Reverse Atom Transfer Radical Polymerization of Methyl Methacrylate in Different Solvents

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ABSTRACT: The reverse atom transfer radical polymerization of methyl methacrylate was investigated in different solvents: xylene, *N,N*-dimethylformamide, and pyridine. The polymerizations were uncontrolled, using 2,2′-bipyridine as a ligand in xylene and pyridine because the catalyst ($CuBr_2$/2,2′-bipyridine complex) had poor solubility in the xylene system. In the pyridine system, the solubility of the catalyst increased, but the solvent could complex with $CuBr_2$, which influenced the control of the polymerization. In the *N,N*-dimethylformamide system, the catalyst could be dissolved in the solvent completely, but the —$N(CH_3)_2$ group in *N,N*-dimethylformamide could also complex with $CuBr_2$, so the polymerization could not be well controlled. The ligand of 4,4′-di(5-nonyl)-2,2′-bipyridine was also investigated in xylene; the introduction of the —$CH(C_4H_9)_2$ group enabled the $CuBr_2$/4,4′-di(5-nonyl)-2,2′-bipyridine complex to easily dissolve in xylene, and the polymerizations were well controlled. The number-average molecular weight increased linearly with the monomer conversion from 4280 to 14,700. During the whole polymerization, the polydispersities were quite low (1.07–1.10). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2543–2547, 2007

Key words: atom transfer radical polymerization (ATRP); kinetics (polym.); living polymerization

INTRODUCTION

In recent years, there has been great interest in controlled/living radical polymerization methods, such as nitroxide-mediated stable free-radical polymerization,[1,2] atom transfer radical polymerization (ATRP),[3–19] and reversible addition–fragmentation chain transfer,[20] which have been developed through the living radical polymerization process. ATRP is one of the most promising systems. It is a versatile technique for the synthesis of well-defined polymers with various architectures, such as block,[21–25] graft,[26–29] and star polymers,[30,31] and narrow molecular weight distributions.

The effects of solvents on ATRP have been studied.[15] We chose different solvents for polymerizations, including the nonpolar solvent xylene and the polar solvent *N,N*-dimethylformamide (DMF), and we investigated their effects on ATRP. In the xylene system, the $CuBr_2$/2,2′-bipyridine (bpy) complex had low solubility, which led to low catalyst efficiency, so the polymerization was uncontrolled. To increase the solubility of the catalyst in the solvent, pyridine was used as the solvent on the basis of the rule of similarity. The polymerization was uncontrolled because pyridine could also complex with $CuBr_2$, which could not be the catalyst. The controllability of the polymerization was better in DMF than in xylene, but the molecular distribution was even higher (weight-average molecular weight/number-average molecular weight > 1.2). From the UV absorbance, we could see that the —$N(CH_3)_2$ group in the DMF molecule could also complex with $CuBr_2$, which also led to low catalyst efficiency, so DMF was not a proper solvent for copper-based reverse ATRP. The results were different from those of Liu and Hu.[14] The ligand of 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) was also investigated in the xylene system. The $CuBr_2$/dNbpy complex could be well dissolved in xylene, and the polymerization was well controlled.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China) and distilled under reduced pressure before use. $CuBr_2$ (98.5%), xylene, DMF, and pyridine all
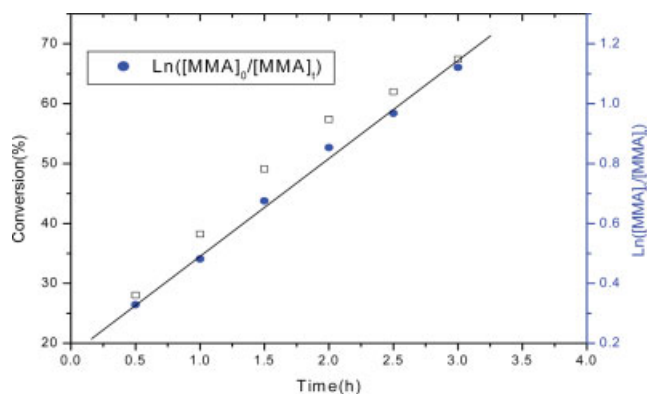
Figure 1 Time dependence of $\ln([MMA]_0/[MMA]_t)$ and the conversion with the $CuBr_2/$bpy complex as the catalyst at 80°C in the xylene solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

came from Chengdu Kelong Chemical Reagent Factory and were used directly. 2,2'-Azobisisobutyronitrile (AIBN; analytical reagent) was obtained from Beijing Chemical Reagent Factory (Beijing, China) and recrystallized from methanol before use. bpy (analytical reagent) came from Beijing Shiying Chemical Reagent Factory (Beijing, China) and was used directly. dNbpy (97%) came from Aldrich and was used as received.

Polymerization

A 150-mL Schlenk flask equipped with a magnetic stirrer was charged with MMA and $CuBr_2$; under argon protection, the mixture was stirred for 0.5 h. AIBN and the ligand were dissolved in the solvent and then added to the Schlenk flask. At room temperature and under an argon atmosphere, the mixture of the ligand, solvent, MMA, $CuBr_2$, and AIBN was stirred for 1 h and then placed in a water bath with magnetic stirring at 80°C. The reactions were carried out with stirring and under argon for 3 h. Samples were taken periodically via a syringe to monitor the conversion and molecular weight. The monomer conversion was determined gravimetrically, and then the samples were dissolved in acetone, precipitated in methanol, and dried.

Characterization

The monomer conversion was determined gravimetrically. The number-average molecular weights and polydispersities (weight-average molecular weight/number-average molecular weight) of the obtained polymers were measured at 35°C by gel permeation chromatography on a Waters 2410 instrument (Agident Technology, Santa Clara, CA) with tetrahydrofuran as the solvent (1.0 mL/min), with polystyrene

standards for calibration, and with Waters Millennium 32 as the data-processing software. The absorbance of the solution was measured on a Beijing Purkinje General Instrument Co., Ltd. (Beijing, China), T5 ultraviolet–visible (UV–vis) spectrophotometer.

RESULTS AND DISCUSSION

The radical polymerization of MMA, with the $CuBr_2/$bpy complex as the catalyst, was carried out in xylene. Figure 1 shows that the conversion of MMA increased from 28.0 to 67.4% within 3 h. Also, the kinetics were first-order in the monomer. Figure 2 shows that the number-average molecular weight increased with the monomer conversion. The increase in the number-average molecular weight was not linear with the monomer conversion, and the polydispersities were too high (weight-average molecular weight/number-average molecular weight = 2.3) for a controlled radical polymerization. The whole polymerization was uncontrolled. The experimental phenomena showed that there was a lot of insoluble $CuBr_2$ at the bottom of the flask throughout the polymerization. The solubility of the $CuBr_2/$bpy complex in xylene was too low to make the polymerization controlled.

On the basis of the rule of similarity, we chose pyridine as the solvent to increase the solubility of the catalyst ($CuBr_2/$bpy complex); the results are shown in Figures 3 and 4. Figure 3 shows the time dependence of the logarithmic data and the conversion of MMA. The plot of $\ln([MMA]_0/[MMA]_t)$ (where $[MMA]_0$ and $[MMA]_t$ are the concentrations of the monomer at time 0 and time t, respectively)
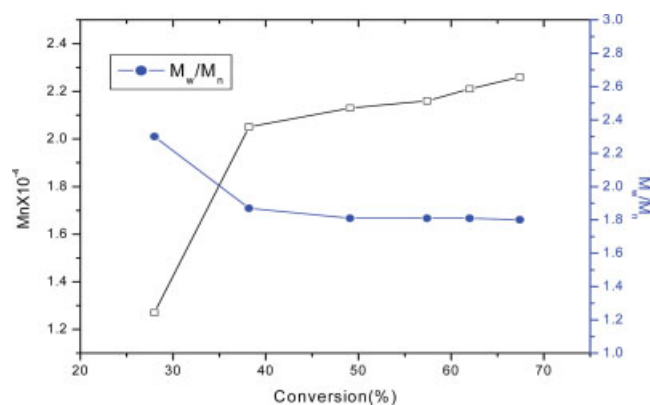

Figure 2 Dependence of the number-average molecular weight (M_n) and polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of poly(methyl methacrylate) on the conversion with the $CuBr_2/$bpy complex as the catalyst at 80°C in the xylene solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 3 Time dependence of $\ln([MMA]_0/[MMA]_t)$ and the conversion with the $CuBr_2$/bpy complex as the catalyst at 80°C in the pyridine solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
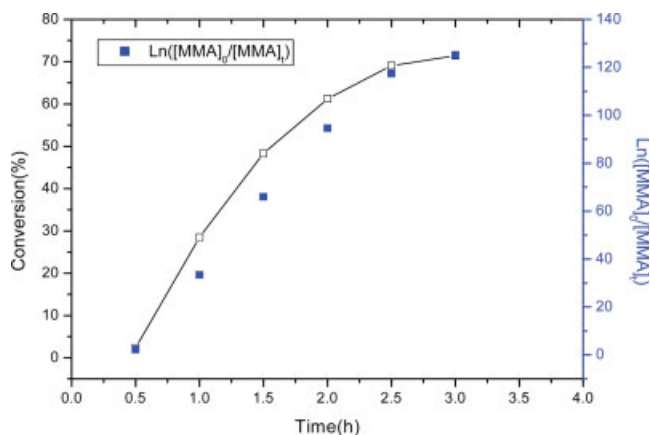

Figure 5 Time dependence of $\ln([MMA]_0/[MMA]_t)$ and the conversion with the $CuBr_2$/bpy complex as the catalyst at 80°C in the DMF solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

versus time t is not a straight line, and this indicates that the kinetics were not first-order in the monomer. Figure 4 shows that the number-average molecular weight increased with the monomer conversion. The molecular weight distribution remained 1.6 during the entire polymerization. The results were not in agreement with a controlled polymerization.

We also chose a polar solvent, DMF, for the polymerization. The results are shown in Figures 5 and 6. The conversions and logarithmic conversion data [$\ln([MMA]_0/[MMA]_t)$ plotted against time t] are shown in Figure 5. The kinetics were not first-order in the monomer. Figure 6 shows that the experimental molecular weight increased with the monomer
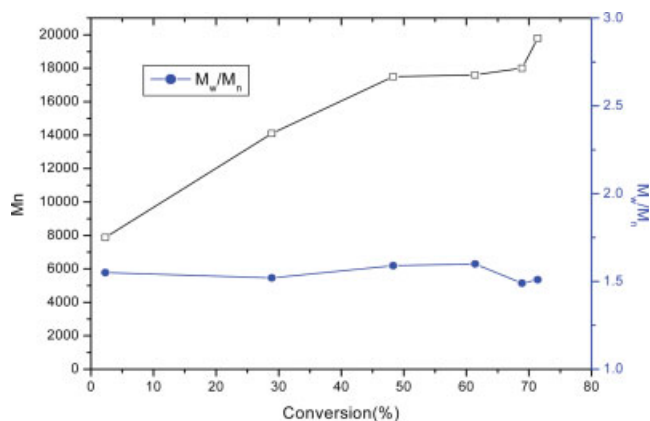
conversion, and the molecular weight distribution also increased from 1.2 to 1.6 with the monomer conversion. In comparison with the polymerizations of MMA in the pyridine system, this polymerization had better controllability. During the experiment, a change in the solution color was observed within 0.5 h, and then the color of the solution was kept.

From the molecular structure, we can conclude that pyridine may be able to complex with $CuBr_2$ and bpy. To observe whether the solvent could complex with $CuBr_2$, we performed the following experiment. A 150-mL Schlenk flask equipped with a magnetic stirrer was charged only with the solvent and $CuBr_2$; under argon protection, the mixture was

Figure 4 Dependence of the number-average molecular weight (M_n) and polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of poly(methyl methacrylate) on the conversion with the $CuBr_2$/bpy complex as the catalyst at 80°C in the pyridine solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
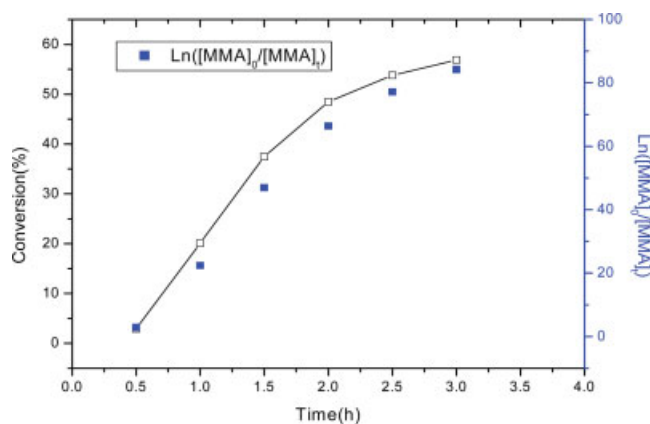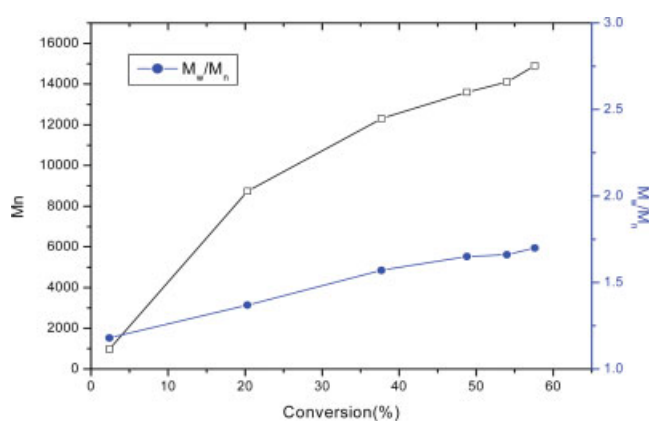

Figure 6 Dependence of the number-average molecular weight (M_n) and polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of poly(methyl methacrylate) on the conversion with the $CuBr_2$/bpy complex as the catalyst at 80°C in the DMF solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 7 Absorbance of a CuBr$_2$/pyridine complex solution in pyridine.

Figure 9 Time dependence of ln([MMA]$_0$/[MMA]$_t$) and the conversion with the CuBr$_2$/bpy complex as the catalyst at 80°C in the xylene solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
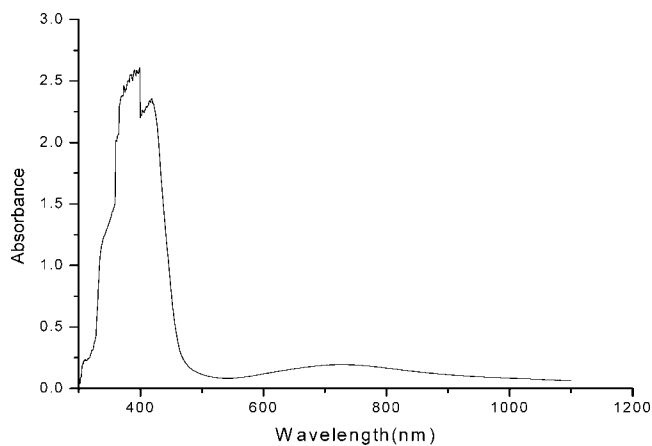
stirred for 1 h under the reaction conditions. The absorbance of the final solution was measured with UV–vis spectrophotometers. Figure 7 shows the absorbance of the CuBr$_2$ solution in pyridine. The weak peak at 730 nm and the intense peak at 430 nm arose from the d–d transition of the CuBr$_2$/pyridine complex.[32] The CuBr$_2$/pyridine complex could not be the catalyst of controlled polymerization because much more CuBr$_2$ complexation with pyridine would reduce the efficiency of the catalyst. Therefore, the results were not in agreement with a controlled polymerization.

The —N(CH$_3$)$_2$ group in DMF also complexed easily with CuBr$_2$. We performed the same experiment, except that pyridine was changed to DMF. The final solution was also measured with UV–vis spectrophotometers. Figure 8 shows the absorbance of a CuBr$_2$ solution in DMF. The weak band at 490 nm and the intense peak at 590 nm arose from the d–d transition of CuBr$_2$/DMF.[32] Therefore, the results were also not good. However, the ability of DMF to complex
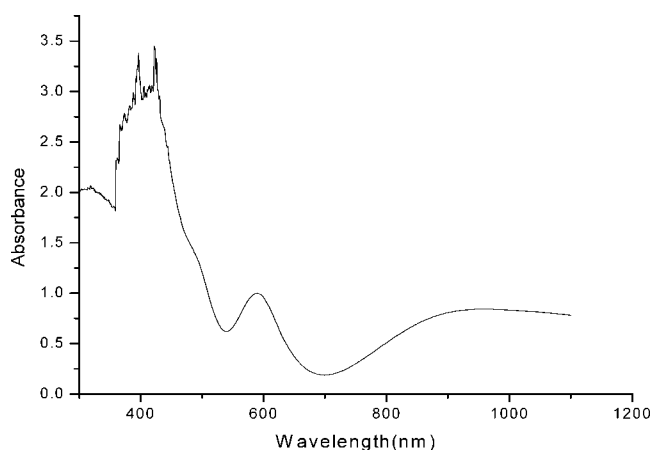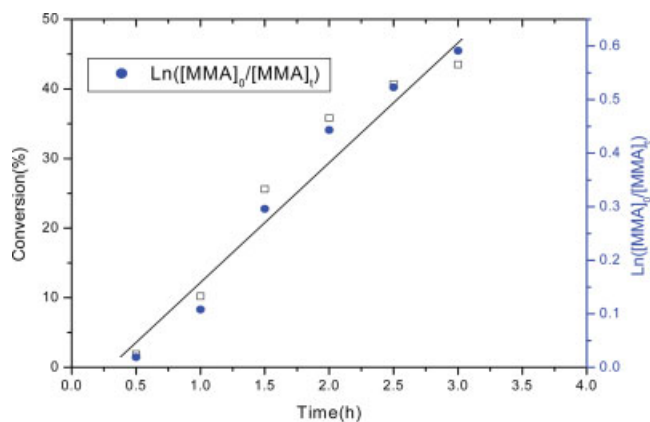
with CuBr$_2$ was lower than that of pyridine and even lower than that of bpy; the CuBr$_2$/bpy complex existed chiefly during the polymerization. Therefore, the controllability of the polymerization in DMF was better than that in pyridine.

To obtain a well-controlled polymerization, we chose dNbpy as a ligand for the xylene system. The CuBr$_2$/dNbpy complex could be well dissolved in the solvent, and the system was homogeneous. The results of the polymerization under the same reaction conditions are shown in Figures 9 and 10. Figure 9 shows that the conversion of MMA reached 1.9% within 0.5 h once the polymerization began; after 3 h, the conversion of MMA reached 43.5%. The increased conversion of the monomer was obviously slower than that in the CuBr$_2$/bpy system. The loga-
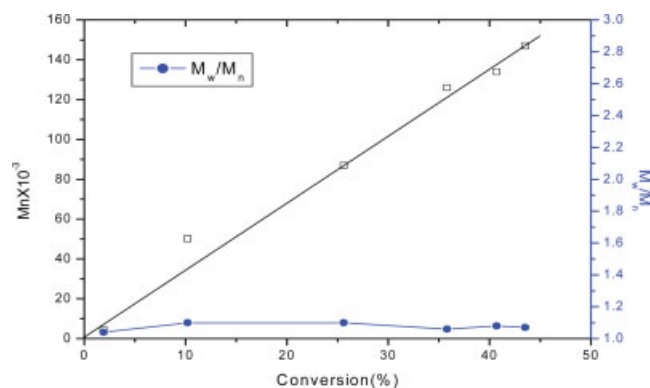

Figure 8 Absorbance of a CuBr$_2$/DMF complex solution in DMF.

Figure 10 Dependence of the number-average molecular weight (M_n) and polydispersity [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of poly(methyl methacrylate) on the conversion with the CuBr$_2$/bpy complex as the catalyst at 80°C in the xylene solution polymerization of MMA. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

rithmic conversion data [ln([MMA]$_0$/[MMA]$_t$) plotted against time t] are also shown in Figure 9 and show that the kinetics were first-order in the monomer. As shown in Figure 10, a well-controlled polymerization, characterized by a linear correlation between the molecular weights and monomer conversion, was realized with this system. During the whole polymerization, the polydispersities were in the range of 1.07–1.10, even for the first sample obtained at 0.5 h.

From these results, we can see that the solubility of a catalyst in a solvent has a notable influence on ATRP. When bpy was chosen as the ligand and xylene was chosen as the solvent, the solubility of the CuBr$_2$/bpy complex in xylene was too low to make the polymerization controlled. When DMF and pyridine were chosen as the solvents, although the polymerization was homogeneous and the solubility of the CuBr$_2$/bpy complex increased obviously in xylene, the solvent could have another influence on ATRP; the controllability was not even good for polymerization. The solubility of the CuBr$_2$/dNbpy complex in xylene was much improved because of the introduction of the —CH(C$_4$H$_9$)$_2$ group into dNbpy, so the control of the polymerization was much improved. To improve the solubility of a CuBr$_2$/ligand complex in a solvent and the controllability of polymerization, choosing a solvent is not a good idea in comparison with choosing a ligand.

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