EPR and Kinetic Studies of Atom Transfer Radical Polymerization of (Meth)acrylates

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ABSTRACT: Electron paramagnetic resonance (EPR) spectroscopy and kinetic analysis were applied to atom transfer radical polymerization (ATRP) of (meth)acrylates. Although only copper(I) species was added to the system initially, EPR signals of copper(II) species were clearly observed in the polymerization mixture of methyl methacrylate (MMA) initiated by either ethyl 2-bromoisobutyrate (EBB) or p-toluenesulfonyl chloride (TsCl) in diphenyl ether. ATRP of methyl acrylate (MA) initiated by methyl 2-bromopropionate (MBP) in diphenyl ether also showed clear EPR signal of copper(II) species. As the polymerization proceeded, the concentration of copper(II) increased gradually until a nearly steady state was reached. The correlation between time dependence of concentration of copper(II) species and kinetics of polymerization is discussed for various ATRP systems. Our results indicate that conversion of 5—6% of initial copper(I) species to copper(II) species is observed for polymerization of MMA at 90°C and ca. 3% conversion was found for MA.
      KEY WORDS   Atom Transfer Radical Polymerization / Electron Paramagnetic Resonance / Kinetics / Controlled Polymerization / Methacrylate / Acrylate /

Radical polymerization is the most utilized method in polymer formation from vinyl and diene compounds.[1−3] Various kinds of general-purpose resins have been produced by radical polymerization processes. Among them, acrylic resins (methacrylate and acrylate polymers) are one of the most essential materials in modern life for their outstanding properties, e.g., clearness, toughness, chemicals-resistant property, etc. If polymerization processes involved during the synthesis of these products can be controlled, the quality of the materials is expected to be improved and the amount of waste from these processes is expected to be decreased. Various kinds of control for precision polymerization have been one of the most interesting fields in radical polymerization.[4−6] However, the control of reactivity of the propagating polymer chain is much more difficult in radical polymerization than in ionic polymerization because bimolecular termination takes place in competition with the propagation of growing ends in radical polymerization. Iniferter methods have been applied for polymerization of methyl methacrylate (MMA) and gave some controlled character, e.g., increase of molecular weight with conversion, formation of block copolymer, etc. On the other hand, control of molecular weight and molecular weight distribution was very difficult.[7−9]

The extension of atom transfer radical addition (ATRA)[10,11] to atom transfer radical polymerization (ATRP) has provided a new and efficient way to conduct controlled/"living" radical polymerization.[12,13] 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 (meth)acrylates proceeds in a controlled "living" fashion.[13−15] The resulting polymers have degrees of polymerization predetermined by $D[M]/[I]_0$, M_n up to 10^5 and low polydispersities, $1.05 < M_w/M_n < 1.5$. Such results appear to satisfy the pheno-

mena of controlled polymerization. However, the mechanism of ATRP is not yet fully understood. A detailed understanding of the mechanism is expected to lead to more effective control for various monomers.

Electron paramagnetic resonance (EPR) spectroscopy is a very useful tool to investigate paramagnetic species.[16] Structures, concentrations, and dynamics of paramagnetic compounds can be obtained from EPR measurements in the study of radical polymerizations.[17,18] EPR has been previously used to determine concentrations of paramagnetic copper(II) species in styrene–ATRP systems.[19,20] Concentrations of free nitroxyl radicals in nitroxide-mediated polymerization of styrene have also been evaluated by EPR.[21,22] Furthermore, EPR spectroscopy can be used to investigate the chemistry of paramagnetic metal complexes. Potentially, EPR can yield information on the local structure, coordination structure, aggregated structure, symmetry, and concentration of paramagnetic copper(II) species.[23]

Recently, we have reported preliminary results of direct measurements of copper(II) concentration in (meth)acrylate ATRP systems.[24] Estimated concentrations of copper(II) species in both cases were in the range of 3—6% relative to the initial amount of copper(I) complex. Of further interest is the correlation of copper(II) species concentrations with the kinetic results of actual ATRP systems, because copper(II) species play an important role in the activation/deactivation processes. Accordingly, the correlation between kinetic ATRP data and copper(II) concentrations was investigated in this research.

EXPERIMENTAL

EPR Measurements

EPR spectra were recorded on a Bruker ESP-300 X-band EPR spectrometer. A 0.2 ml sample of the polymerization mixtures were taken from the polymerization systems and put into an EPR tube (o.d. 4 mm)

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R = CH$_3$ or H
X = halogen atom
M = MMA or MA

coupling/disproportionation
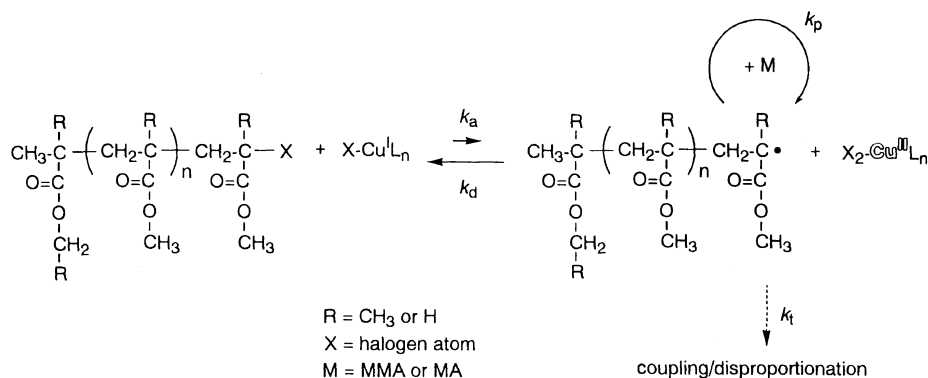
Scheme 1. Reaction scheme of ATRP.

under argon.[25] The mixture was degassed 3 times by freeze–pump–thaw cycles and sealed under vacuum. Spectra were recorded at either room temperature or in the frozen state at low temperature after polymerization at a controlled temperature for a given time. It is evidenced from kinetics that concentration of growing radicals is much higher at polymerization temperature ($[P^{\cdot}] \sim 10^{-7}$ M at 90°C) than at room temperature ($[P^{\cdot}] \ll 10^{-8}$ 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 the spectra. Spectra of Cu^{II}(trifluoroacetylacetonate) in the same media under the same condition were used as standards.

Materials

MMA and methyl acrylate (MA) from Aldrich were distilled over CaH$_2$ under reduced pressure just before use. The ligand, 4,4-di(5-nonyl)-2,2'-dipyridyl (dNbipy) was prepared according to the procedure reported previously.[26] CuBr was washed with glacial acetic acid to remove residual CuBr$_2$. Initiators, ethyl 2-bromoisobutyrate (EBB), *p*-toluenesulfonyl chloride (TsCl), and methyl 2-bromopropionate (MBP) were obtained from Aldrich and used without any further purification. Ph$_2$O was purified by distillation over CaH$_2$.

Polymerization

An argon-filled dry round-bottomed flask was charged with CuBr and dNbipy. 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 dNbipy were completely dissolved, mixture of initiator and diphenyl ether was added by a degassed syringe.[25] After taking out a part of the solution for EPR measurements, the flask was immersed in an oil bath held by a thermostat at the desired temperature. At timed intervals, samples were withdrawn from the flask using a degassed syringe and added to tetrahydrofuran (THF). A typical polymerization system is monomer/initiator/CuX (X = Cl or Br)/dNbipy (= 200/1/1/2) with 50% of diphenyl ether. The polymerization temperature was 90°C. The polymerization systems used in this research are followings[24]:

System 1 MMA/ethyl 2-bromoisobutyrate/CuBr/ dNbipy = 200/1/0.5/1 in diphenyl ether (50%).

System 2 MMA/*p*-toluenesulfonyl chloride/CuBr/ dNbipy = 200/1/0.5/1 in diphenyl ether (50%).

System 3 MA/methyl 2-bromopropionate/CuBr/ dNbipy = 200/2/1/2 in diphenyl ether (50%).

Characterization

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

RESULTS AND DISCUSSION

Concentrations and Structures of Copper(II) Species

A typical scheme of (meth)acrylate 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 through a halogen atom transfer reaction. The organic radical then initiates radical polymerization, which is controlled by the reversible deactivation of the propagating radical by the paramagnetic copper(II) species. During the activated state, the propagation process is considered to occur for several monomer units, depending on the rate of propagation and the rate of deactivation. In the investigation of this reaction by EPR spectroscopy, the 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 organic radicals. Initiating radicals, whose lifetimes are usually very short, 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^{-1}.[17,18] The concentrations of copper(II) species in these system are
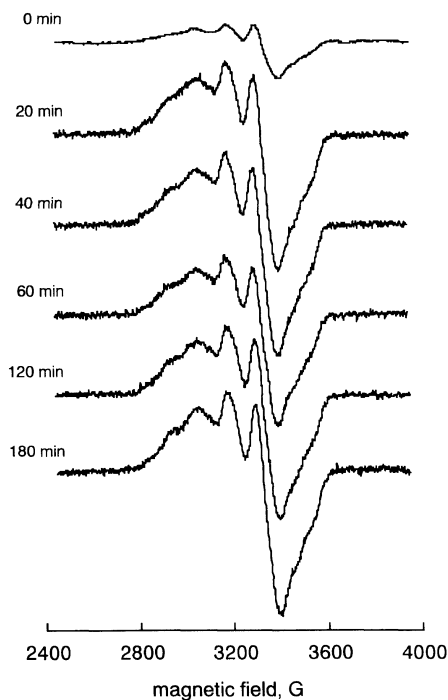
Figure 1. EPR spectra of the polymerization mixture of MMA ATRP measured at 20 K after 0, 20, 40, 60, 120, and 180 min at 90°C. MMA/p-toluenesulfonyl chloride/CuBr/dNbipy ($=200/1/0.5/1$) in diphenyl ether (50 vol%).
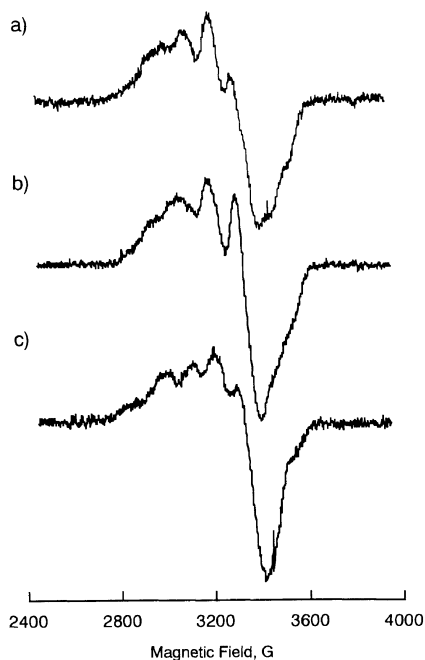

Figure 2. EPR spectra in various systems at 20 K after 120 min heating. Systems 1, 2, and 3 correspond to a, b, and c, respectively.

Figure 3. a) Plots of time dependence of concentration of copper(II) species for MMA ATRP initiated by ethyl 2-bromoisobutyrate (open circles) and p-toluenesulfonyl chloride (open triangles) in diphenyl ether solution and MA ATRP initiated by methyl 2-bromopropionate (filled circles). b) Plots of time dependence of proportion of copper(II) species formed from copper(I) species by ATRP initiated by ethyl 2-bromoisobutyrate (open circles) and p-toluenesulfonyl chloride (open triangles) in diphenyl ether solution and MA ATRP initiated by methyl 2-bromopropionate (filled circles).

EPR signals of polymerization systems 1, 2, and 3 after 2 h heating are shown in a, b, and c in Figure 2, respectively. Basically, the signal features are considered to be almost the same. Small difference may be found between EBB initiated and TsCl initiated systems. The difference may be considered to come from the different coordination structures of copper(II) complexes in these systems (i.e., $Cu(II)Br_2$ and $Cu(II)BrCl$). When the monomer was changed from MMA to MA, the signal features also changed, especially in the relative intensities of some hyperfine split peaks. Some information on the structure of the copper(II) complex can be deduced from these spectra. We will discuss the detailed analysis of these spectra, which would provide more information about the ATRP mechanism, separately in a forthcoming article.[28]

The concentration of copper(II) species was estimated by double integration of these signals. The conversion dependence of copper(II) concentrations in the ATRP systems 1—3 are shown in Figure 3a. In System 1 (MMA ATRP initiated by EBB), the concentration of copper(II) increased until 30% conversion and reached a steady state. The steady state concentration was about 0.6—0.7 mmol L^{-1}. The percentage of copper(II) formed from copper(I) was calculated and the results are shown 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 initial amount of copper(I) species still in monovalent state. This also means that about 5% of chains termi-

above 10^{-3} mol L^{-1} (*vide infra*) which is 10^4 or 10^5 times higher than the initiating and propagating radicals according to persistent radical effect.[27] Thus, the copper(II) species is the predominant species observed by EPR in the (meth)acrylate ATRP Systems.

An example of the time dependence of the EPR signals from the copper species in the ATRP of MMA initiated with TsCl is shown in Figure 1. Since these signals were observed in frozen state, they present characteristic anisotropic pattern.[23]
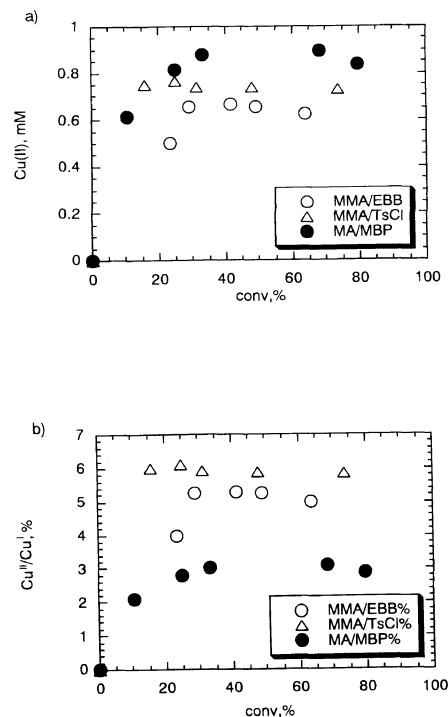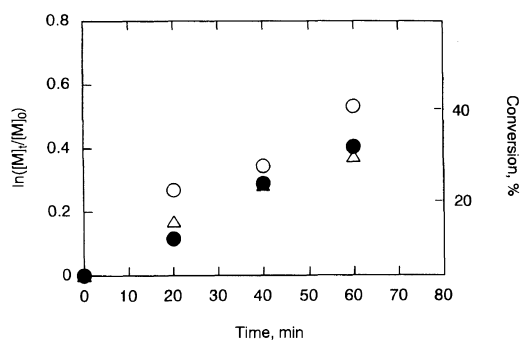
Figure 4. First order kinetic plots for Systems 1 (open circle), 2 (open triangle), and 3 (filled triangle).

nated and at least 95% of chains are in the dormant state capable of activation and further growth. In the case of the MMA ATRP system initiated by TsCl (System 2), the concentration of copper(II) increased rapidly, reaching a nearly steady state before the first measurement, i.e., 15% conversion. In the case of System 3 (MA ATRP initiated by MBP), the concentration of copper(II) species increased steadily in the initial 10% conversion, and then increased more gradually to reach steady state at about 40% conversion. Conversion from copper(I) to copper(II) species was relatively low (ca. 3%) in this system, in spite of the twice higher $[RX]_0$ and $[CuX]_0$.

Correlation of Concentrations of Copper(II) Species and Kinetics of Polymerizations in ATRP Systems

The first order plots of the rate of polymerization for Systems 1—3 are shown in Figure 4. During the initial 60 min of polymerization, the plots are reasonably linear, and the following discussion about the kinetics of the polymerization systems pertain to this region (less than 30% conversion). The linear relationship implies that the concentration of propagating radicals is in the steady state. Since the EPR technique used in this study is not sensitive enough to detect the signal from the propagating radicals directly, confirmation that the propagating radical concentration is in the steady state cannot be obtained directly. However, the results of the first order kinteic plots indirectly suggest that this is the case. The first order kinetic plots of MMA and MA ATRP show similar apparent polymerization rates.

The correlation between the copper(II) concentration and kinetics of the same polymerization system has been now examined. Such a correlation is important in the discussion regarding the mechanism of ATRP of (meth)acrylates.

System 1: Plots of copper(II) concentration, M_n, and M_w/M_n as a function of monomer conversion are shown in Figure 5. Until 40% monomer conversion, M_n is larger than the theoretical prediction (solid line). After 40% conversion, it becomes smaller than the theoretical one. This may be explained by relatively slow and/or inefficient initiation with EBB in the polymerization of MMA and some transfer with the entirely Br-based system.[14] M_w/M_n is around 1.3 during the polymerization. On the other hand, the copper(II) concentration in the same system increased monotonously and reached a steady state at about 30% conversion.
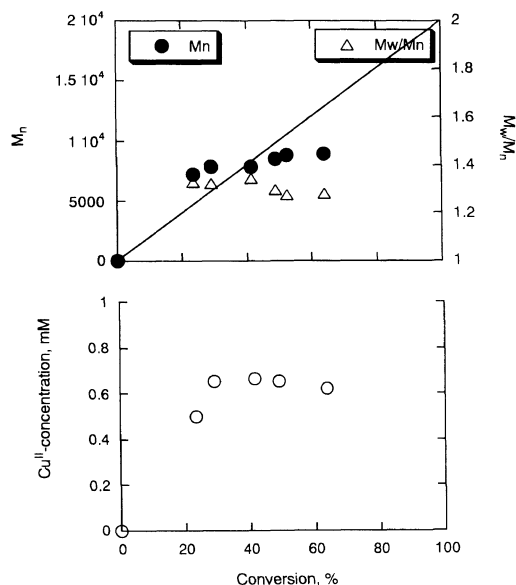

Figure 5. Number average molecular weight, M_n, and molecular weight distribution, M_w/M_n, as a function of monomer conversion for the polymerization system 1 along with copper(II) concentration dependence on the conversion for the same system.
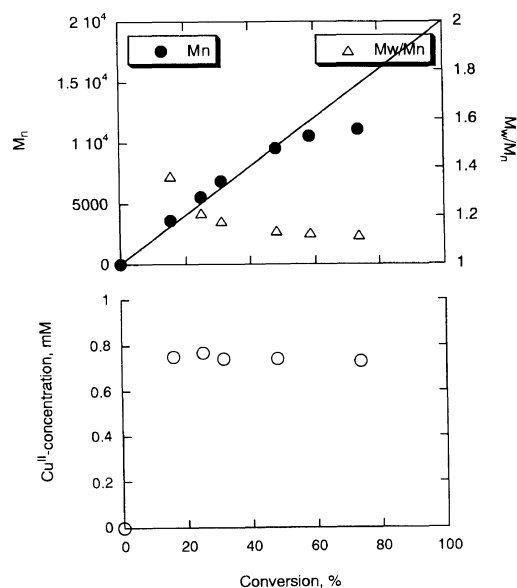

Figure 6. Number average molecular weight, M_n, and molecular weight distribution, M_w/M_n, as a function of monomer conversion for the polymerization system 2 along with copper(II) concentration dependence on the conversion for the same system.

System 2 (Figure 6): Until 50% conversion, M_n shows good agreement to the theoretically predicted value. M_w/M_n decreased gradually from 1.4 to 1.1 from 15 to 30% conversion. The relatively small polydispersity (ca. 1.1) at about 75% conversion indicates that propagation was still controlled even after M_n deviated from the theoretical values. The copper(II) concentration reached a nearly steady state quickly and it kept at this value beyond 15% conversion. The initiation with TsCl is sufficiently fast in the polymerization of MMA.[14] Thus, the molecular weights of the resulting poly(MMA) showed good agreement with the predictions.

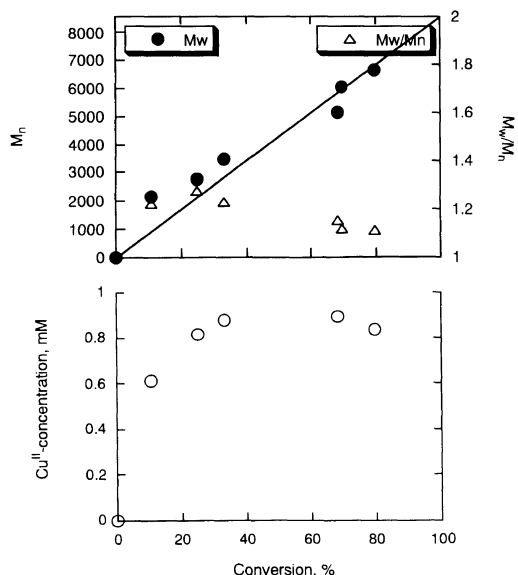System 3 (Figure 7): In the initial stage (until 40% conversion), M_n is slightly larger than the theoretical

Figure 7. Number average molecular weight, M_n, and molecular weight distribution, M_w/M_n, as a function of monomer conversion for the polymerization system 3 along with copper(II) concentration dependence on the conversion for the same system.

Table I. Description of studied ATRP systems 1—3

System 1:
MMA/EBB/CuBr/dNbipy = 200/1/0.5/1 in 50 % Ph$_2$O (v/v)

System 2:
MMA/TsCl/CuBr/dNbipy = 200/1/0.5/1 in 50 % Ph$_2$O (v/v)

System 3:
MA/MBP/CuCl/dNbipy = 200/2/1/2 in 50 % Ph$_2$O (v/v)

prediction, and after 60% conversion it follows the theoretical value. When M_n was larger than predicted, the copper(II) concentration in the polymerization system was increasing and reached a steady value at about 40% conversion. Below 30% conversion, the amount of copper(II) species may not be enough to allow fast deactivation to take place. This may be correlated with the faster rate constant of propagation of MA than that of MMA. M_w/M_n decreased slightly from 20% to 80% conversion. 0.6 to 0.8 mmol L^{-1} of copper(II) species seemed to be enough for control of molecular weight distribution.

In the above results, M_n increased monotonously with conversion, and seems to be independent of the change of concentration of copper(II) species. However, there may be some correlation between M_w/M_n and copper(II) concentration. When the steady state concentration was observed above some value (0.5—0.6 mM), the M_w/M_n has a relatively small value, and when copper(II) concentration has low value (<0.5 mM), M_w/M_n has relatively larger value. This correlation may be explained by the mechanism of activation/deactivation process of polymerization. At lower concentrations of copper(II) species, the rate of deactivation may not be fast enough to compete with propagation and also with radical-radical termination. The amount at a nearly steady state is 5 to 6% of copper(II) species in total copper species for MMA and 2 to 3% of them for MA under the studied conditions. It is recognized that

proportion of copper(II) species depends not only on the monomer structure but also on the concentrations of the involved reagents, temperature and reaction time since termination continues during the polymerization. Initially, [Cu^{II}] builds up rapidly because termination is relatively faster due to chains being short. With the progress of the reaction a nearly constant concentration of copper(II) species is observed due to slower termination because of the persistent radical effect and chains becoming longer and viscosity becoming higher.

In summary, we have observed the EPR signals of copper(II) species in (meth)acrylate ATRP systems. The pseudostationary steady state concentration of copper(II) species was clearly evident in these controlled polymerization systems. A correlation between the kinetic data (such as the molecular weight and molecular weight distribution dependence on monomer conversion) and copper(II) concentration indicates that a certain amount of copper(II) species is required to control ATRP systems. The structure and chemical properties of the copper(II) species remain as future areas of investigation.

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25. The method of sample preparation is very important in the evaluation of the percentage of Cu^{II} formed from Cu^{I}. In previous experiments, we mixed CuBr, dNbipy, and initiator first, and then we added (meth)acrylate and diphenyl ether. In this manner of preparation, the concentration of Cu^{II} was three times larger than in the present experiments. A high local concentration of CuBr and initiator is considered to produce the higher concentration of Cu^{II} species. This finding highlights the importance of sample preparation for ATRP experiments.

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