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ATRP of MMA in Polar Solvents Catalyzed by $FeBr_2$ without Additional Ligand

Yu Wang and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering,
Department of Chemistry, Carnegie Mellon University,
4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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Atom transfer radical polymerization (ATRP)[1−5] is one of the most extensively studied controlled radical polymerization methods.[6] Several transition metals, such as Cu, Ru, Fe, Ni, and Os, have been successfully employed as ATRP catalysts.[7] From an economic standpoint Fe is very attractive because it has the lowest toxicity and lowest price. Successful Fe-based ATRP, in the presence of various phosphine, amine, or pyridine containing ligands, was first reported in 1997 by Sawamoto[8] and Matyjaszewski.[9] During the past decade, other Fe-based catalyst systems were developed for ATRP. The active catalyst complexes contained half-metallocene,[10] amines,[11] diimines,[12] substituted phosphines,[13] carbenes,[14] carboxylic acids,[15,16] or halide ligands forming anionic Fe species[17,18] or ionic liquids.[19] Most of these reactions were carried out in bulk monomer or relatively nonpolar solvents. In this report we present results of ATRP of methyl methacrylate (MMA) in polar solvents without any additional ligand. This system provides a low cost and environmentally friendly ATRP process.

$FeBr_2$-catalyzed ATRP of MMA was well controlled when the reaction was conducted in several polar solvents, such as NMP, DMF, and MeCN (Table 1). The polymerizations were carried out at 60 °C with the ratio [MMA]:[EBrPA]:[$FeBr_2$] = 100:1:1 (EBrPA:ethyl 2-bromo-2-phenylacetate), MMA/solvent = 2/1 (v/v), without any additional ligand. After 8 h, the conversions had reached 68.4%, 41.4%, and 34.2% in NMP, DMF, and MeCN, respectively. In these three solvents, the molecular weights of the obtained PMMA agreed with the theoretical values, while the M_w/M_n values remained low (1.26−1.28). However, when DMSO was used as the solvent, the polymerization was not controlled. The conversion reached 36.4% with a molecular weight of 4500 after 8 h, higher than the theoretical value, while the M_w/M_n value was as high as 2.16. Since $FeBr_2$ is not soluble in anisole, the polymerization did not occur, even after 8 h. However, in the presence of tri(*n*-butyl)phosphine (TBP) as a ligand, the polymerization was well controlled in anisole but with a relatively low activity. Conversion reached 27% in 8 h, providing a PMMA with molecular weight of 2700 (M_w/M_n = 1.18). However, in an identical system, when 1 equiv of DMSO (vs Fe) was added, a decrease in activity was observed, although the control was retained. The conversion reached 19.1% in 8 h with a molecular weight of 2100 (M_w/M_n = 1.19). The addition of 10 equiv of DMSO resulted in an uncontrolled polymerization. The molecular weight was nearly 3 times higher than the theoretical value, while M_w/M_n values reached 2.24.

These experiments suggest that certain polar solvents can act as ligands for Fe species. Solvents containing either an amide or a cyano group can facilitate $FeBr_2$ dissolution and lead to controlled polymerization, although the coordination of the solvent with the Fe could be weak. Fe(II) complexes with MeCN as one of the ligands were previously isolated; however, these complexes lost MeCN rapidly at ambient conditions.[20] DMSO coordinates much stronger to Fe and can displace halide ligands.[21] This leads to a negative effect on the catalytic activity, and therefore the polymerization in DMSO was not well controlled.

Table 1. ATRP of MMA in Different Solvents Catalyzed by $FeBr_2$ in the Absence of Additional Ligands[a]

solvent	conv (%)	$M_{n,GPC}$	$M_{n\ th}$	M_w/M_n
NMP	68.4	6900	7080	1.27
DMF	41.4	4600	4380	1.28
MeCN	34.2	3100	3660	1.26
DMSO	36.4	4500	3880	2.16
anisole	no polymer			
anisole[b]	27.0	2700	2940	1.18
anisole/DMSO[c]	19.1	2100	2140	1.19
anisole/DMSO[d]	35.0	10300	3730	2.24

[a] [MMA]:[EBrPA]:[$FeBr_2$] = 100:1:1, MMA/solvent = 2/1 (v/v), at 60 °C, after 8 h polymerization. [b] 1 equiv of TBP was added as ligand. [c] 1 equiv of DMSO vs Fe was added with 1 equiv of TBP as ligand. [d] 10 equiv of DMSO was added with 1 equiv of TBP as ligand.

Since NMP has the highest activity among the solvents investigated for $FeBr_2$-catalyzed ATRP of MMA, NMP was chosen for the subsequent studies.

NMP was added at different concentrations (10%, 33.3%, and 66.7% v/v) for the $FeBr_2$-catalyzed ATRP of MMA at 60 °C with the ratio [MMA]:[EBrPA]:[$FeBr_2$] = 100:1:1 (Figure 1). With 10% NMP, the polymerization was relatively fast and conversion reached 55.3% in 100 min, yielding PMMA with a molecular weight 5200 and M_w/M_n = 1.21. Increased amounts of NMP resulted in slower polymerizations. Conversions reached 40.4%, 15.9%, and 8% after 1 h with 10%, 33.3%, and 66.7% NMP, respectively, yielding polymers with the following molecular weights and M_w/M_n values: M_n = 3600, M_w/M_n = 1.25; M_n = 2300, M_w/M_n = 1.42; M_n = 1700, M_w/M_n = 1.52. M_w/M_n values were relatively high at the beginning of the polymerization reactions but decreased to lower values with the progress of ATRP. Slightly curved kinetic plots were observed for the polymerizations with 10% and 33.3% NMP, indicating that limited radical terminations occurred. Experimental molecular weights agreed well with the theoretical values. When 66.7% NMP was used, the polymerization rate decreased after 4 h and the molecular weights were slightly higher than calculated values, indicating the lower initiation efficiency (83%). The minimum amount of NMP could be close to 10% since the reaction mixture became slightly heterogeneous when lower levels were examined. ATRP of MMA at 60 °C with the ratio [MMA]:[EBrPA]:[$FeBr_2$] = 200:1:1 with 10% NMP reached 88.6% conversion after 24 h, yielding PMMA with molecular weight 17 400 and M_w/M_n = 1.20.

In order to determine whether it was possible to achieve a better control over polydispersity, a small amount of $FeBr_3$ was added at the beginning of polymerization. With the ratio [MMA]:[EBrPA]:([$FeBr_2$] + [$FeBr_3$]) = 100:1:1 in 33.3% NMP at 60 °C, when the initial ratio [$FeBr_2$]:[$FeBr_3$] was 9.5:0.5, the polymerization rate and M_w/M_n values were nearly the same as in the absence of $FeBr_3$. This could indicate that more than 5% $FeBr_3$ is formed by radical termination at the beginning of the polymerization, although it was not purposely added. When the initial ratio of added iron bromide salts was [$FeBr_2$]:[$FeBr_3$] = 9:1, the polymerization became slower and better control (M_w/M_n = 1.2−1.25) was observed (Figure 2).

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*Corresponding author. E-mail: km3b@andrew.cmu.edu.

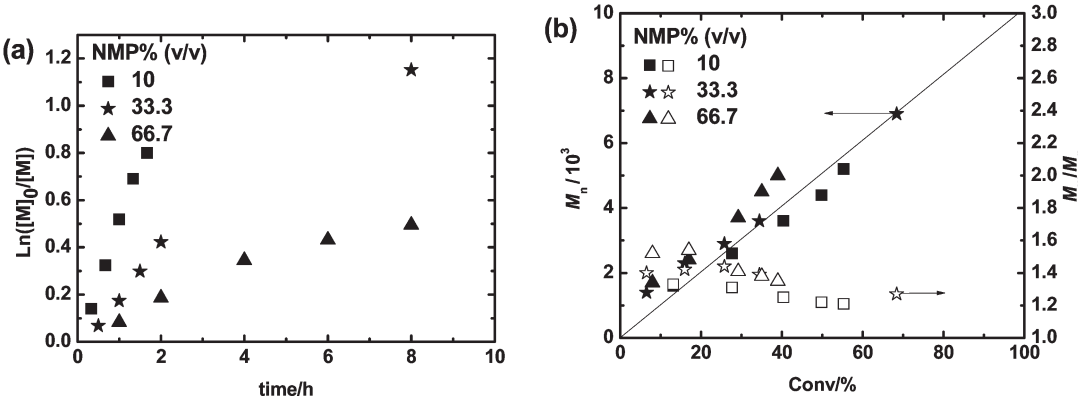

Figure 1. (a) Kinetic plots of ln([M]$_0$/[M]) vs time and (b) Plot of number-average molecular weights M_n and M_w/M_n values vs conversion for FeBr$_2$-catalyzed ATRP of MMA with different amounts of NMP. [MMA]:[EBrPA]:[FeBr$_2$] = 100:1:1 at 60 °C.

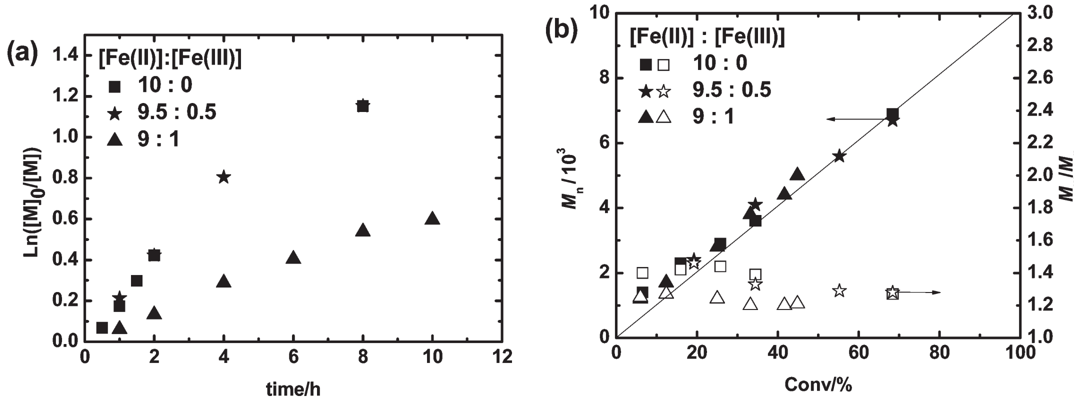

Figure 2. (a) Kinetic plots of ln([M]$_0$/[M]) vs time and (b) plot of number-average molecular weights M_n and M_w/M_n values vs conversion for FeBr$_2$-catalyzed ATRP of MMA in the presence of different amounts of FeBr$_3$. [MMA]:[EBrPA]:([FeBr$_2$] + [FeBr$_3$]) = 100:1:1 at 60 °C in 33.3% (v/v) NMP.

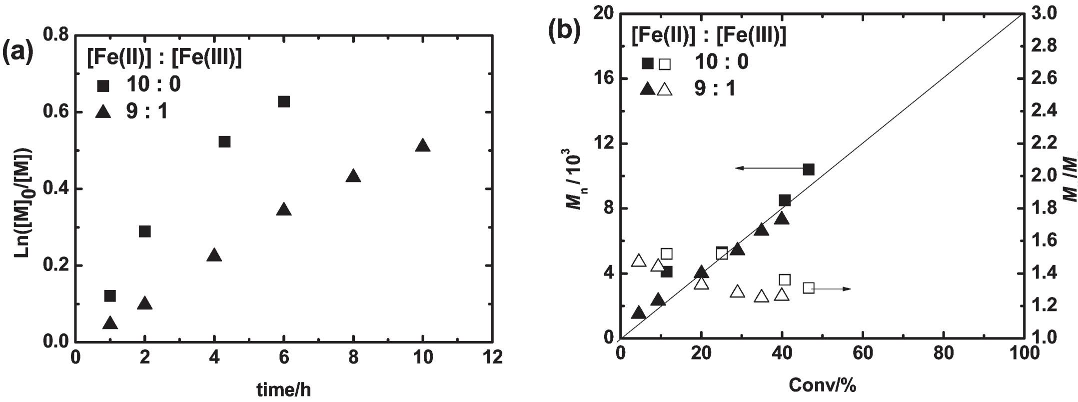

Figure 3. (a) Kinetic plots of ln([M]$_0$/[M]) vs time and (b) plot of number-average molecular weights M_n and M_w/M_n value vs conversion for FeBr$_2$-catalyzed ATRP of MMA in the presence of different ratio of FeBr$_3$. [MMA]:[EBrPA]:([FeBr$_2$] + [FeBr$_3$]) = 200:1:1 at 60 °C in 33.3% (v/v) NMP.

The polymerization was also well controlled at 60 °C with a targeted degree of polymerization of 200, [MMA]:[EBrPA]:([FeBr$_2$] + [FeBr$_3$]) = 200:1:1 in 33.3% NMP, and conversion reached 46.6% in 6 h, while the M_w/M_n values decreased from 1.52 to 1.31. The molecular weights according to GPC analysis agreed very well with the theoretical values. In the presence of small amount of FeBr$_3$ ([FeBr$_2$]:[FeBr$_3$] = 9:1) polymerization was slower and control was improved (M_w/M_n values decreased from 1.47 to 1.26) (Figure 3).

In summary, FeBr$_2$ successfully catalyzed ATRP of MMA in NMP, DMF, and MeCN in the absence of additional ligand, but the polymerization was not controlled in DMSO. Certain polar solvents might act as ligands that dissolve FeBr$_2$ and also adjust the catalytic activity (i.e., ATRP equilibrium constant), leading to well-controlled polymerization. The amount of NMP could be reduced to as low as 10% and still dissolve most of the FeBr$_2$ and maintained control over polymerization. Addition of a small amount of FeBr$_3$ can further improve the control over molecular weight distribution.

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