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Atom transfer radical polymerization of styrene catalyzed by copper carboxylate complexes[a]

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SUMMARY: The atom transfer radical polymerization (ATRP) of styrene has been studied using complexes of copper carboxylates. Compared with systems employing copper halides as the catalyst, the use of copper carboxylates resulted in faster polymerization rates and higher polydispersities. A ligand (dNbpy) to Cu(I) carboxylate ratio of 1 was sufficient to achieve the maximum rate of polymerization. The addition of a small amount of either Cu(II) or Cu(I) halide to the copper carboxylate system yielded polymers with better controlled molecular weights and lower polydispersities yet the polymerization still remained relatively fast.

Introduction

Free radical polymerization is one of the most widely used polymerization processes. In spite of its commercial importance, controlled radical polymerization has long been considered impossible because of the inevitable bimolecular radical termination process. Only in recent years has controlled radical polymerization been obtained by maintaining a low and stationary concentration of growing radicals based on a fast, dynamic equilibrium between active (free radicals) and dormant species. Several well controlled radical polymerizations have been developed including nitroxyl radical-mediated polymerizations[2–5], cobalt(II)-mediated polymerizations[6,7] and several transition metal-catalyzed (Ru[8,9], Cu[10–14], Ni[15,16], and Fe[17,18]) atom transfer radical polymerizations (ATRP).

The Cu(I) halide/bipyridine catalyzed polymerization, an atom transfer radical polymerization, has provided for the well controlled polymerization of various monomers (styrene, acrylates, methyl methacrylate, acrylonitrile, etc.)[10–14,19–21], various polymer architectures (linear, star, comb, and (hyper)branched polymers)[22] and polymer compositions (random, block, graft and gradient copolymers)[23–25]. This paper reports the controlled radical polymerization of styrene by ATRP using copper carboxylates as catalysts. The effect of the counter anions of the Cu(I) complexes on the polymerization has been investigated.

Experimental part

Styrene was stirred over CaH_2 overnight and vacuum distilled before use. 4,4′-Bis(5-nonyl)–2,2′-bipyridine (dNbpy) was synthesized through a coupling reaction of 4-(5-nonyl)-pyridine using Pd-C as the catalyst. CuBr was purified according to the procedure of Keller and Wycoff[26]. Cu(I) 2-thiophenecarboxylate (CuTC) was synthesized according to the procedure of Liebeskind et al.[27] All other reagents were purchased from commercial sources and used as received.

The general procedure for the polymerization of styrene is described as follows: Cu(I) complex, ligand (dNbpy), initiator 1-phenylethyl bromide (1-PEBr) and styrene in an appropriate ratio were added to a glass tube purged with argon. The solution was degassed three times by “freeze-pump-thaw“ cycles and sealed under vacuum. The tubes were placed in an oil bath thermostatted at 90 °C and were removed from the oil bath at timed intervals.

Monomer conversions were determined by gas chromatography (GC) with *p*-dimethoxybenzene as an internal standard. Molecular weights and polydispersities were determined by gel-permeation chromatography (GPC) using commercially available polystyrene standards for calibration.

Results and discussion

The principle of atom transfer radical polymerization is to establish an equilibrium between dormant and active species as shown by Eqs. 1 and 2. The rate law for ATRP is given by Eq. 3.

$$\text{P–X} + \text{Cu(I)} \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftarrows}} \text{P}^\bullet + \text{Cu(II)–X} \tag{1}$$

$$K_\mathrm{eq} = \frac{k_\mathrm{a}}{k_\mathrm{d}} = \frac{[\mathrm{P}^\bullet][\mathrm{Cu(II)-X}]}{[\mathrm{Cu(I)}][\mathrm{P-X}]} \tag{2}$$

$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}][\mathrm{P}^\bullet] = k_\mathrm{p}K_\mathrm{eq}[\mathrm{M}][\mathrm{P-X}]\frac{[\mathrm{Cu(I)}]}{[\mathrm{Cu(II)-X}]} = k_\mathrm{p}^\mathrm{app}[\mathrm{M}] \tag{3}$$

While the controlled living radical polymerization by ATRP follows the general equations 1, 2 and 3, the equili-

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[a] Part of this work was presented at the 214th American Chemical Society National Meeting in San Francisco (ref.[1]).

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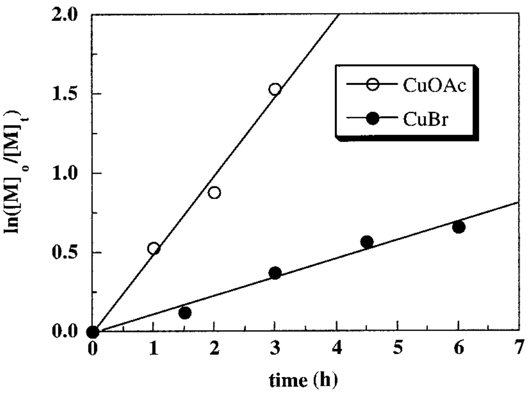

Fig. 1. First order kinetic plot of bulk polymerization of styrene at 90 °C with CuOAc and CuBr as catalysts, respectively. $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{Cu(I)}]_0 : [\text{dNbpy}]_0 = 100:1:1:2$

brium constant and kinetics of individual polymerization may vary depending on the monomer, catalyst and reaction conditions, i.e., temperature, solvent, etc. Cu(I) halides such as CuCl and CuBr have been widely used as catalysts in the previous studies of ATRP. In order to study the effect of the counter anion of Cu(I) complex on the polymerization, especially non-halogen anions, we have studied the polymerization of styrene catalyzed by copper(I) acetate (CuOAc) and copper(I) 2-thiophenecarboxylate (CuTC). Some new features have been observed which are different from those polymerizations using Cu(I) halides.

The bulk polymerization of styrene initiated by CuBr and CuOAc was carried out at 90 °C in a ratio of $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{Cu(I)}]_0 : [\text{dNbpy}]_0 = 100:1:1:2$. As shown in Fig. 1, both polymerizations were first order with respect to monomer conversion, which indicated that the concentration of radicals was constant throughout the polymerization. However, the polymerization catalyzed by CuOAc was much faster than that catalyzed by CuBr. Since the polymerization rate is directly related to the propagating radical concentration (Eq. 3), this result can be interpreted as that when CuOAc was used, the equilibrium in Eq. 1 is shifted to the right by decreasing the deactivation rate constant k_d, and/or increasing the activation rate constant k_a.

The effect of the ratio of ligand (dNbpy) to Cu(I) on the polymerization rate was investigated. In the ATRP of styrene by CuBr/dNbpy, the optimal polymerization rate was reached when $[\text{dNbpy}]_0/[\text{CuBr}]_0 = 2$, while the polymerization rate was only half of it when $[\text{dNbpy}]_0/[\text{CuBr}]_0 = 1$[19]. The possible explanation is that a 2:1 ratio of dNbpy to CuBr is required to form the active species even though other more complexed mechanisms may operate. A new feature in the polymerization of styrene by copper carboxylates is that the polymerization rate was very similar when 1:1 and 2:1 ratios of dNbpy to CuOAc were used (Fig. 2). The same result was observed when Cu(I) 2-thiophenecarboxylate (CuTC) was employed (Fig. 3). It suggests that both the acetate and the 2-thiophenecarboxylate ligands may act as bidentate ligands in the absence of a second dNbpy ligand to fulfill the coordination requirement.

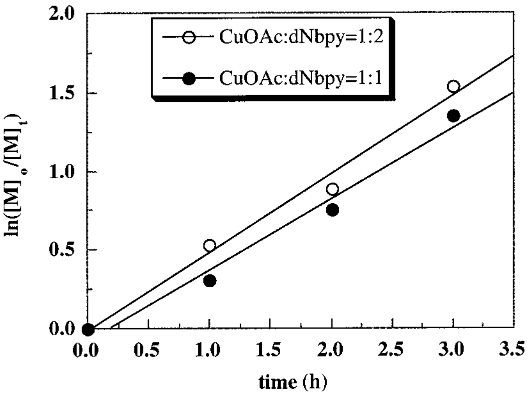

Fig. 2. First order kinetic plot of bulk polymerization of styrene at 90 °C with 1:1 and 1:2 ratios of CuOAc to dNbpy, respectively. $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{CuOAc}]_0 : [\text{dNbpy}]_0 = 100:1:1:1$ and $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{CuOAc}]_0 : [\text{dNbpy}]_0 = 100:1:1:2$

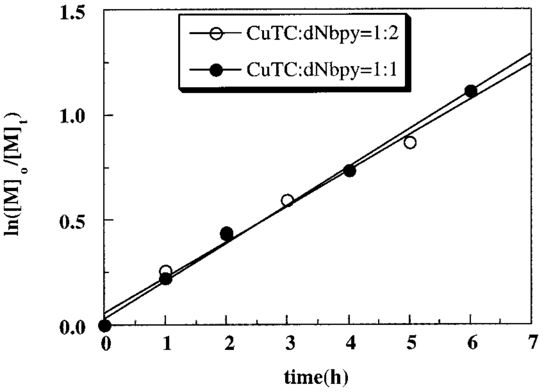

Fig. 3. First order kinetic plot of bulk polymerization of styrene at 90 °C with 1:1 and 1:2 ratios of CuTC to dNbpy, respectively. $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{CuTC}]_0 : [\text{dNbpy}]_0 = 100:1:1:1$ and $[\text{styrene}]_0 : [\text{1-PEBr}]_0 : [\text{CuTC}]_0 : [\text{dNbpy}]_0 = 100:1:1:2$

In the polymerization of styrene catalyzed by copper carboxylates, the molecular weights were usually higher than the theoretical values calculated from Eq. 4, where $\Delta[\text{M}]$, $[\text{R–X}]_0$, and $(\text{MW})_0$ represent the concentration of consumed monomer, the initial concentration of initiator, and the molecular weight of monomer, respectively. The polydispersities obtained were also relatively higher ($\overline{M}_w/\overline{M}_n > 1.2$), as compared with $\overline{M}_w/\overline{M}_n \approx 1.1$ for the CuBr/dNbpy system.

$$\overline{M}_n = (\Delta[\text{M}]/[\text{R–X}]_0)(\text{MW})_0 \qquad (4)$$

Fig. 4 shows the result of the polymerization of styrene using CuOAc at 90 °C. The relatively higher molecular

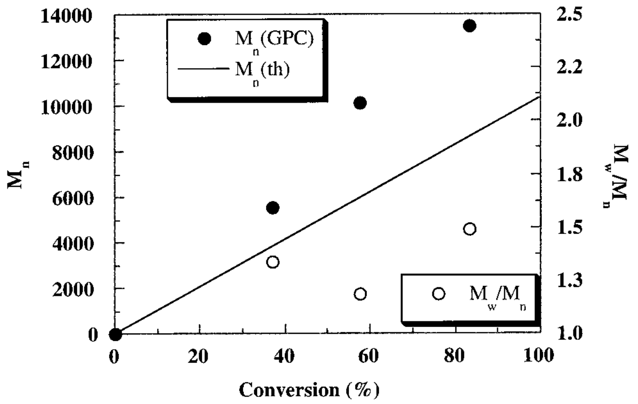

Fig. 4. Plot of polymer molecular weight and polydispersity vs. monomer conversion in the bulk polymerization of styrene at 90 °C. $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{dNbpy}]_0 = 100:1:1:2$

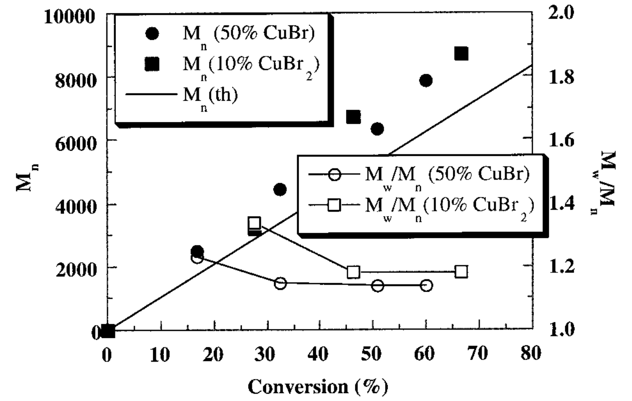

Fig. 5. Plot of polymer molecular weight and polydispersity vs. monomer conversion in the bulk polymerization of styrene at 90 °C by CuOAc with 10% $CuBr_2$ and 50% CuBr, respectively. A: $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{CuBr}_2]_0:[\text{dNbpy}]_0 = 100:1:1:0.1:2.2$. B: $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{CuBr}]_0:[\text{dNbpy}]_0 = 100:1:0.5:0.5:2$

weights than predicted, suggest a lower initiator efficiency which probably results from larger equilibrium constant K_{eq} in Eq. 2. A high concentration of radicals at the beginning of the polymerizations could lead to bimolecular termination, thus lowering the initiation efficiency. The higher polydispersities of the resulting polymers are most likely caused by a slower deactivation process and/or additional side reactions.

The relatively higher molecular weights and higher polydispersities, presumably caused by initial termination of the initiator and slow deactivation, respectively, were improved by the addition of a co-catalyst which has a faster deactivation process. $CuBr_2$ reacts with polystyryl radicals with a nearly diffusion-controlled rate[19,28]. Therefore, by adding a small amount of $CuBr_2$ into the CuOAc system, the initial concentration of radicals can be reduced and the overall deactivation process can be accelerated. A similar effect has also been observed in the presence of CuBr. Thus, by combining the CuOAc system, with a larger equilibrium constant, with the CuBr system, having a faster deactivation process, the molecular weights and polydispersities were better controlled while the polymerization still remained relatively fast. Fig. 5 and 6 show the polymerizations of styrene catalyzed by CuOAc in the presence of 10 mol-% added $CuBr_2$ (relative to CuOAc) and by 1 : 1 of CuOAc to CuBr, respectively.

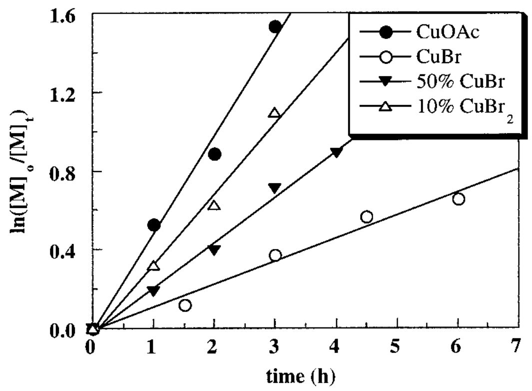

Fig. 6. Comparison of the first order kinetics for the bulk polymerization of styrene at 90 °C with various catalytic systems. A. $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{dNbpy}]_0 = 100:1:1:2$. B: $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{CuBr}]_0:[\text{dNbpy}]_0 = 100:1:0.5:0.5:2$. C: $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuOAc}]_0:[\text{CuBr}_2]_0:[\text{dNbpy}]_0 = 100:1:1:0.1:2.2$. D. $[\text{styrene}]_0:[\text{1-PEBr}]_0:[\text{CuBr}]_0:[\text{dNbpy}]_0 = 100:1:1:2$

The molecular weights were close to the theoretical values and the polydispersities were reduced from about 1.4 to below 1.2. The polymerization rates in both cases were slower than for the CuOAc system due to the addition of CuBr, but were still faster than those when CuBr was used alone. It is possible that several copper species may be formed in the solution (Eq. 5). If the copper dicarboxylate, $Cu(OAc)_2$, is formed, this would not be able to deactivate the propagating radicals as the carboxylate ligand is not a group that can be radically transferred, as is the halogen, i. e., bromine.

$$\text{CuOAc} + \text{CuBr}_2 \rightleftharpoons \text{Cu(OAc)(Br)} + \text{CuBr} \qquad (5)$$

ATRP is proposed to proceed by a free radical polymerization mechanism. Each growing polymer chain does not bind to a specific metal center. The polymer chain can react freely with any metal complexes. Even though more than one catalytic species may be involved, polymers with unimodal molecular weight distribution are produced when there is a fast, dynamic exchange between the propagating radicals and the halogen-terminated polymer chains.

When polymers of high molecular weight (>30 000) were desired, some slow side reactions were observed as evidenced by broader molecular weight distributions and a deceleration in the rate of polymerization. In order to understand the nature of the side reactions, the reaction between 1-phenylethyl bromide, as a model of macromolecular polystyryl bromide, and the complex of CuOAc with two equivalents of dNbpy was studied in benzene. The corresponding products were analyzed by NMR. When a benzene solution of 1-PEBr and CuOAc/2dNbpy was heated at 90 °C in a sealed NMR tube, the coupling product (2,3-diphenylbutane) was observed. In addition to the coupling product, styrene and 1-phenylethyl acetate (1-PEOAc) were also detected, and their concentrations increased with time. The mechanism for the formation of 2,3-diphenylbutane and styrene have been studied previously[29]. The possible mechanism for the formation of 1-phenylethyl acetate might involve the displacement of Br^- on 1-phenylethyl bromide, by OAc^- of the copper complex. This hypothesis is supported by the results of the reaction of 1-phenylethyl bromide with $Cu(OAc)_2$ (Eq. 6). When a benzene solution of 1-phenylethyl bromide ($[\text{1-PEBr}]_0 = 0.2$ M) and $Cu(OAc)_2$ ($[Cu(OAc)_2]_0 = [\text{dNbpy}]_0/2 = 0.05$ M) was heated in a sealed NMR tube at 90 °C, after 20 h, 1-PEOAc was formed in 28.5% yield, in addition to the formation of styrene in 6.5% yield.

$$\text{1-PEBr} + Cu(OAc)_2 \longrightarrow \text{1-PEOAc} + Cu(OAc)(Br) \qquad (6)$$

The formation of styrene can be formed by disproportionation of two 1-phenylethyl radicals, or by reaction of Cu(II) species with RBr and $R^\bullet$. In the presence of RBr, the Cu(II) may act as a Lewis acid to form the 1-phenylethyl cation. Loss of a proton would result in the formation of styrene. Similarly, $R^\bullet$ can be oxidized to the cation by outer sphere electron transfer with Cu(II).

Conclusions

The atom transfer radical polymerization of styrene has been studied using complexes of copper carboxylates. ATRP of styrene by copper carboxylates resulted in a faster polymerization rate, higher molecular weights than the calculated values, and higher polydispersities compared with ATRP catalyzed by CuBr. Cu(I) to ligand (dNbpy) ratios of 1 : 1 and 1 : 2 yielded similar polymerization rates. The molecular weight control and molecular weight distributions were improved by adding $CuBr_2$ or CuBr to the copper carboxylate system while the polymerization rate still remained relatively fast.

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