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Atom Transfer Polymerization of Methyl Methacrylate. Effect of Acids and Effect with 2-Bromo-2-Methylpropionic Acid Initiation

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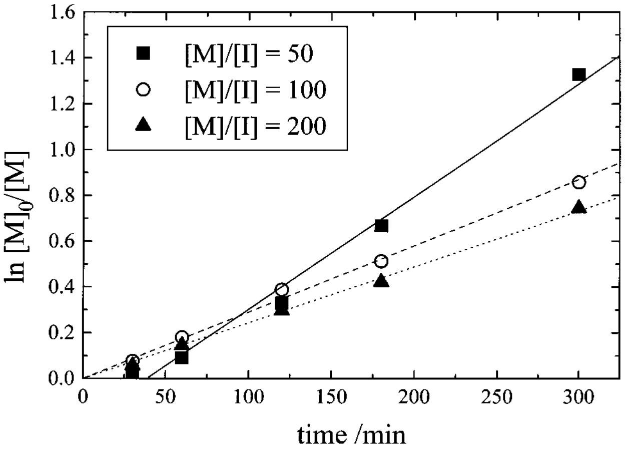

Figure 1. First-order kinetic plots for the ATP of MMA initiated by **1**, mediated by (*N*-*n*-pentyl-2-pyridylmethanimine)copper(I) bromide in xylene solution at 90 °C.

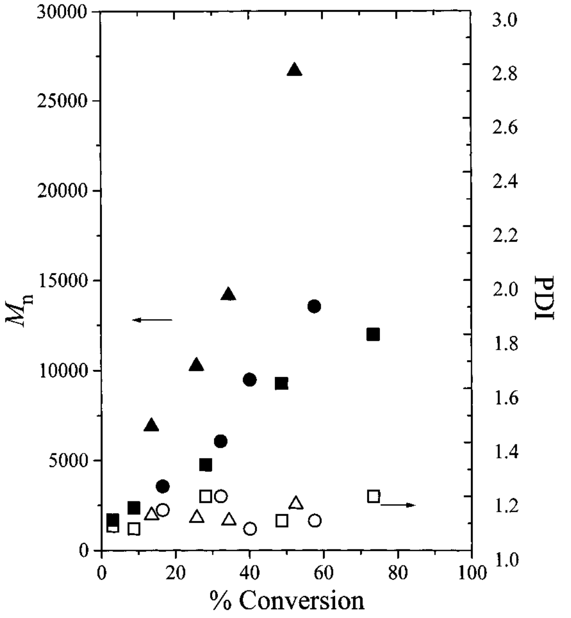

Figure 2. Evolution of M_n (solid) and PDI (open) with conversion for ATP of MMA initiated by **1**, mediated by (*N*-*n*-pentyl-2-pyridylmethanimine)copper(I) bromide in xylene solution at 90 °C: (□, ○, and △) [MMA]/[initiator] = 50, 100, and 200, respectively.

Synthesis of polymers with well-controlled architecture and predictable molecular weight is currently of great academic and industrial interest. Transition metal mediated atom transfer polymerization (ATP) has emerged as an effective living/controlled method for the polymerization of styrenes, methacrylates, acrylates, and acrylonitrile.[1−10] Although the mechanism is not yet fully established, the current belief is that a halogen atom is abstracted, either fully or partially, in a homolytic bond cleavage from either an alkyl halide or sulfonyl halide[7,8] by a transition metal complex. This produces a carbon center which can initiate polymerization in a radical or radical-like fashion with subsequent propagation.[11] Termination is greatly reduced as the halogen atom remains as the ω-terminal end of the propagating chain; thus polymeric radical−radical reactions, resulting in either combination and/or disproportionation, are greatly reduced with the overall concentration of *free* radicals in the reaction extremely small, whichever mechanism operates. Bis(2,2′-bipyridine)- and (substituted 2,2′-bipyridine)copper(I) complexes,[3,12] tris(triphenylphosphine)ruthenium(II) chloride,[1] $Ni[C_6H_3(CH_2NMe_2)_2]Br$,[9] and bis(*N*-*n*-alkyl-2-pyridylmethanimine)copper(I) bromide[10] have all been shown to be efficient mediators/catalysts of such reactions. The polymers made by ATP contain a halogen ω-terminal end group and an α-terminal group originating from the initiator. Thus, ATP is a viable process for producing end-functionalized polymers. Matyjaszewski has reported the use of functional initiators to prepare polystyrene with a variety of α-functionality[13] and we have previously reported the synthesis of α-hydroxyl-functionalized PMMA using 2-hydroxyethyl 2′-methyl-2′-bromopropionate as an ATP initiator.[14] A range of functional initiators have been reported for styrene including allyl, hydroxyl, epoxy, aryl bromide, primary amino, etc.;[13] however, acid functional initiators were not reported and *tert*-butyl protecting groups were used in this instance. Also, although ATP has been demonstrated to be tolerant to, or not poisoned by, a range of functional groups present in the monomer, solvent, etc., polymers of carboxylic acid containing monomers such as methacrylic acid have not been reported, the acids being generally believed to deactivate the metallo-organic catalyst.[2,13,15] The aim of the work described here was 2-fold: first, to investigate the use of 2-bromo-2-methylpropionic acid, **1**, as an initiator for the ATP of MMA to produce α-carboxyl-functionalized PMMA and second, to investigate the effect of carboxylic acids on ATP initiated by a nonfunctional alkyl halide in conjunction with copper(I) *N*-*n*-alkyl-2-pyridylmethanimine complexes.

Methyl methacrylate was polymerized by ATP at 90 °C in xylene solution, initiated with three different concentrations of 2-bromo-2-methylpropionic acid, **1**, relative to MMA in conjunction with a (*N*-*n*-pentyl-2-pyridylmethanimine)copper(I) bromide complex formed in situ.[16] When [MMA]/[**1**] = 50, a conversion of 48.7% was reached within 300 min. After a slow increase in the rate of polymerization for approximately 60 min, a steady rate is achieved, Figure 1. The number average molecular mass, M_n, increases with conversion and the PDI remains at 1.20 or below, Figure 2. Thus the system shows characteristics of a controlled polymerization. The observed M_n, however, is consistently about

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Table 1. Molecular Weight Data for PMMA with Initiation by 1 Mediated by (*N*-*n*-Pentyl-2-pyridylmethanimine)copper(I) Bromide

$[M]_0/[I]_0$	time (min)	conversion (%)	$M_{n(th)}$[a]	$M_{n(SEC)}$	PDI_{SEC}	$10^5 k_p[Pol^*]$[b] (s^{-1})
50	300	73.5	3 850	12 000	1.20	8.20
100	300	57.6	5 930	13 500	1.11	4.83
200	300	52.5	10 700	26 600	1.17	4.07

[a] $M_{n(th)} = [M]_0/[I]_0 \times (MW_{MMA}) \times \text{conversion} + (MW_{init})$, where MW_{MMA} is the molecular weight of MMA monomer (100.12) and MW_{init} is the molecular weight of the initiator (167.01). [b] Calculated from the rate of polymerization: $-d[M]/dt = R_p = k_p[Pol^*][M]$, where [M] is the monomer concentration, R_p is the rate of polymerization, k_p is the propagation rate coefficient, and [Pol*] is the concentration of active species.

Table 2. Data for the ATP of MMA in the Presence of Benzoic Acid (for All Reactions [MMA]:[2]:[CuBr]:[*N*-*n*-butyl-2-pyridylmethanimine] = 100:1:1:3 in Xylene Solution (50 wt %) at 90 °C)

[benzoic acid]/[Cu]	time (min)	conversion (%)	$M_{n(th)}$[a]	$M_{n(SEC)}$	PDI_{SEC}	$k_p[Pol^*]$[b] (s^{-1})
0	120	44.2	4620	6470	1.24	7.98×10^{-5}
0.25	120	66.5	6850	7960	1.29	1.50×10^{-4}
0.5	120	71.1	7310	9590	1.25	1.73×10^{-4}
1	120	81.1	8310	9170	1.49	2.32×10^{-4}
2	120	75.8	7780	10300	1.52	1.98×10^{-4}
4	120	85.1	8720	10000	1.54	2.61×10^{-4}

[a] Defined in footnote *a* of Table 1; $MW_{init} = 195.06$. [b] Defined in footnote *b* of Table 1.

3 times greater than the theoretical value throughout the polymerization. When the [MMA]/[**1**] is increased to 100 the rate approximately is cut in half and the observed M_n values increase, although again they stay well above that expected, Table 1. A further increase in [MMA]/[**1**] to 200 results in an increase in M_n but no apparent change in rate of polymerization. In all cases the PDI remains at 1.20 or below. 2-Bromo-2-methylpropionic acid is an effective initiator for the ATP of MMA under these conditions. The acid functionality does not totally deactivate the catalyst; indeed, the values of PDI obtained are very narrow. The acid does, however, cause an increase in the observed M_n, i.e., a decrease in initiator efficiency. Thus, **1** has more than one role in the reaction. We can ascribe the decrease in initiator efficiency as a proportion of **1** complexing with copper to produce an, as yet unidentified, new copper species accompanied by a corresponding reduction in active initiator present.

To further investigate this dual role of the carboxylic acid functionality we carried out ATP of MMA in the presence of benzoic acid with ethyl 2-bromoisobutyrate, **2**, as initiator in the presence of CuBr and *N*-*n*-butyl-2-pyridylmethanimine.[17] When the ratio of benzoic acid to copper(I) bromide is 0.5 or less, the PDI of the product remains fairly narrow, Table 2. The addition of benzoic acid increases the rate of polymerization, and the first order kinetic plots are linear, indicating that little termination occurs, Figure 3. When the amount of benzoic acid is increased, until there is a stoichiometric amount relative to copper(I), a further increase in rate is observed, but this is accompanied by a broadening of the PDI. Further increasing the amount of acid causes a broadening of PDI but no further increase in the rate of polymerization, Figure 4. Again, these results suggest that the carboxylic acid functionality has a role in ATP of MMA under these conditions. Low levels of acid increase the rate, but when the concentration of acid is relatively high, a poisoning of the copper catalyst occurs.

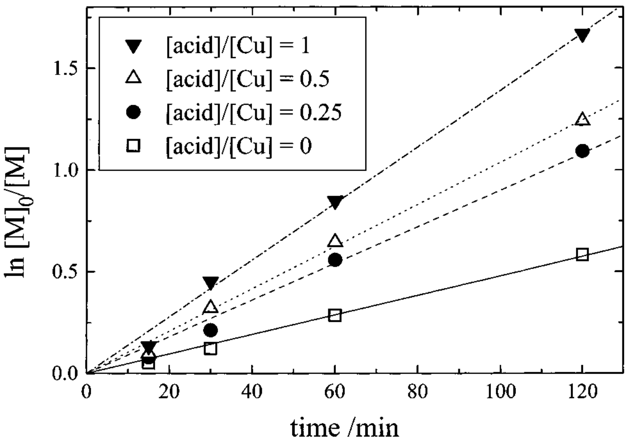


Figure 3. First-order kinetic plots for the ATP of MMA in the presence of benzoic acid initiated by **2** and mediated by (*N*-*n*-butyl-2-pyridylmethanimine)copper(I) bromide in xylene solution at 90 °C.

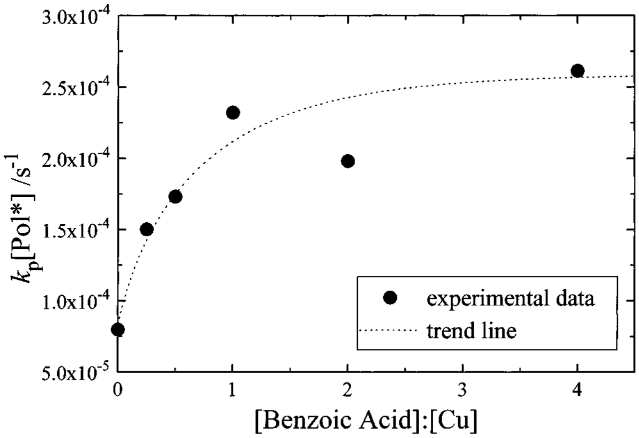
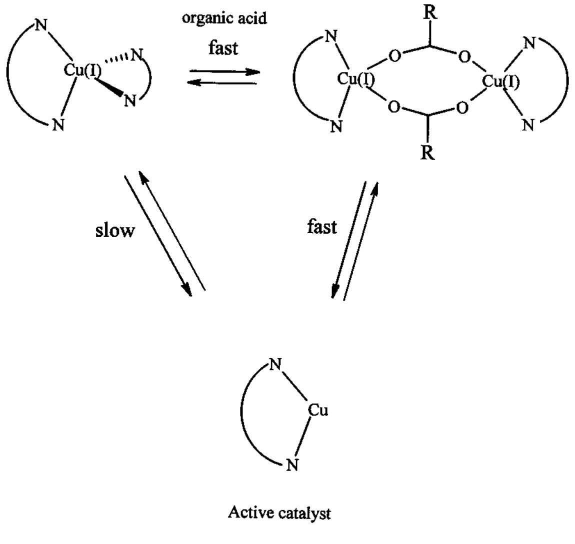


Figure 4. Dependence of $k_p[Pol^*]$ on the amount of benzoic acid present relative to copper(I) bromide for the ATP of MMA initiated by **2** and mediated by (*N*-*n*-butyl-2-pyridylmethanimine)copper(I) bromide in xylene solution at 90 °C.

Scheme 1



We envisage that the initial role of the acid is to complex with the copper, displacing one Schiff base ligand and creating a coordination site on the metal allowing propagation to occur; for example, Scheme 1. In the absence of acid the loss of the Schiff base ligand is slower, reducing the rate of formation of the active species during both initiation and propagation. This is currently under investigation in our laboratory.

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Supporting Information Available: Tables giving further polymerization conversion and molecular weight data (2 pages). Ordering and access information is given on any current masthead page.

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(16) Degassed MMA (10 mL) was added to CuBr (0.134 g) in a Schlenk tube previously purged with nitrogen. *N*-*n*-pentyl-2-pyridylmethanimine (0.33 g) and degassed xylene (20 mL) were added and the solution heated to 90 °C prior to addition of 2-bromo-2-methylpropionic acid, **1** (0.156 g). [MMA]:[CuBr]:[*N*-*n*-pentyl-2-pyridylmethanimine]:[**1**] = 100:1:2:1. Conversion was measured by gravimetry.
(17) Polymerizations carried out as in ref 16 except for 10 mL of xylene (50 wt %), *N*-*n*-butyl-2-pyridylmethanimine used as Schiff base ligand, and ethyl-2-bromoisobutyrate, **2**, used as initiator. [MMA]:[CuBr]:[*N*-*n*-pentyl-2-butylmethanimine]:[**2**] = 100:1:3:1.

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