

Rate Enhancement by Carboxylate Salts in the CuCl, Cu₂O, and Cu(0) Catalyzed “Living” Radical Polymerization of Butyl Methacrylate Initiated with Sulfonyl Chlorides

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Introduction. Sulfonyl chlorides are universal initiators for the heterogeneous metal-catalyzed “living” radical polymerization of styrene, methacrylates, and acrylates.^{1–6} In contrast, the structure of alkyl halide initiators should be tailored for each class of monomers in order to obtain a rate of initiation at least equal to that of propagation.⁷ The preferred catalytic system for both classes of initiators is based on CuCl in combination with an organic ligand such as substituted or unsubstituted 2,2'-bipyridine (bpy).^{1–8}

One of the challenges in the field of metal-catalyzed “living” radical polymerization is the enhancement of the rate of polymerization with preservation of the control of the molecular weight and polydispersity (M_w/M_n). A step in this direction was made by using phase-transfer catalysts (PTC) as additives in the CuCl/bpy-catalyzed polymerization of butyl methacrylate (BMA) initiated with sulfonyl chlorides. The rate was enhanced by a factor of 1.5 while the narrow polydispersity of 1.2 was maintained.⁶ Furthermore, we demonstrated that Cu₂O, Cu(0), and combinations of both in conjunction with bpy and PTCs self-regulate the in situ generation of the CuCl/CuCl₂ catalyst leading to higher polymerization rates or polymers with lower M_w/M_n . This method provides the simplest and the most convenient tool to control the rate and M_w/M_n in the polymerization of BMA and styrene (S).⁶

Reports of a rate acceleration by LiCl⁹ in the copper salt-catalyzed addition of CCl₄ to acrylates indicated the potential use of LiCl for the rate enhancement of the polymerization of BMA. The mechanism proposed by these authors considers the formation of a complex, i.e., Li₂CuCl₄,⁹ which would change both the rate of propagation and the rate of termination. Recently, reports about the rate-enhancing effect of copper(I) carboxylates,¹⁰ carboxylic acids,^{11a} and phenols^{11b,c} on the metal-catalyzed “living” radical polymerization of styrene (S) and methyl methacrylate (MMA) attracted our attention because of two seemingly unrelated reports on copper-assisted syntheses. The mechanisms proposed for the Hurtley reaction¹² and the copper-catalyzed synthesis of diaryl ethers¹³ show that cuprate-type intermediates [ArCOOCuX]⁻M⁺, formed by coordination of a carboxylate salt to the copper(I) center, play an important role. This knowledge inspired us to investigate the effect of carboxylates on the Cu(I)-catalyzed “living” radical polymerization of BMA.

Results and Discussion. The addition of sodium benzoate (NaBz) to the CuCl/bpy-catalyzed “living” radical polymerization initiated with *p*-methoxyben-

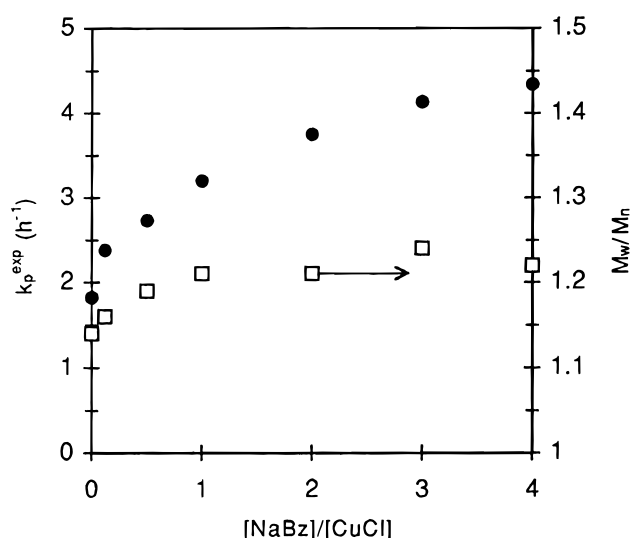


Figure 1. Rate dependence of the “living” radical polymerization of BMA on the NaBz/CuCl (mol/mol) ratio in diphenyl ether initiated with MBSC and catalyzed by CuCl/bpy. Reaction conditions: [BMA] = 4.5 M, [BMA]/[MBSC]/[CuCl]/[bpy] = 200/1/1/2 molar ratio, reaction temperature 120 °C.

zenesulfonyl chloride (MBSC) enhances the rate of polymerization of BMA in diphenyl ether (entries 1 and 3, Table 1). Figure 1 shows the dependence of the experimental rate constant of propagation (k_p^{exp}) on the NaBz/CuCl ratio. Upon the addition of 4 equiv of NaBz, a rate enhancement of 2.4 times is observed while the M_w/M_n values do not increase or exceed 1.24. A series of salts were investigated for the potential rate-enhancing effect. The addition of 1 equiv of NaCl, LiCl, NaOH, Na₂CO₃, NaHCO₃, K₂CO₃, Li₂CO₃, Cs₂CO₃, or ZnCl₂ did not enhance the rate of the polymerization of BMA. The addition of Cu(0) to the heterogeneous Cu(I)/bpy-catalyzed “living” radical polymerization of methacrylates, acrylates, and styrene enhances the rate by reduction of the CuCl₂ formed in situ.^{6,14} To exclude the possibility of the reduction of CuCl₂ by NaBz, a mixture of NaBz and CuCl₂/bpy as a catalyst was used in the polymerization of BMA. However, after 24 h no polymer was observed; therefore, NaBz did not reduce CuCl₂ to generate in situ Cu(I)Cl.

The observed rate enhancement by NaBz is ligand dependent. When 2-(2'-pyridyl)-4,5-dihydrooxazole¹⁵ (pyrox) is used as a ligand instead of 2,2'-bipyridine (bpy), the rate is enhanced 5.1 times upon the addition of only 1 equiv of NaBz (entries 2 and 5, Table 1). The use of a Cu/bpy ratio of 1/1 instead of 1/2 does not affect the value of the rate constant (entries 3 and 4, Table 1), suggesting that the active species contains only one bpy ligand. It is expected that the addition of bpy ligand to the heterogeneous polymerization mixture will first complex more catalyst (CuCl) and, then, eventually interact with the complex **3** to a smaller extent (entry 3 vs 4, Table 1).

The addition of sodium carbonate (Na₂CO₃) (entry 7, Table 1) or benzoic acid (entry 6, Table 1) does not show a rate-enhancing effect. The latter observation is different from the results reported by Haddleton et al.,¹¹ who claim that benzoic acid enhances the rate of polymerization of MMA catalyzed by (*N*-*n*-butyl-2-

Table 1. Rate Enhancement of the CuCl, Cu₂O, and Cu(0) Catalyzed Polymerization of Butyl Methacrylate ([BMA] = 4.5 M) Initiated with *p*-Methoxybenzenesulfonyl Chloride (MBSC) at 120 °C in PhOPh

no.	cat.	ligand	additive	[M]/[I]/[cat.]/[ligand]/[additive]	k_p^{exp} (h ⁻¹)	M_w/M_n (conv) (%)	time (min)	init effic ^g
1	CuCl	bpy		200/1/1/2	1.82	1.14 (95)	80	0.99
2	CuCl	pyrox		200/1/1/2	0.69	1.18 (95)	240	0.89
3	CuCl	bpy	NaBz ^a	200/1/1/2/1	3.20	1.21 (93)	60	0.93
4	CuCl	bpy	NaBz	200/1/1/1/1	3.01	1.17 (95)	60	0.86
5	CuCl	pyrox	NaBz	200/1/1/2/1	3.53	1.22 (97)	60	0.93
6	CuCl	bpy	HBz	200/1/1/2/1	1.83	1.24 (93)	90	0.99
7	CuCl	bpy	Na ₂ CO ₃	200/1/1/2/1	1.64	1.14 (90)	85	0.99
8	CuCl	bpy	NaAc ^b	200/1/1/2/1	2.45	1.25 (90)	57	0.82
9	CuCl	bpy	Na ₂ CO ₃ /HTc ^c	200/1/1/2/1/1	3.11	1.25 (95)	60	0.93
10	CuTc	bpy		200/1/1/2	3.28	1.38 (91)	45	0.88
11	CuAc	bpy		200/1/1/2	2.10	1.38 (90)	60	0.84
12	CuCl	bpy	Na ₂ CO ₃ /HFBz ^d	200/1/1/2/1/1	2.39	1.22 (90)	60	0.99
13	CuCl	bpy	Na ₂ CO ₃ /HMeOBz ^e	200/1/1/2/1/1	3.00	1.19 (95)	60	0.75
14	CuCl	bpy	Li ₂ CO ₃ /HBz	200/1/1/2/1/1	1.67	1.17 (93)	90	0.93
15	CuCl	bpy	Na ₂ CO ₃ /HBz	200/1/1/2/1/1	2.53	1.15 (92)	60	0.79
16	CuCl	bpy	K ₂ CO ₃ /HBz	200/1/1/2/1/1	2.48	1.27 (91)	60	0.72
17	CuCl	bpy	Cs ₂ CO ₃ /HBz	200/1/1/2/1/1	3.35	1.30 (97)	60	0.78
18	CuCl	bpy	Na ₂ CO ₃ /HBz/EC ^f	200/1/1/2/1/1	3.62	1.14 (84)	30	0.70
19	Cu ₂ O	bpy		200/1/1/2	0.80 ^f	1.09 (95)	240	0.97 ^h
20	Cu ₂ O	bpy	NaBz	200/1/1/2/1	1.08	1.28 (96)	180	0.82
21	Cu ₂ O	bpy	NaAc	200/1/1/2/1	1.10	1.19 (91)	120	0.93
22	Cu(0)	bpy		200/1/2/6	3.11	1.26 (95)	60	0.99
23	Cu(0)	bpy	NaBz	200/1/2/6/2	6.99	1.67 (90)	21	0.75
24	Cu(0)	bpy	NaBz	200/1/0.5/1.5/0.5	5.04	1.30 (99)	55	0.90

^a Bz = benzoate. ^b Ac = acetate. ^c Tc = 2-thiophene carboxylate. ^d FBz = *p*-fluorobenzoate. ^e MeOBz = *p*-methoxybenzoate. ^f Induction period observed. ^g Determined as the slope of the plot of M_n vs M_{th} ($M_{th} = 200 \times 142 \times \text{conv} (\%) / 100 + 206$). ^h Deviation of M_n from M_{th} . ⁱ A PhOPh/EC ratio of 50/50 (vol %) was used.

pyridylmethanimine)copper(I) bromide and initiated with 2-bromoisobutyric acid. They reported that, upon the addition of 4 equiv of benzoic acid, the rate was enhanced by a factor of 3. However, an increase of the M_w/M_n from 1.2 to 1.5 was observed. The addition of a mixture of benzoic acid and sodium carbonate in a 1:1 ratio does enhance the rate which can be explained by the in situ formation of NaBz. The formation of NaBz in situ is not very efficient in the nonpolar polymerization mixture, and therefore, the rate of polymerization is slower than in the case when NaBz is added directly (entry 15 vs 4, Table 1).

To gain structural insight into the active copper species, the rate enhancement was studied as a function of substitution of the benzoate cation, the electronegativity of the metal cation, and the polarity of the solvent (Table 1). The addition of a 1:1 mixture of *p*-methoxybenzoic acid/Na₂CO₃ (entry 13) results in a higher rate, while the addition of *p*-fluorobenzoic acid/Na₂CO₃ (entry 12) results in a slightly lower rate compared to the addition of benzoic acid/Na₂CO₃ (entry 15). The substituent-dependent rate of polymerization increases in the order F < H < MeO and shows for this limited set that electron-donating groups on the benzoate increase the rate. The effect of the electronegativity of the cation was investigated by adding 1:1 mixtures of benzoic acid and Li₂CO₃, Na₂CO₃, K₂CO₃, and Cs₂CO₃, which generate the corresponding metal benzoates in situ. In the case of lithium benzoate the rate is not enhanced (entry 14), whereas sodium and potassium benzoate show an equal rate enhancement (entries 15 and 16). Cesium benzoate shows the largest enhancement (entry 17), however, the M_w/M_n increases to 1.30. Clearly, the rate of the polymerization depends on the electronegativity of the cation and increases in the order Li < Na ≈ K < Cs. Finally, Figure 2 shows the influence of in situ generated NaBz and ethylene carbonate (EC), a polar solvent, on the rate of polymerization of BMA initiated with MBSC and catalyzed by CuCl/bpy. The use of EC enhances the in situ generation of NaBz and, therefore,

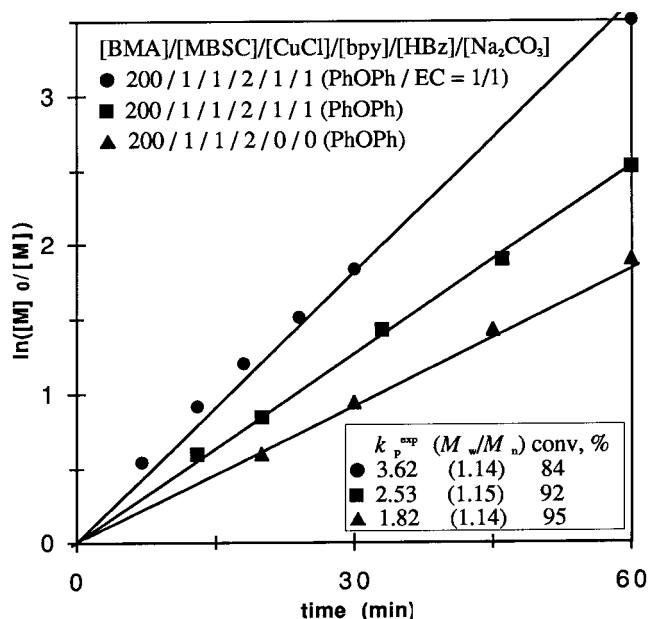
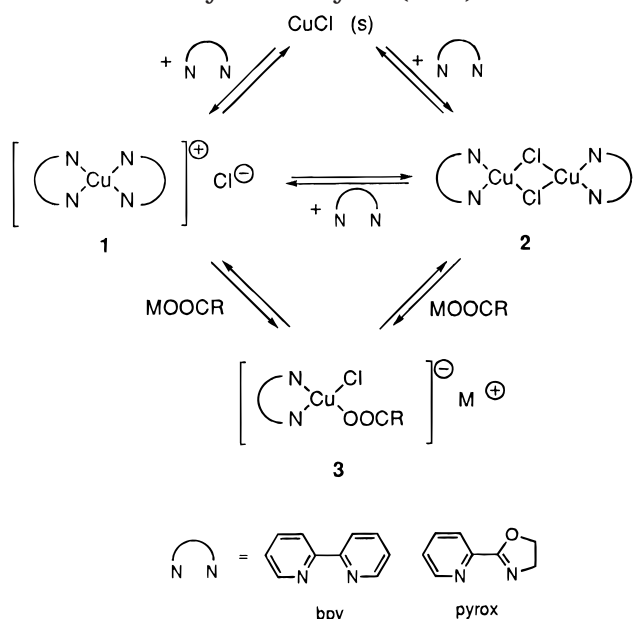


Figure 2. First-order kinetic plots for the polymerization of BMA initiated with *p*-methoxybenzenesulfonyl chloride (MBSC) and catalyzed by CuCl/bpy at 120 °C in PhOPh. Reaction conditions: [BMA] = 4.5 M, [BMA]/[MBSC]/[CuCl]/[bpy]/[HBz]/[Na₂CO₃] = 200/1/1/2/1/1 (●) (in PhOPh/EC = 50/50 (vol %)), 200/1/1/2/1/1 (■), 200/1/1/2/0/0 (▲).

shows the largest rate enhancement while a low polydispersity (i.e., 1.14) is maintained (entry 18, Table 1). However, the initiator efficiency decreases with increasing rate. Part of the initiator is most likely lost during the initial stage of the polymerization while the Cu(I)/Cu(II) system reaches quasi-equilibrium (persistent radical effect).¹⁶

The effect of carboxylates on the rate of the CuCl/bpy catalyzed polymerization of BMA can be explained by the formation of a cuprate-type active species **3** (Scheme 1). Recently, the intermediacy of a similar

Scheme 1. Proposed Mechanism for the Formation of Cuprates from CuCl/bpy and Benzoates in the Metal-Catalyzed "Living" Radical Polymerization of Butyl Methacrylate (BMA)



species has been proposed to play a role in the Hurtley reaction¹² and the copper-catalyzed synthesis of diaryl ethers.¹³ It has been reported that the CuCl/bpy complex can exist as a monomeric $[\text{Cu}(\text{bpy})_2]\text{Cl}$ (**1**) complex or as a $\text{bpyCu}(\mu\text{-Cl})_2\text{Cu}(\text{bpy})$ (**2**) dimer with bridging chlorine ligands.¹⁷ The carboxylate anion can generate the cuprate by either removing a bpy ligand from **1** or replacing a bridging chlorine ligand in **2** to form monomeric **3**. All the catalyst species **1–3** are active and coexist in equilibrium with the heterogeneous Cu(I)Cl catalyst. The formation of the cuprate facilitates the buildup of negative charge on the copper center. This facilitates the oxidation of Cu(I) to Cu(II) and therefore results in a higher radical concentration and higher polymerization rates. The buildup of negative charge on the Cu(I) center is increased by using benzoates with electron-donating groups such as *p*-methoxybenzoate or using benzoates with less electronegative cations such as cesium which increases the ionic character of the cuprate. The ionic character of the cuprate is further enhanced by the use of the polar solvent EC (entry 18 vs 15, Table 1). Furthermore, cesium carboxylates are relatively soluble in organic solvents which may additionally enhance the rate through better solubility of the formed cuprate.¹³ Although the intermediacy of cuprate **3** may play a key role in the rate enhancement, the exact mechanism of the formation of the growing radical species from the initiator or the dormant "living" polymer remains unclear. Due to the heterogeneous nature of the polymerization and the equilibrium between various catalyst species, a quantitative analysis of this catalytic process requires further experiments.

The self-regulating Cu_2O and Cu(0) systems which generate the CuCl/CuCl₂ catalyst in situ should show higher rates upon addition of carboxylates. The addition of NaBz (entry 20, Table 1) or sodium acetate (NaAc) (entry 21, Table 1) to the Cu_2O regulated system (entry 19, Table 1) not only enhances the rate but also removes the induction period and the observed deviation of M_n from M_{th} . Similarly, the Cu(0) (entries 22–24, Table 1) regulated polymerizations of BMA in the presence of

NaBz show higher rates, but M_w/M_n values simultaneously increase up to 1.67.

Recently, Matyjaszewski et al. reported the use of copper acetate (CuAc) and copper 2-thiophene carboxylate (CuTc) as catalysts for the living radical polymerization of styrene initiated with 1-phenylethyl bromide.¹⁰ Higher rates were observed while the initiator efficiencies were low and the M_w/M_n increased to 1.5. To compare CuAc and CuTc with CuCl/NaAc and CuCl/NaTc, respectively, polymerizations of BMA were performed with these catalytic systems (entries 8, 9 and 10, 11; Table 1). The use of the thiophene carboxylate (Tc) salts results in higher rates ($k_p^{\text{exp}} = 3.1\text{--}3.3$) compared to the acetate (Ac) salts ($k_p^{\text{exp}} = 2.1\text{--}2.5$). Both the Tc systems and the Ac systems show the same rate which may indicate the formation of similar active species. However, the use of carboxylic acid salts results in lower M_w/M_n . The lower polydispersity obtained by using carboxylic acid salts can be explained by the slow in situ formation of the active cuprate species. The slow generation of the active catalyst in situ facilitates a better control of the initial stage of the polymerization. This trend is analogous to that found for polymerization of BMA and S, catalyzed by the in situ formed CuCl from Cu_2O .⁶

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Supporting Information Available: Characterization techniques, a typical procedure for polymerization kinetics, and 22 figures containing 22 kinetic plots (24 pages). See any current masthead page for ordering information and Internet access instructions.

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