II) species during the polymerization, leaving 94–95% of the initial amount of copper(I) species still in the monovalent state. This also means that only 5% of the chains terminated and 95% of the chains are in the dormant state capable of further growth. The termination usually happens at the early stages of polymerization when mobility of radicals is higher and termination rate coefficients, which are chain length dependent, are also higher. However, in the case of the

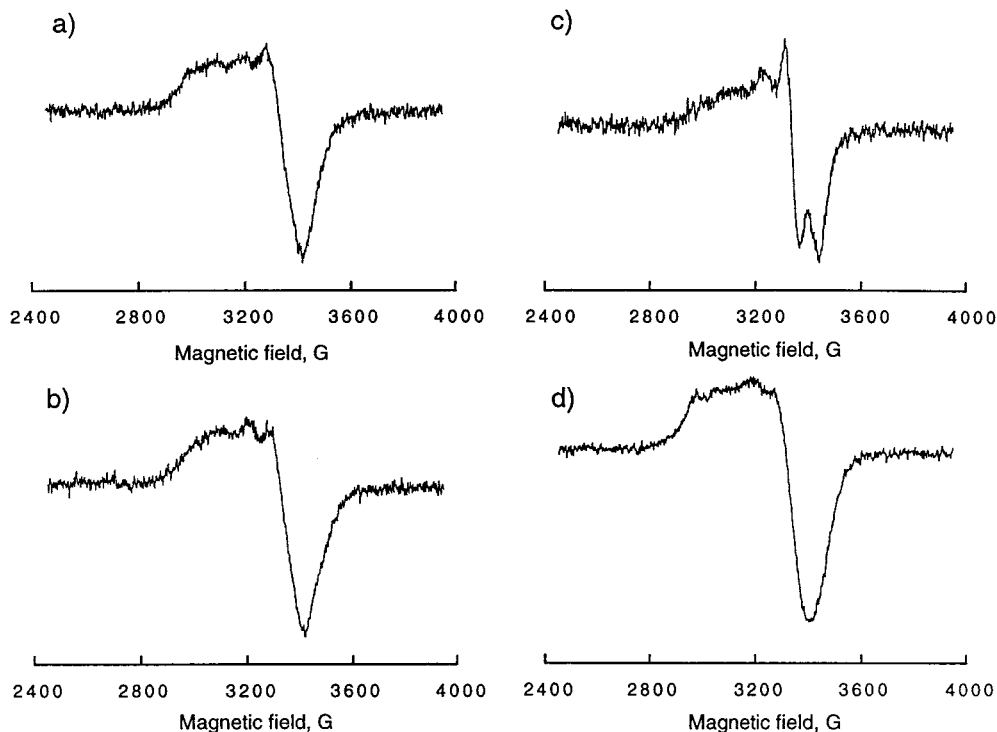


Figure 2. EPR spectra recorded for various systems after 120 min heating at 110 °C: (a) 1 (1PEBr/CuBr); (b) system 2 (BzBr/CuBr); (c) system 3 (1PECl/CuCl); (d) system 4 (1PEBr/CuBr/bulk).

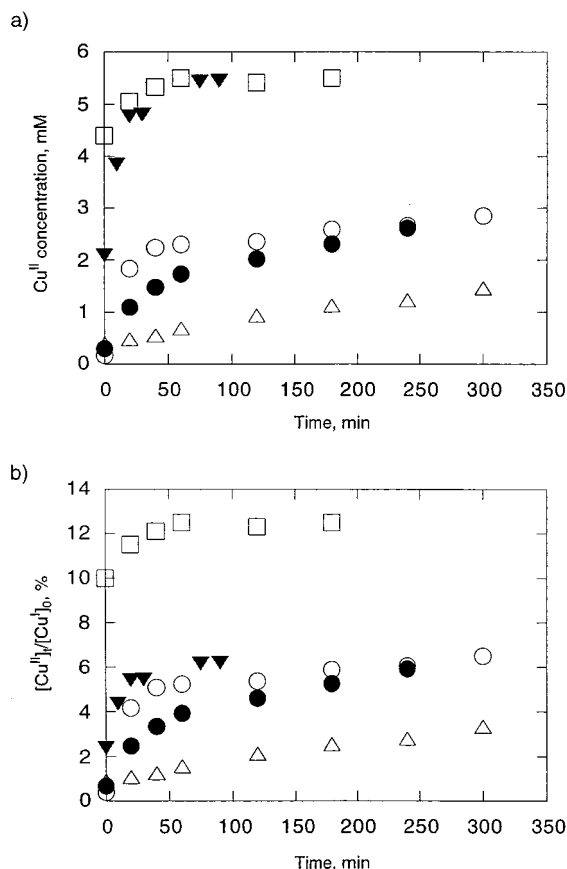


Figure 3. (a) Plots of time dependence of concentration of copper(II) species for ATRP initiated by 1-phenylethyl bromide (system 1, ○), benzyl bromide (system 2, ●), and 1-phenylethyl chloride (system 3, △) in toluene solution and bulk polymerization initiated by 1-phenylethyl bromide (system 4, ▼) as well as in the presence of externally added $CuBr_2$ (system 5, □). (b) Plots of time dependence of proportion of copper(II) species formed from copper(I) species by ATRP initiated by 1-phenylethyl bromide (○), benzyl bromide (●), and 1-phenylethyl chloride (△) in toluene solution and bulk polymerization initiated by 1-phenylethyl bromide (▼) as well as in the presence of externally added $CuBr_2$ (□).

benzyl bromide initiated system (system 2), the concentration 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 indicate that benzyl bromide is a slow initiator. In the case of system 3, the concentration of copper(II) species increased continuously to the range of 1–1.5 mM. The copper(II) concentration was low relative to that of $CuBr$ -catalyzed systems in agreement with lower rates and lower equilibrium constants for the $RCI/CuCl$ system.¹⁴ The correlation between this concentration and the kinetics of polymerization will be discussed in the latter part of this article. In the bulk polymerization of styrene (system 4), the apparent copper(II) concentration was higher than those systems utilizing a solvent due to a twice larger initial concentration of $CuBr$ and $R-X$. As shown in Figure 3b, the proportion of conversion of copper(I) to copper(II) in system 4 is similar to those of systems 1 and 2. The time dependence of concentration of Cu^{II} species in a polymerization system with $CuBr$ and 10% $CuBr_2$ (relative to $CuBr$) initially added (system 5) is also shown in Figure 3a and 3b. The Cu^{II} concentration stabilized after 60 min resulting in a steady-state concentration of 12.5%; consistent with the observed slower polymerization rate.¹⁴ Thus, de-

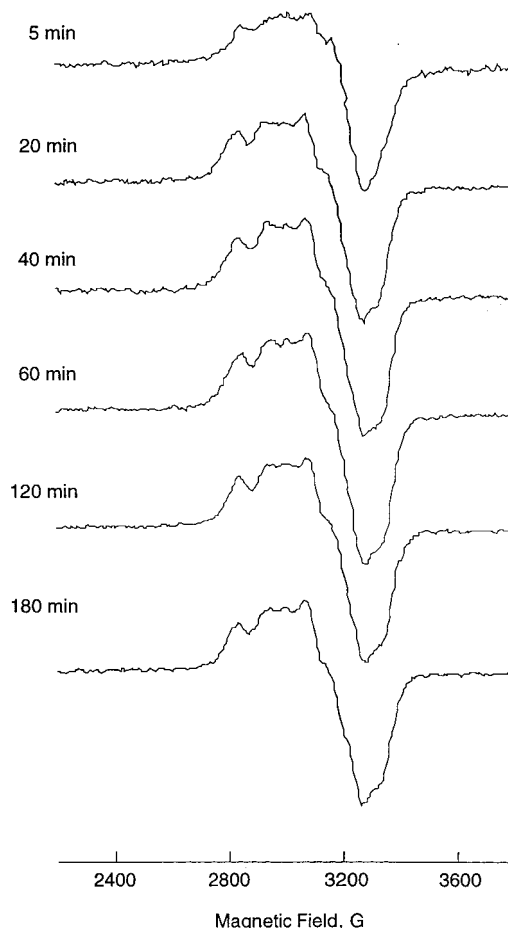


Figure 4. EPR spectra of styrene ATRP recorded at 110 °C under otherwise the same conditions as in Figure 1.

spite excess copper(II) species, some termination occurred at early stages of polymerization resulting in the increase of Cu^{II} concentration.

EPR Signals of the Cu^{II} Species and Its Concentration at 110 °C. EPR signals at the styrene polymerization temperature (110 °C) have been measured and investigated (Figure 4). The features of the signals were very similar to those measured at room temperature (25 °C). Estimated concentrations of copper(II) species were comparable to those observed at room temperature. These results indicate that the EPR data recorded at room temperature can be useful for discussions of ATRP systems.

Correlation of the Concentration of $Cu(II)$ Species with the Kinetics of Polymerizations in ATRP Systems. First-order kinetic plots of the rate of polymerization for systems 1–5 are shown in Figure 5. Within 120 min, the semilogarithmic plots were nearly linear. Discussions about the kinetics of the polymerization system are limited to this range.

A correlation of the copper(II) concentration and kinetics of the same polymerization system was examined. This correlation should be considered to be important for discussions of the mechanism of the ATRP of styrene.

For system 1 (styrene/1-phenylethyl bromide/ $CuBr$ /dNbipy = 100/1/1/2 in toluene (50%)), plots of copper(II) concentration, M_n , and M_w/M_n as the dependence of monomer conversion are shown in Figure 6. Copper(II) concentration reached a steady state within 30 min. M_n increased linearly with conversion and showed a

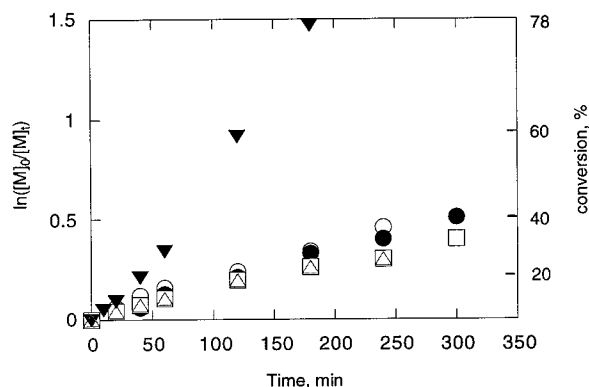


Figure 5. First-order kinetic plots for polymerization in systems 1–5 (same legend as in Figure 3).

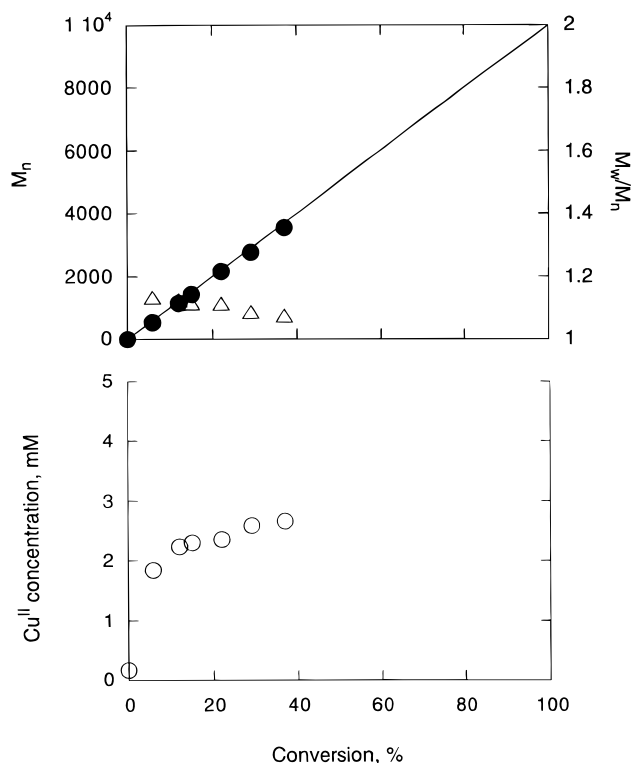


Figure 6. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for polymerization system 1 as well as copper(II) concentration dependence on the conversion.

good agreement with the theoretical prediction (solid line). Polydispersities decreased with conversion and remained low, $M_w/M_n < 1.15$, during the polymerization.

In system 2 (styrene/benzyl bromide/CuBr/dNbipy = 100/1/1/2 in toluene (50%)), the copper(II) concentration increased gradually until ca. 40% conversion (Figure 7). The copper(II) concentration reached a steady state only after 4–5 h. Molecular weights of polymers initiated with benzyl bromide showed a slightly higher M_n values relative to the theoretically predicted values in the initial stages (range of 0–30% conversion), and the M_n obeyed theoretical prediction after 40% conversion. The continuous increase of copper(II) concentration and the deviation in the lower conversion can be ascribed to slower initiation with benzyl bromide. However, the polydispersities were relatively low in this system.

In system 3 (styrene/1-phenylethyl chloride/CuCl/dNbipy = 100/1/1/2 in toluene (50%)), the copper(II) concentration increased slowly and did not reach a

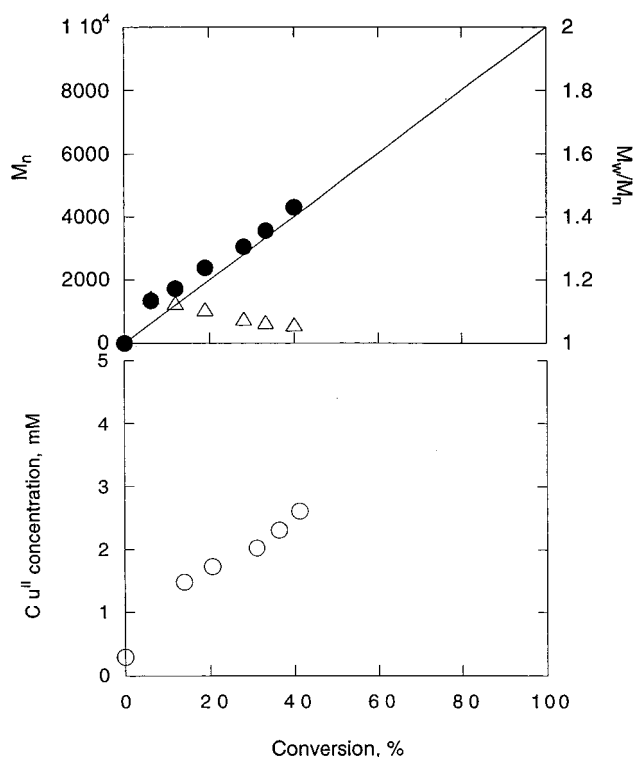


Figure 7. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for polymerization system 2 as well as copper(II) concentration dependence on the conversion.

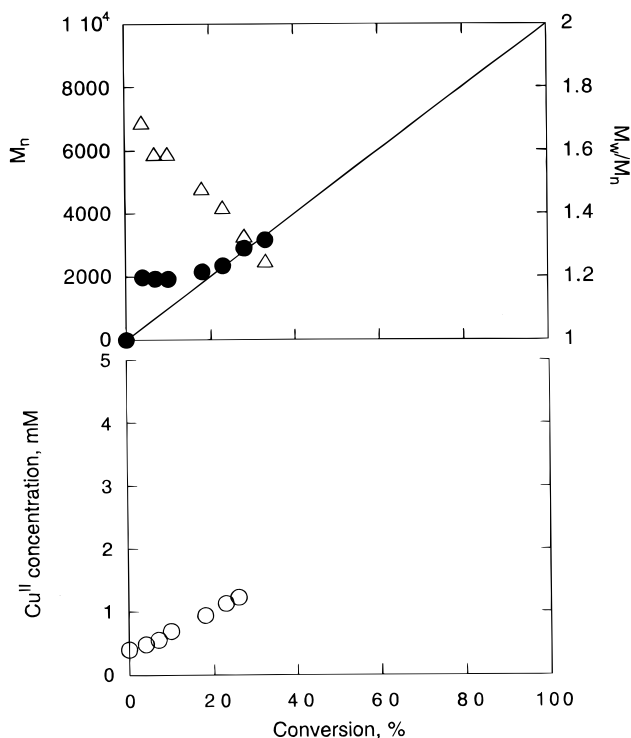


Figure 8. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for polymerization system 3 as well as copper(II) concentration dependence on the conversion.

steady state (Figure 8). Cu^{II} concentration was more than 1 mM above 20% conversion. At less than 10% conversion, M_n remained almost constant at 2000, which is significantly larger than the theoretical prediction. Above 20% conversion, M_n showed a linear relationship

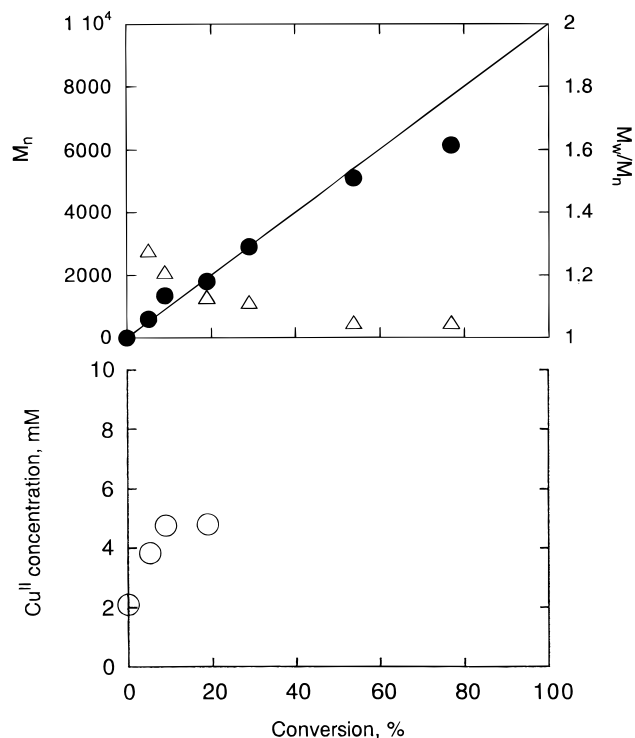


Figure 9. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for polymerization system 4 as well as copper(II) concentration dependence on the conversion.

to conversion and agreed with the theoretical prediction. The higher than predicted M_n in the initial stage of polymerization indicates incomplete initiation and slow deactivation. The Cu^{II} concentrations in the polymerization process which showed a steady M_n are relatively low in this polymerization system. This may mean that the concentration of Cu^{II} species is too low to control the radical polymerization. After a considerable amount of Cu^{II} species is formed, the system starts to become self-controlled. This is indicated by the observation that with the continuous increase of the copper(II) concentration, polydispersities decreased dramatically (relative to other cases) from $M_w/M_n = 1.7$ –1.2.

In system 4 (styrene/1-phenylethyl bromide/ $\text{CuBr}/\text{dNbipy} = 100/1/1/2$ in bulk), the copper(II) concentration increased rapidly and reached a steady state within 20 min (Figure 9). M_n increased linearly with conversion and obeyed the theoretical prediction under 60% conversion. The polydispersities decreased to $M_w/M_n = 1.05$.

In system 5 (styrene/1-phenylethyl bromide/ $\text{CuBr}/\text{CuBr}_2/\text{dNbipy} = 100/1/1/0.2/2$ in toluene (50%)), the copper(II) concentration was initially about 4.4 mM (10% of the initial copper(I) concentration) and increased slowly, reaching a steady state (Figure 10). The polymerization proceeded at a slower rate than in the system without the initial addition of CuBr_2 . However, the concentration of copper(II) species still increased slightly with conversion, indicating some termination of low molar mass growing radicals which have not been trapped efficiently by copper(II).

In most of these examples, M_n increased linearly with conversion, independent of the change of concentration of copper(II) species. However, there is some correlation between M_w/M_n and the concentration of copper(II) species. When the steady-state concentration was observed above some value (2–4 mM), the M_w/M_n was

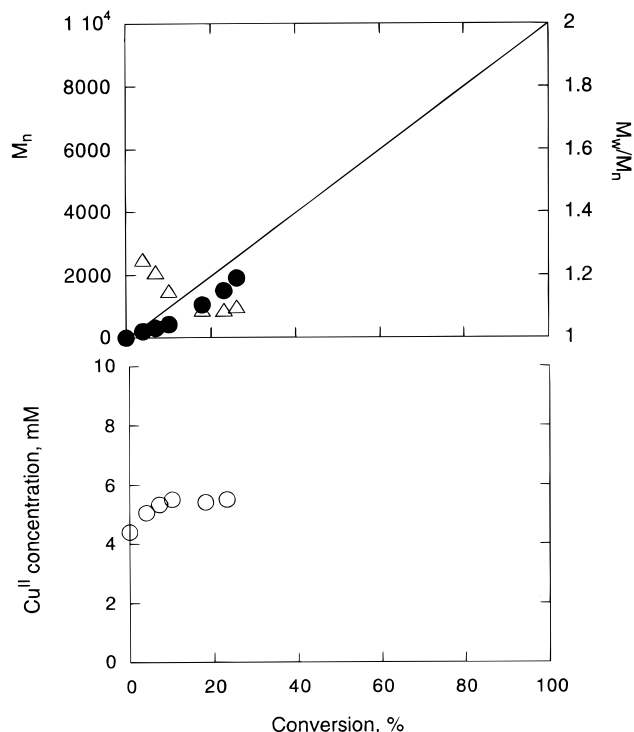


Figure 10. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for polymerization system 5 as well as copper(II) concentration dependence on the conversion.

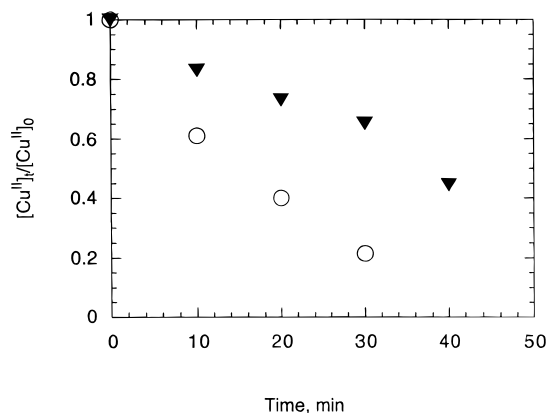


Figure 11. Time dependence of copper(II) concentration in the systems of Cu(0)/CuBr_2 (▼) and Cu(0)/Cu(OTf)_2 (○) with 2 equiv of dNbipy in toluene solution (5 mM).

relatively low. And when the copper(II) concentration was smaller (< 1 mM), M_w/M_n was relatively larger. This correlation may be explained by the mechanism of the activation–deactivation process of polymerization.¹⁴

Cu(0)-Containing Systems. Recently, an effective ATRP system utilizing Cu(0) powder was reported.²⁶ The system is composed of Cu(0)/CuBr (or Cu(OTf)_2)/ dNbipy /styrene = 3/1/2/100. In this system, successively formed Cu^{II} species are considered to be able to react with Cu(0) and form 2 equiv of Cu^{I} species. The reaction of CuBr_2 and Cu(OTf)_2 with Cu(0) was examined by EPR. The time dependence of the concentration of Cu^{II} species for the cases of CuBr_2 and Cu(OTf)_2 in the presence of an excess amount of Cu(0) powder were recorded by EPR spectroscopy, and the results are shown in Figure 11. The Cu^{II} concentration decreased monotonously. This means that the $\text{Cu(0)/Cu}^{\text{II}}$ mixture can be used as an effective system for the in situ

formation of Cu^{I} species. The ATRP system with Cu^{I} (0) still enables good control and faster polymerization, provided that the system can adjust the concentration of Cu^{II} species to an appropriate amount. This amount depends strongly on stirring, temperature and size of copper zero. For example, with very small copper particles ($1\ \mu\text{m}$), uncontrolled rapid polymerization is observed. Better results are obtained with larger copper particles (-100 or -300 mesh) and even with copper turnings.

In summary, we observed EPR signal of copper(II) species in ATRP system. The steady concentration of copper(II) species was noticed for well-controlled systems. Correlation between kinetic results (molecular weight and molecular weight distribution dependence on monomer conversion) and copper(II) concentration indicates that some critical amount of copper(II) species is necessary to control ATRP systems.

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