

EPR study of the atom transfer radical polymerization (ATRP) of (meth)acrylates

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SUMMARY: Electron paramagnetic resonance (EPR) spectroscopy was applied to atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) and methyl acrylate (MA) in order to investigate the mechanism of the controlled/"living" radical polymerization system. Although initially only copper(I) species was added to the system as a catalyst, EPR signals of copper(II) species were observed during the polymerization of MMA initiated by ethyl 2-bromoisobutyrate and *p*-methylbenzenesulfonyl chloride, and polymerization of MA initiated by methyl 2-bromopropionate. As the polymerization proceeded, the concentration of copper(II) increased gradually until a steady state was reached. The EPR results indicate that 5–6% of copper(I) species converted to copper(II) species in polymerization of MMA and about 3% in polymerization of MA at 90 °C.

Introduction

Controlled/"living" polymerization methods enable preparation of well-defined (co)polymers (with controlled molecular weight, low polydispersities, precise terminal functionalities, as well as with predefined chain architecture and composition). In such systems the contribution of chain breaking reactions should be 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 polymerization⁶. 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^{7,8}. The resulting polymers have degrees of polymerization predetermined by $\Delta[M]/[I]_0$ up to $\bar{M}_n \approx 10^5$ and low polydispersities, $1.05 < \bar{M}_w/\bar{M}_n < 1.5$. 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 polymerized by repetitive atom transfer radical additions to yield a well-defined polymer with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \approx 1.05^{8a}$) and $\bar{M}_w/\bar{M}_n \approx 1.30^{8b}$).

According to kinetic and mechanistic studies of ATRP of vinyl monomers, 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 groups⁹. 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 by the so-called persistent radical effect¹⁰. A rough estimate of the amount of formed CuBr₂/dNbipy species from kinetic studies was $\approx 5\%$ based on CuBr/dNbipy catalyst⁹. Direct measurements of Cu(II) species by EPR in styrene ATRP confirmed this value¹¹. In this communication the direct EPR determinations of Cu(II) species in MMA and MA ATRP are reported.

Electron paramagnetic resonance (EPR, or electron spin resonance ESR) spectroscopy is a very powerful tool to investigate paramagnetic species¹². Structures, concentrations, and dynamics of paramagnetic compounds can be obtained from EPR measurements in the study of radical polymerizations^{13,14}. EPR has been previously used to determine concentrations of free TEMPO in nitroxide-mediated polymerization of styrene^{15,16}. 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) species¹⁷.

Experimental part

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. The mixture was degassed 3 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. Comparison of the apparent rate constants of propagation with the absolute rate constants of radical propagation ($-\ln[M]/dt = k_p^{app} = k_p \cdot [P^*]$) indicate that concentration of growing radicals is much higher at polymerization tempera-

ture ($[P^*] \approx 10^{-7}$ M at 100°C) than at either room temperature or 150 K ($[P^*] \ll 10^{-8}$ M). However, this does not affect concentration of Cu(II) species which can change by less than 0.01%, since $[\text{Cu(II)}] > 10^{-3}$ M.

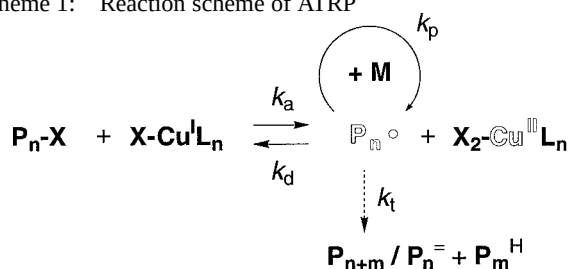
Concentrations of copper(II) species were estimated by double integration of spectra. Spectra of Cu(II)(trifluoroacetylacetonate) in the same media at the same temperature were used as standards.

Typical polymerization systems employ the following reagents ratios: MMA/initiator/CuBr/dNbipy (=200/1/0.5/1) with 50% of Ph_2O and MA/methyl 2-bromopropionate/CuBr/dNbipy (=200/1/1/2) with 50% of Ph_2O . Polymerization temperature was 90°C for MMA and MA.

Results and discussion

A typical scheme of ATRP system is shown in Scheme 1.

Scheme 1: Reaction scheme of ATRP



X = halogen atom
M = MMA or MA

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. In principle, all of these species could be observed by EPR spectroscopy; however, 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 rapidly 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 concentration of copper(II) species in this system is above 10^{-3} mol/L (vide infra), which is 10^4 or 10^5 times higher than that of the initiating and propagating radicals according to persistent radical effect¹⁰. Thus, the copper(II) species is the predominant species observed by EPR in ATRP systems.

The results of time dependence of EPR signals of copper species in the ATRP of methyl methacrylate are shown in Fig. 1.

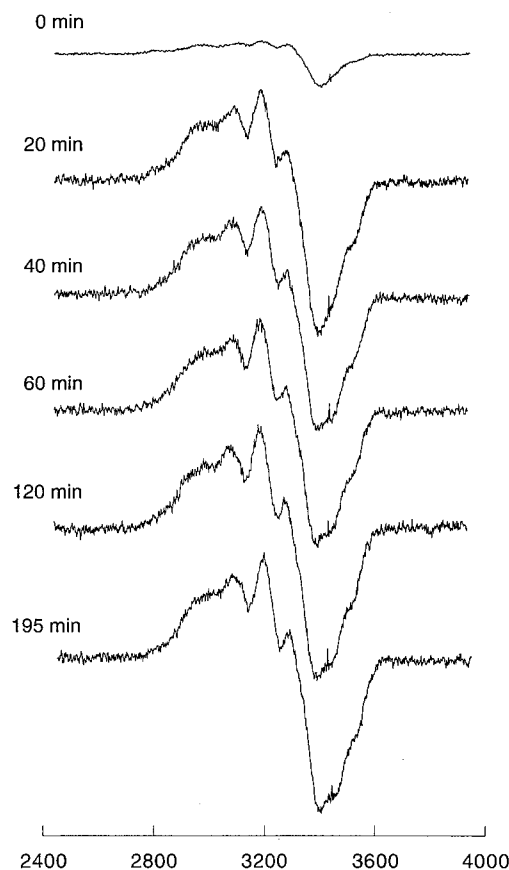


Fig. 1. EPR spectra of the polymerization mixture measured at 150 K after 0, 20, 40, 60, 120, and 195 min at 90°C . $[\text{MMA}]_0/[\text{Ethyl 2-bromoisobutyrate}]_0/[\text{CuBr}]_0/[\text{dNbipy}]_0$ (200/1/0.5/1) in diphenyl ether (50 vol.-%)

Signals were measured at 150 K because monomer and solvent (Ph_2O) are polar. The signal feature present after 20 min heating is considered to be a copper(II) signal of trigonal bipyramidal structure¹⁷. The concentration of copper(II) species was estimated by double integration of these signals. Time dependence of copper(II) concentrations in the ATRP of MMA and MA in diphenyl ether (Ph_2O), initiated by ethyl 2-bromoisobutyrate, *p*-methylbenzenesulfonyl chloride, and methyl 2-bromopropionate are shown in Fig. 2.

In the case of the solution polymerization of MMA initiated by ethyl 2-bromoisobutyrate, the concentration of copper(II) increased rapidly and reached a steady state value within 10 min. The steady state concentration was about 0.6–0.8 mM. In the case of the tosyl chloride initiated system, the concentration of copper(II) increased gradually, reaching a steady state within 60 min. The slightly higher steady state concentration of copper(II) in RBr/CuBr system than in RCl/CuBr system may be attributed to higher equilibrium constant and higher radical concentrations in the former systems. Higher radical concentration results in more pronounced termination and leads to higher overall concentration of Cu(II) species.

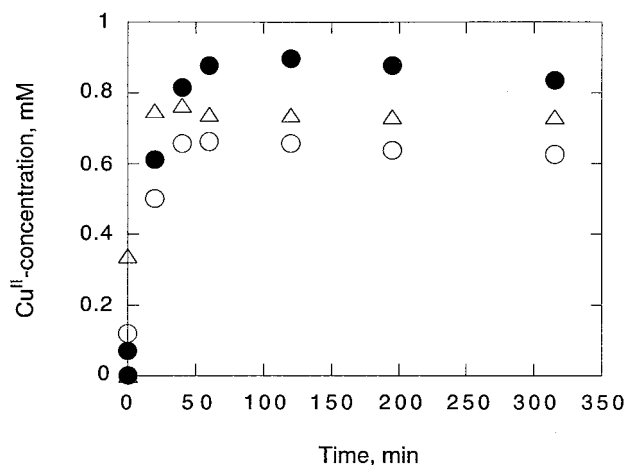


Fig. 2. Plots of time dependence of concentration of copper(II) species for ATRP of MMA initiated by ethyl 2-bromoisobutyrate (Δ) and tosyl chloride ($\circ$) in Ph_2O solution (50 vol.-%; $[\text{MMA}]_0/[\text{RX}]_0/[\text{CuBr}]_0/[\text{dNbipy}]_0: 200/1/0.5/1$) and ATRP of MA initiated by methyl 2-bromopropionate ($\bullet$) in Ph_2O (50 vol.-%; $[\text{MA}]_0/[\text{Methyl 2-bromopropionate}]_0/[\text{CuBr}]_0/[\text{dNbipy}]_0: 200/1/1/2$)

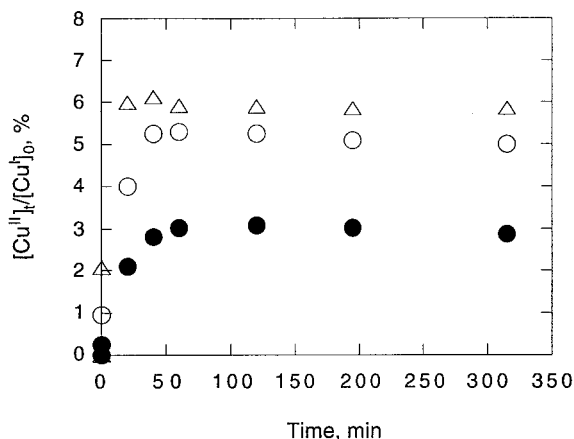


Fig. 3. Plots of time dependence of proportion of copper(II) species formed from copper(I) species by ATRP of MMA initiated by ethyl 2-bromoisobutyrate (Δ) and tosyl chloride ($\circ$) in Ph_2O solution (50 vol.-%; $[\text{MMA}]_0/[\text{RX}]_0/[\text{CuBr}]_0/[\text{dNbipy}]_0: 200/1/0.5/1$) and ATRP of MA initiated by methyl 2-bromopropionate ($\bullet$) in Ph_2O (50 vol.-%; $[\text{MA}]_0/[\text{Methyl 2-bromopropionate}]_0/[\text{CuBr}]_0/[\text{dNbipy}]_0: 200/1/1/2$)

The solution polymerization of MA was initiated with methyl 2-bromopropionate and catalyzed with $\text{CuBr}/2\text{dNbipy}$ at concentration twice higher than in MMA polymerization. In this system, the concentration of copper(II) species also increased rapidly and reached steady state at 0.8–0.9 mM. In the initial stage, the concentration of Cu(II) was slightly higher than the steady state concentration.

The percentage of Cu(II) formed from Cu(I) was calculated, and the results are shown in Fig. 3. In the case of the ATRP of MMA, approximately 5–6% of the copper(I) was converted to copper(II) species during the polymerization, leaving 94–95% of copper(I) species still in monovalent state. This also means that only 3% of

chains terminated, and 97% of chains are in the dormant state capable of growth. In the case of MA, about 3% of Cu(II) species was formed. The proportion of formed Cu(II) species in MA polymerization is smaller than in MMA polymerization, but the proportion of terminated chains is similar due to different concentrations of the catalyst.

In summary, we observed EPR signal of copper(II) species in ATRP of MA and MMA. The steady state concentration of copper(II) species is approximately 5–6% for MMA and 3% for MA of the original copper(I) species under typical conditions. These results are consistent with our previous kinetic data¹⁸⁾.

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