

# Effects of the Solvent Polarity on the Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by 4-(Chloromethyl)phenyltrimethoxysilane

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**ABSTRACT:** The controllability of the atom transfer radical polymerization of methyl methacrylate in the polar solvent *N,N*-dimethylformamide and the nonpolar solvent xylene with 4-(chloromethyl)phenyltrimethoxysilane as an initiator and with CuCl/2,2'-bipyridine and CuCl/4,4'-di(5-nonyl)-2,2'-bipyridine as catalyst systems was studied. Gel permeation chromatography analysis established that in the nonpolar solvent xylene, much better control of the molecular weight and polydispersity of poly(methyl methacrylate) was achieved with the CuCl/4,4'-di(5-nonyl)-2,2'-

bipyridine catalyst system than with the CuCl/2,2'-bipyridine as catalyst system. In the polar solvent *N,N*-dimethylformamide, unlike in xylene, the polymerization was more controllable with the CuCl/2,2'-bipyridine catalyst system than with the CuCl/4,4'-di(5-nonyl)-2,2'-bipyridine catalyst system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2751–2754, 2007

**Key words:** atom transfer radical polymerization (ATRP); living polymerization

## INTRODUCTION

Nanostructured organic/inorganic hybrid materials combine the properties of both inorganic nanoparticles and polymers.<sup>1,2</sup> In our previous work, we have focused on the synthesis of nanoparticle/polymer composites by grafting a polymer chain through a monomer covalently linked to the inorganic particle surface.<sup>3</sup> Because the grafting efficiency is very low, we decided to graft a polymer chain from the surface of nanoparticles modified with a polymerization initiator in our further work. In this process, a controlled/living polymerization technique would be optimal because such methods afford control over the molecular weight, molecular weight distribution, and structure of the resulting polymers.<sup>4,5</sup> Therefore, 4-(chloromethyl)phenyltrimethoxysilane (CMTMS), which has three methoxyl groups and a benzyl chlo-

ride group, was chosen both as the silane coupler, which can be linked to the inorganic particles, and as the atom transfer radical polymerization (ATRP) initiator.

There are many reports of ATRP catalyzed by copper halides complexed with 2,2'-bipyridine (bpy) and its derivatives<sup>5–12</sup> and studies of solvent effects on ATRP.<sup>13–17</sup> In different systems, ligand and solvent effects on ATRP are diverse to some extent. To well control the ATRP initiated by CMTMS linked to the inorganic particle surface, first we studied the ATRP of methyl methacrylate (MMA) initiated by free initiator CMTMS. Because the solvents and the ligands affect the control of polymerization very much, in the context of this work, we focused on the effects of the solvent polarity on the ATRP of MMA initiated by CMTMS.

## EXPERIMENTAL

### Materials

MMA was purchased from the Chengdu Kelong Chemical Reagent Factory (Chengdu, China) and distilled under reduced pressure before use. CuCl, purchased from the Chengdu Kelong Chemical Reagent Factory, was purified through washing with 5% HCl and methanol and then dried under argon. Xylene, tetrahydrofuran (THF), and bpy (analytical reagent) were used as received from the Chengdu Kelong Chemical Reagent Factory. 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy; 97%) was used as received

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from Aldrich (Schnelldorf, Germany). CMTMS (97%) was used as received from Fluorochem (Derbys, UK). *N,N*-Dimethylformamide (DMF) was used as received from the Chengdu Changlian Chemical Reagent Factory (Chengdu, China).

### Polymerization

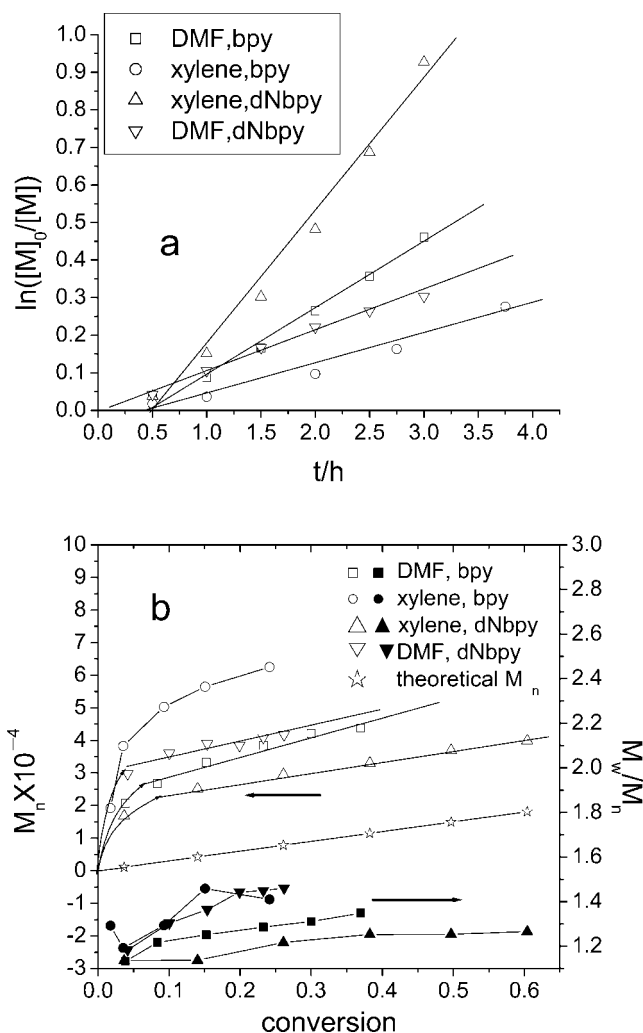
All experiments described in this work were conducted with the following ratios:  $[MMA]/[CMTMS]/[CuCl]/[ligand] = 300/1/1/2$  and  $MMA/solvent = 1/1$  (v/v). The polymerization was carried out under argon in a dried flask equipped with a magnetic stirring bar. The flask was charged with MMA and CuCl, sealed with a rubber septum, and then degassed to remove oxygen for 0.5 h at room temperature. Then, the ligand, solvent, and CMTMS were added in turn. The mixture was continually stirred under argon at room temperature for 40 min, and then the flask was quickly immersed in a water bath heated at 95°C. Samples were taken periodically via syringe to determine the conversion (gravimetry), molecular weight, and molecular weight distribution [gel permeation chromatography (GPC) analysis]. Before the GPC analysis, the samples should be dissolved in THF, treated with 10% HF, precipitated in methanol, and dried.

### Analysis

The monomer conversion was determined by gravimetry. The number-average molecular weight ( $M_n$ ) and polydispersities ( $M_w/M_n$ , where  $M_w$  is the weight-average molecular weight) of the obtained polymers were measured by GPC at 35°C on a Waters 2410 instrument (Agilent Technology, Inc., CA) with THF as the solvent (1.0 mL/min), with calibration with polystyrene standards, and with Waters Millennium 32 as the data-processing software. Thin-layer chromatography (TLC) was used to compare the polarities of bpy and dNbpy, and the developing agent was 4/1 (v/v) petroleum ether/ethyl acetate.

## RESULTS AND DISCUSSION

The polar solvent DMF and the nonpolar solvent xylene were chosen to study the effects of solvent polarity on the ATRP of MMA initiated by CMTMS. DMF has a relatively high polarity (dipole moment = 3.82 D), and xylene has a relatively low polarity (dipole moment = 0.62 D).<sup>18</sup> TLC experiments have shown that bpy has higher polarity than dNbpy. According to the rule of similarity, bpy is more soluble in DMF than dNbpy, and dNbpy is more soluble than bpy in xylene. This leads to poor solubility of the CuCl/bpy complex and CuCl<sub>2</sub>/bpy complex in



**Figure 1** Polymerizations of MMA in solution at 95°C with different solvents (DMF and xylene) and different ligands (bpy and dNbpy): (a) first-order kinetic plots and (b) dependence of  $M_n$  and  $M_w/M_n$  of PMMA on the conversion (experimental conditions:  $[MMA]/[CMTMS]/[CuCl]/[ligand] = 300/1/1/2$ ,  $MMA/solvent = 1/1$  v/v).

xylene, poor solubility of the CuCl/dNbpy complex and CuCl<sub>2</sub>/dNbpy complex in DMF, good solubility of the CuCl/dNbpy complex and CuCl<sub>2</sub>/dNbpy complex in xylene, and good solubility of the CuCl/bpy complex and CuCl<sub>2</sub>/bpy complex in DMF.

The polymerizations of MMA show approximately first-order kinetics with respect to the monomer concentration for all polymerization systems used, as shown in Figure 1(a), and this indicates that the number of active species remained constant during the polymerizations. The slopes of the kinetic plots reflect the polymerization rates. The bigger the slope is, the faster the polymerization rate is. In other words, the slope of the kinetic plot stands for the apparent propagation rate constant ( $k_p^{app}$ ).<sup>19</sup> Assuming that propagation occurs via normal free radicals, the stationary concentration of radicals,  $[P^*]$ , can be

**TABLE I**  
Values of  $k_p^{\text{APP}}$  and  $[P\cdot]$  for the ATRP of  
MMA in Solution at 95°C

Solvent/ligand	$k_p^{\text{APP}} \times 10^5 \text{ (s}^{-1}\text{)}$	$[P\cdot] \times 10^8 \text{ (mol/L)}$
Xylene/bpy	1.00	0.59
Xylene/dNbpy	7.63	4.49
DMF/bpy	3.96	2.33
DMF/dNbpy	2.93	1.72
DMF/bpy <sup>a</sup>	0.98	0.58

[MMA]/[CMTMS]/[CuCl]/[ligand] = 300/1/1/2; MMA/solvent = 1/1 (v/v).

<sup>a</sup> [CuCl]/[CuBr<sub>2</sub>] = 10/1.

estimated from the ratio of  $k_p^{\text{APP}}$  and the rate constant of radical propagation ( $k_p$ ), which can be calculated by the equation

$$k_p \text{ (L mol}^{-1} \text{ s}^{-1}\text{)} = 2.39 \times 10^6 \exp(-5300 \text{ cal mol}^{-1}/RT)$$

where R is the universal gas constant, and T is the absolute temperature.<sup>20</sup> That is,  $[P\cdot] = k_p^{\text{APP}}/k_p$ .<sup>19</sup> Detailed data for  $k_p^{\text{APP}}$  and  $[P\cdot]$  for all the polymerization systems are listed in Table I.

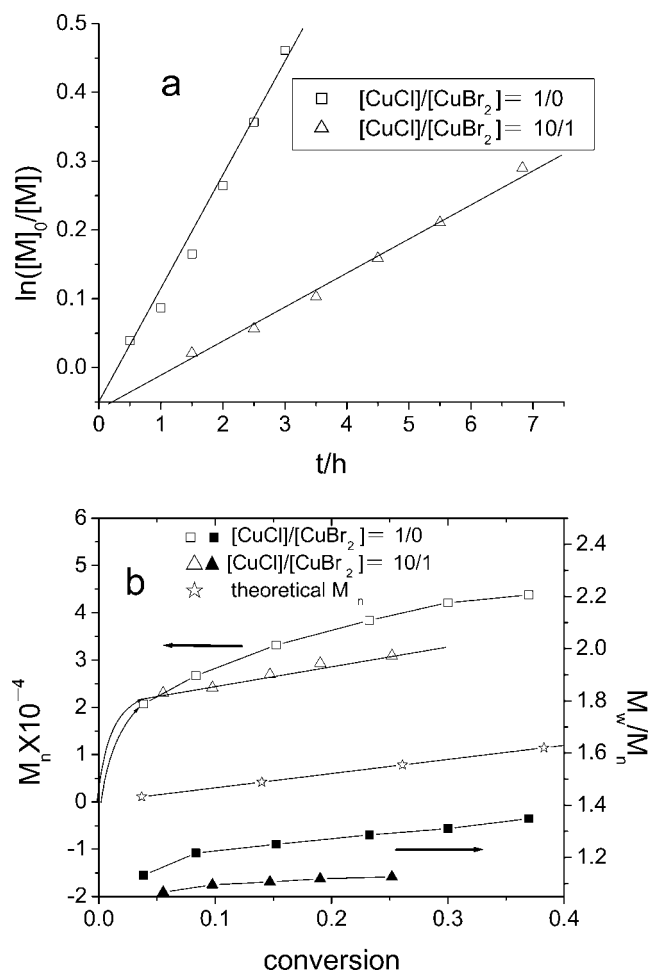
In the nonpolar solvent xylene, the polymerization is much slower with ligand bpy than dNbpy; that is,  $k_p^{\text{APP}}$  (xylene/bpy) is about  $1.00 \times 10^{-5} \text{ s}^{-1}$  and  $k_p^{\text{APP}}$  (xylene/dNbpy) is about  $7.63 \times 10^{-5} \text{ s}^{-1}$  (Table I).  $[P\cdot]$  ( $0.59 \times 10^{-8} \text{ mol/L}$ ) is quite low when polymerization occurs in xylene with bpy as the ligand (Table I); however, the controllability of the polymerization is very poor, as indicated by high molecular weights and broad molecular weight distributions [ $M_w/M_n = 1.41$ ; Fig. 1(b)]. This is attributed to the poor solubility of the CuCl/bpy complex and CuCl<sub>2</sub>/bpy complex in xylene. Without enough activator CuCl/bpy complex in the solution, few radicals are produced, and this leads to a low polymerization rate. At the same time, the concentration of the deactivator is also low, and this results in slower deactivation of the propagating radicals. A lower deactivation rate makes it advantageous to add monomer units to the active radical during a single activation/deactivation cycle. Therefore, the polymer molecular weights are much higher than the theoretical ones, and the molecular weight distributions are relatively broad.

In xylene, when the long alkyl group was introduced to bpy (e.g., dNbpy), the control of the polymerization was improved. When dNbpy was used as the ligand, the polymerization rate was much higher [ $k_p^{\text{APP}}$ (xylene/bpy) =  $1.00 \times 10^{-5} \text{ s}^{-1}$  and  $k_p^{\text{APP}}$ (xylene/dNbpy) =  $7.63 \times 10^{-5} \text{ s}^{-1}$ ], and the molecular weight distribution ( $M_w/M_n = 1.26$ ) was narrower than that when bpy was used as the ligand [ $M_w/M_n = 1.41$ ; Fig. 1(b)]. The good solubility of the CuCl/dNbpy complex and CuCl<sub>2</sub>/dNbpy complex in xylene quickly establishes the equilibrium between

the radicals and alkyl halides, and this results in controllable polymerizations.

In the polar solvent DMF, unlike in the nonpolar solvent xylene, the polymerization is more controllable with bpy as the ligand than dNbpy. As shown in Figure 1, not only is the polymerization rate higher [ $k_p^{\text{APP}}$ (DMF/bpy) =  $3.96 \times 10^{-5} \text{ s}^{-1}$  and  $k_p^{\text{APP}}$ (DMF/dNbpy) =  $2.93 \times 10^{-5} \text{ s}^{-1}$ ], but the molecular weight distributions are also narrower [ $M_w/M_n$ (bpy) = 1.35 and  $M_w/M_n$ (dNbpy) = 1.46]. The different solubilities of bpy and dNbpy in DMF and xylene, respectively, may cause the differences in the polymerization control in DMF and xylene. The CuCl/bpy complex and CuCl<sub>2</sub>/bpy complex are more soluble in DMF than the CuCl/dNbpy complex and CuCl<sub>2</sub>/dNbpy complex. With bpy as the ligand, the equilibrium is quickly established between the radicals and alkyl halides, and this is helpful for the polymerization controllability.

Therefore, in DMF, the polymerization is more controllable with bpy as the ligand than with dNbpy. On



**Figure 2** Polymerizations of MMA in DMF at 95°C with or without CuBr<sub>2</sub> ([MMA]/[CMTMS]/[CuCl + CuBr<sub>2</sub>]/[ligand] = 300/1/1/2, MMA/DMF = 1/1 v/v): (a) first-order kinetic plots and (b) dependence of  $M_n$  and  $M_w/M_n$  of PMMA on the conversion.

the contrary, in xylene, the polymerization is more controllable with dNbpy as the ligand than with bpy.

Figure 1(b) shows that, in all cases, initially the molecular weights are higher than predicted, and there are two reasons that may account for this. One is the inefficient initiation; the other is the slow deactivation at the beginning of the polymerization. To prove the second reason, some CuBr<sub>2</sub> as a deactivator was added to the polymerization system for comparison with the polymerization without CuBr<sub>2</sub>. The results are shown in Figure 2. Figure 2(a) shows the first-order kinetic plots, and Figure 2(b) shows the dependence of  $M_n$  and  $M_w/M_n$  of poly(methyl methacrylate) (PMMA) on the conversion. Figure 2(b) shows that even when some deactivator is added at the beginning of the polymerization, just like the systems without CuBr<sub>2</sub>, initially the molecular weights are higher than predicted, and this indicates that slow deactivation at the beginning is not the main reason for the high molecular weights. The main reason is thought to be the inefficient initiation. Polymerization with a small amount of CuBr<sub>2</sub> is about 4 times slower [ $k_p^{\text{app}}([\text{CuCl}]/[\text{CuBr}_2] = 10/1) = 0.98 \times 10^{-5} \text{ s}^{-1}$  and  $k_p^{\text{app}}([\text{CuCl}]/[\text{CuBr}_2] = 10/0) = 3.96 \times 10^{-5} \text{ s}^{-1}$ ], and the molecular weight distribution is narrower than the one without CuBr<sub>2</sub> [ $M_w/M_n([\text{CuCl}]/[\text{CuBr}_2] = 10/1) = 1.15$  and  $M_w/M_n([\text{CuCl}]/[\text{CuBr}_2] = 10/0) = 1.35$ ], as shown in Table I and Figure 2. The increase in the concentration of the deactivator makes  $[P\cdot]$  very low, about  $0.58 \times 10^{-8} \text{ mol/L}$  (Table I), and suppresses the termination of radicals and chain transfer of radicals. Therefore, except for the lower polymerization rate, the polymerization is more controllable when some deactivators are added at the beginning of the polymerization.

Besides, we have found that DMF affects the ATRP of MMA. Some works have also found that DMF can not only affect the thermal decomposition of initiators<sup>21</sup> but also affect the rate of polymerization.<sup>22–24</sup> It is thought that DMF can also affect the ATRP of MMA not only as a solvent but also as a catalyst for the polymerization to some extent, this will be studied in our further work.

## CONCLUSIONS

The polarity of the solvents affects the solubility of transition-metal complexes in solution. The better solubility of the transition-metal complex, CuCl/ligand, in solution leads to better controllability of the polymerization. The inefficient initiation is thought to be the main reason for the molecular weights being initially higher than predicted.

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