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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Online publication date: 31 March 2003

To cite this Article Cheng, Zhenping , Zhu, Xiulin , Zhang, Lifen , Zhou, Nianchen and Chen, Jianying(2003) 'Homogeneous Solution Reverse Atom Transfer Radical Polymerization of Methyl Methacrylate', Journal of Macromolecular Science, Part A, 40: 4, 371 – 385

To link to this Article: DOI: 10.1081/MA-120019065

URL: <http://dx.doi.org/10.1081/MA-120019065>

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JOURNAL OF MACROMOLECULAR SCIENCE®

Part A—Pure and Applied Chemistry

Vol. A40, No. 4, pp. 371–385, 2003

Homogeneous Solution Reverse Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT

A homogeneous reverse atom transfer radical polymerization (RATRP) of methyl methacrylate (MMA) was successfully carried out in *N,N*-dimethylformamide (DMF) (25%, v/v) at 69°C, using an initiating system azobisisobutyronitrile (AIBN)/CuBr₂/N, N, N', N''-pentamethyldiethylenetriamine (PMDETA). The kinetics of homogeneous solution polymerizations showed linear first-order rate plots, indicating a constant number of growing species throughout the polymerization as well as a negligible contribution of termination or transfer reactions; a linear increase of the number-average molecular weight with conversion, and relatively low polydispersities, but low initiator efficiency. The dependence of the rate of polymerization on the concentrations of initiator, catalyst, ligand and temperature were presented.

Key Words: Reverse atom transfer radical polymerization; Living polymerization; Methyl methacrylate; Homogeneous polymerization; *N, N, N', N'', N''*-pentamethyldiethylenetriamine; Radical polymerization.

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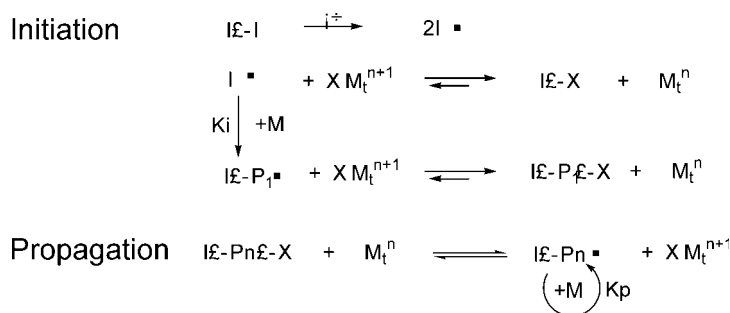
INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers.^[1-7] It has many advantages, such as easily available materials, remarkable tolerance of functional group,^[8,9] mild polymerization conditions and great industrialization prospects, as compared with other processes of living polymerization. In direct ATRP, an initiation system generally consists of activated halides (RX, i.e., 1-chloro-1-phenylethane, ethyl α -bromoisobutyrate, etc.), lower oxidation state metal (M_t^n) and a suitable ligand. This type of ATRP suffers two major drawbacks: firstly, the use of a halide species RX, which often is toxic or not easily handled or obtained; secondly, the oxidation of the catalyst by the oxygen included in air. To circumvent this problem, alternative/reverse ATRP was introduced^[10-18] and a well-controlled polymerization was observed although with low initiator efficiencies. In alternative/reverse ATRP (RATRP), living polymerization is carried out in the presence of conventional radical initiator like AIBN and catalyst consisting of metal in higher oxidation (M_t^{n+1}), no longer air-sensitive, instead of its lower oxidation state (M_t^n) so that the halide initiator and lower oxidation state transition metal catalyst are generated *in situ*. The situation then becomes exactly the same as in a direct ATRP. Its mechanism is illustrated in Scheme 1.

According to Scheme 1, the following rate law is derived (Eq. 1).

$$\begin{aligned}
 R_p &= k_p^{\text{app}}[M] = k_p[P \cdot][M] = k_p \frac{k_{\text{act}} [1 - P_n - X][\text{Cu}(\phi\tilde{n}X/L)]}{k_{\text{dact}} [\text{Cu}(\phi\delta)X_2/L]} [M] \\
 &= k_p K_{\text{eq}} [M] \frac{[1 - P_n - X][\text{Cu}(\phi\tilde{n}X/L)]}{[\text{Cu}(\phi\delta)X_2/L]} \quad (1)
 \end{aligned}$$

Generally, homogeneous ATRP was conducted under some expensive and special ligands (such as, 4, 4'-di-n-heptyl-2, 2'-bipyridine (dHbipy), 4, 4'-di(5-nonyl)-2, 2'-bipyridine (dNbpy), *N*-(n-hexyl)pyridylmethanimine (NHPMI), etc.). On homogeneous ATRP of MMA, Zhang^[19] studied the kinetics of CuBr-mediated homogeneous atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) using 2-hydroxyethyl-2-bromoisobutyrate (HEBIB) as initiator and *N*-(n-hexyl)pyridylmethanimine (NHPMI) as



Scheme 1. Mechanism of RATRP.

ligand and Matyjaszewski^[20] studied the homogeneous controlled/'living' radical polymerization of methyl methacrylate (MMA) using the atom transfer radical polymerization (ATRP) with CuCl/4,4'-di(5-nonyl)-2,2'-bipyridine catalytic system and diphenyl ether as the solvent. Cheng and Zhu^[21] also studied the homogeneous RATRP of MMA in DMF under pulsed microwave irradiation (PMI), using AIBN/CuBr₂/tetramethylethylenediamine (TMEDA) as an initiating system. In addition, Liu and Hu,^[22] using AIBN/CuCl₂/2,2'-bipyridine as an initiating system, studied the RATRP of MMA in acetonitrile and DMF.

N,N,N',N'',N'''-pentamethyldiethylenetriamine as a tridentate amine ligand has been employed in direct ATRP^[23-27] due to the lower redox potential of the copper(I)-PMDETA complex than copper(I)-2,2'-bipyridine (BPY) complex, however, so far, the homogeneous RATRP using PMDETA as ligand, has not been reported.

In this work, we select cheap and commercially available PMDETA as ligand, azobisisobutyronitrile (AIBN)/CuBr₂ as initiator/catalyst in RATRP and report a kinetic investigation of the homogeneous solution RATRP of MMA in DMF at a lower temperature (69°C), including the reaction orders of each component.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (chemically pure; Shanghai Chemical Reagent Co., Ltd.) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with sodium sulfate anhydrous overnight, and finally distilled under vacuum. Azobisisobutyronitrile (AIBN) (chemically pure; Shanghai Chemical Reagent Co., Ltd.) was recrystallized with ethanol anhydrous. Cupric bromide (CuBr₂) (analytical reagent; Shanghai Zhenxin Reagent Factory) was dissolved in deionized water, filtered, condensed under vacuum at 30°C, then crystallized at a vacuum dryer with P₂O₅, filtered, dried. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (chemically pure; Jiangsu Liyang Jiangdian Chemical Factory) was dried with 4Å molecular sieve and distilled under vacuum. *N,N*-dimethylformamide (DMF) (analytical reagent; Shanghai No.1 Chemical Reagent Factory), tetrahydrofuran (THF) (analytical reagent; Shanghai Chemical Reagent Co., Ltd.), HCl (analytical reagent; Jiangsu Jincheng Chemical Reagent Co., Ltd.) and methanol (commercially available) were used as received.

General Procedures of Polymerization

A dry glass tube was filled with CuBr₂, AIBN, PMDETA, DMF and MMA. Vibrating until the mixture becomes a homogeneous solution. Then it was degassed under vacuum and charged with N₂ (five times), sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature (69°C) to polymerize. At timed intervals, cooling the tube into cold water stopped the polymerization. Afterward, the tube was opened and contents were dissolved in THF, precipitated into a large amount of methanol/HCl (100/0.05, v/v). The dried polymer was then characterized by gravimetry.

Characterizations

Conversion of monomer was determined by gravimetry. Molecular weights and molecular weight distributions were measured using Waters 1515 GPC with THF as a mobile phase and with column temperature of 30°C. Polystyrene standards were used to calibrate the columns. ^{13}C NMR and ^1H NMR spectra were recorded in CDCl_3 with an INOVA 400 MHz spectrometer at ambient temperature.

RESULTS AND DISCUSSION

Effect of Concentrations of Initiator on RATRP of MMA

Figure 1 shows the kinetics of $\ln([M]_0/[M])$ vs. polymerization time at different concentrations of initiator at 69°C. The polymerizations of MMA show approximately first-order kinetics with respect to monomer concentration for all initiator concentrations, indicating a constant concentration of living species throughout the polymerization. As expected, increasing the concentrations of initiator increases the apparent rate constant of polymerization, k_p^{app} , as determined from the kinetic slopes, indicating the increase of the rate of polymerization. From Fig. 1, longer induction periods for different concentrations of initiator can also be observed and become shorter (~ 300 min for $n = 0.5$, ~ 50 min for $n = 3$) with increasing of the concentrations of initiator. The induction periods correspond to the decomposition of AIBN and the establishment of the equilibrium between

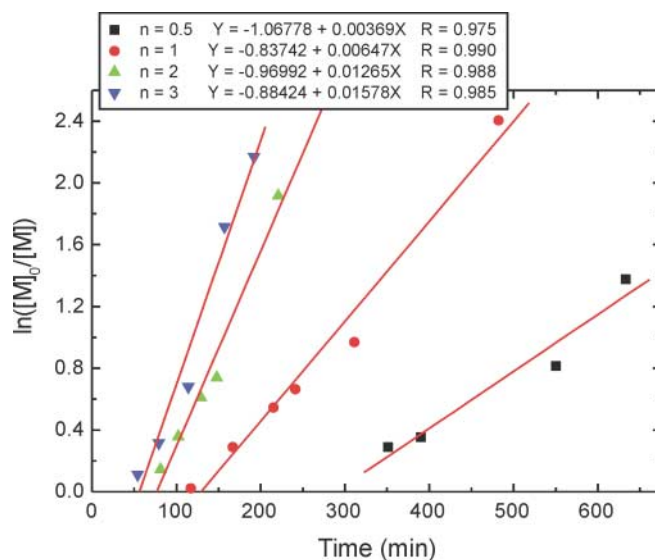


Figure 1. Kinetics of solution RATRP of MMA in DMF at various concentrations of initiator. Conditions: $[\text{MMA}]_0/[\text{AIBN}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 600/n/1/1$ ($n = 0.5, 1, 2, 3$); $\text{MMA}/\text{DMF} = 3/1$ (v/v); 69°C.

Cu(I)/Cu(II) as predicted by the “persistent radical effect”^[28] in the presence of large excess of CuBr₂ at the beginning of the polymerization or the consumption of residual oxygen or some impurity.^[11,29–31]

Figure 2 shows the dependence of molecular weight (M_n) on monomer conversion. For all concentrations of initiator, M_n s increase with monomer conversion but their values are higher than those expected $M_n(\text{cal})$ s. This fact indicates a low efficiency of the initiator system used in this work. The low apparent initiator efficiencies could be caused by the incomplete initiation under a lower temperature^[32] and the possible termination reactions, including the AIBN geminate termination in the solvent cage, at the very beginning of the polymerization.^[12]

PDI (Fig. 3) are very narrow, $1.07 < M_w/M_n < 1.5$, but increase progressively with conversion. It can be believed that there is, in this initiation system (AIBN/CuBr₂/PMDETA), a higher deactivation rate at the beginning of reaction. This is to say, in the initiation step, once generated, the initiating radicals or the propagating radicals, $I\bullet$ or $I\text{-P}_1\bullet$, can abstract the halogen atom Br from the oxidized transition metal species, CuBr₂, to form the reduced transition-metal species, CuBr, and the dormant species, $I\text{-X}$ or $I\text{-P}_1\text{-X}$, and a reversible equilibrium between growing radicals and dormant species is established quickly after the induction periods, keeping the concentrations of active species or propagating radicals sufficiently low, which resulting in the narrow PDIs. However, the increase of PDIs could be caused by the possible termination reactions due to the insufficient deactivation of the propagating PMMA radicals, especially in the last step of polymerizations.

Plotting $\ln([M]_0/[M])$ vs. $\ln[AIBN]_0$ elucidated the dependence of the rate of polymerization on the concentration of initiator. For this system, the slope of the line indicated an apparent 0.84 order with respect to initiator (Fig. 4). This is similar to the ATRP of MA^[33] (0.8 order dependence of the rate on the initiator concentration), but differs from the first order dependence of the rate on the initiator concentration observed

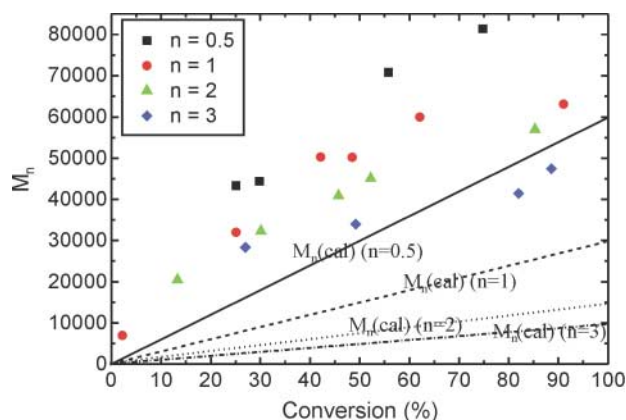


Figure 2. Dependence of molecular weights on monomer conversion in solution RATRP of MMA in DMF at different concentrations of initiator. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/n/1/1$ ($n = 0.5, 1, 2, 3$); $MMA/DMF = 3/1$ (v/v); 69°C.

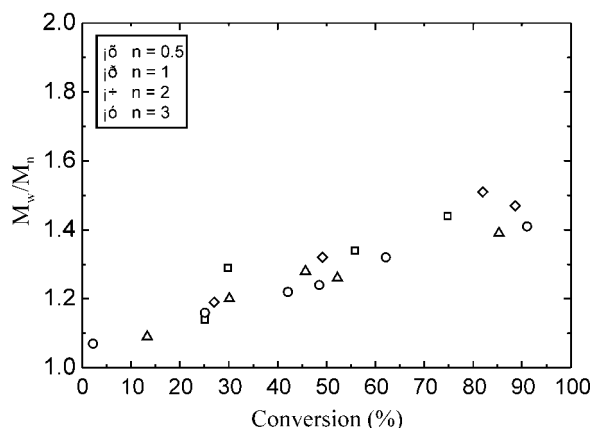


Figure 3. Dependence of molecular weight distributions on monomer conversion in solution RATRP of MMA in DMF at different concentrations of initiator. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/n/1/1$ ($n = 0.5, 1, 2, 3$); $MMA/DMF = 3/1$ (v/v); $69^\circ C$.

for ATRP of both styrene^[34] in 1-PECl(Br)/CuX/dNbpy initiation system and MMA^[2,20] in p-TsCl/CuCl/dNbpy initiation system. This may be due to the low initiator efficiency discussed above in this system.

Effect of Concentrations of Catalyst on RATRP of MMA

The effects of concentrations of catalyst on RATRP of MMA in DMF were also investigated, as shown in Figs. 5, 6 and 7. The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for

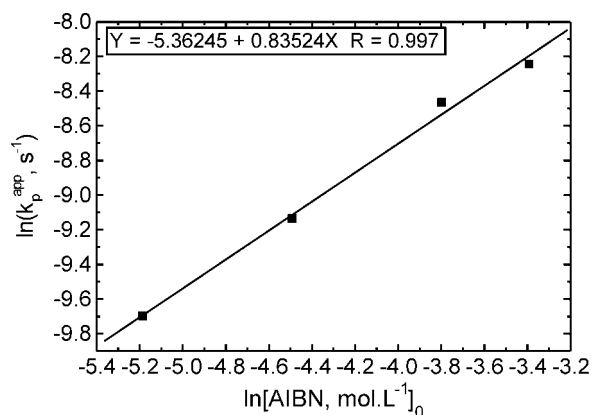


Figure 4. Plot of $\ln(k_p^{app})$ vs. $\ln([AIBN]_0)$ in solution RATRP of MMA in DMF at $69^\circ C$. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/n/1/1$ ($n = 0.5, 1, 2, 3$); $MMA/DMF = 3/1$ (v/v); $69^\circ C$.

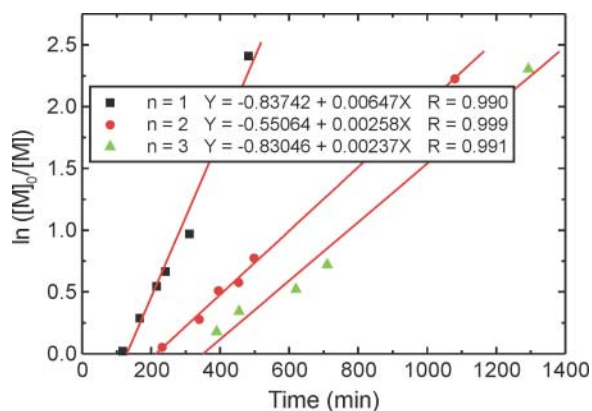


Figure 5. Kinetics of solution RATRP of MMA in DMF at different concentrations of catalyst. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/n/n$ ($n = 1, 2, 3$); MMA/DMF = 3/1(v/v); 69°C.

the duration of the reactions; therefore, the contribution of termination reactions could be neglected. As expected, increasing the catalyst concentration decreased the apparent rate constant of polymerization, k_p^{app} , as determined from the kinetic slopes (Fig. 5). From Fig. 5, longer induction periods (from 130 min to 350 min) can also be observed. Figure 6 shows that M_n s increase with conversion and relatively low polydispersities, PDIs < 1.4, demonstrating the “living” characteristics of this system. Also the deviation of M_n s determined by GPC from the corresponding theoretical M_n ($M_n(cal) = [MMA]_0/(2[AIBN]_0) \times MW(MMA) \times Conversion$), indicating a low initiator efficiency as discussed above. Figure 7 shows the dependence of $\ln(k_p^{app})$ on $\ln[Cu(II)]_0$. The slope

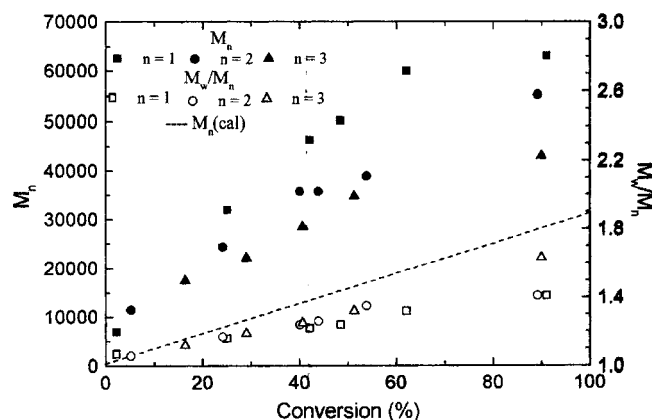


Figure 6. Dependence of molecular weights and molecular weight distributions on monomer conversion in solution RATRP of MMA in DMF at different concentrations of catalyst. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/n/n$ ($n = 1, 2, 3$); MMA/DMF = 3/1(v/v); 69°C.

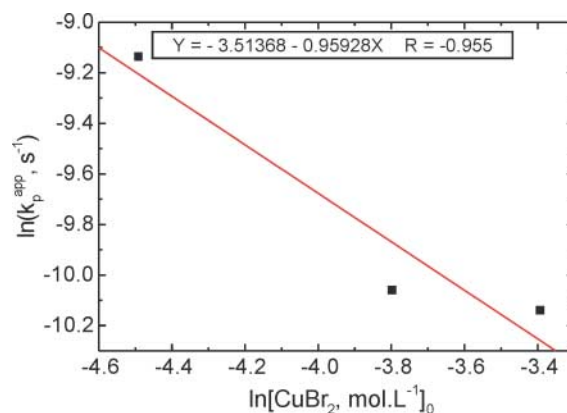


Figure 7. Plot of $\ln(k_p^{\text{app}})$ vs. $\ln([\text{CuBr}_2]_0)$ in solution RATRP of MMA in DMF at 69°C. Conditions: $[\text{MMA}]_0/[\text{AIBN}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 600/1/n/n(n = 1, 2, 3)$; MMA/DMF = 3/1(v/v); 69°C.

of the line indicates an inverse first-order dependence of the rate on the concentration of Cu(II) in this system, as expected by Eq. 1.

Effect of Concentrations of Ligand on RATRP of MMA

The effect of concentrations of ligand (PMDETA) on the solution polymerization of MMA has been investigated, and the results are shown in Figs. 8, 9 and 10. The linearity of the semilogarithmic plot of $\ln([M]_0/[M])$ vs. time for various concentrations of ligand indicates the polymerizations were first-order with respect to monomer and that the

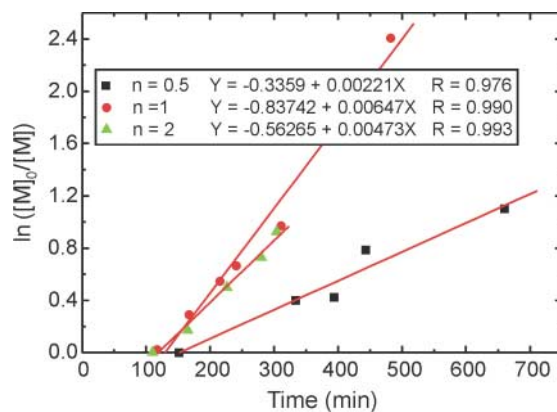


Figure 8. Kinetics of solution RATRP of MMA in DMF at different concentrations of ligand. Conditions: $[\text{MMA}]_0/[\text{AIBN}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 600/1/1/n(n = 0.5, 1, 2)$; MMA/DMF = 3/1(v/v); 69°C.

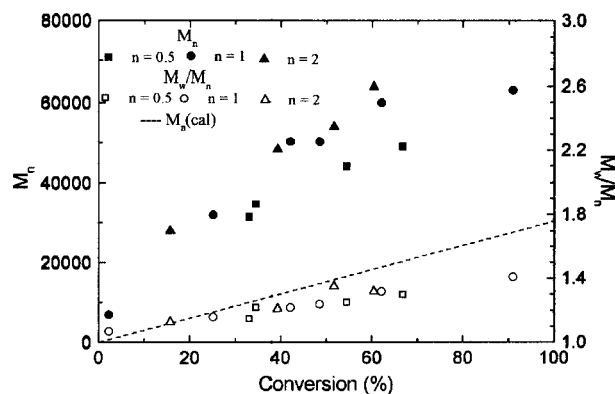


Figure 9. Dependence of molecular weights and molecular weight distributions on monomer conversion in solution RATRP of MMA in DMF at different concentrations of ligand. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/1/n$ ($n = 0.5, 1, 2$); $MMA/DMF = 3/1$ (v/v); $69^\circ C$.

concentration of the growing radicals remained constant (Fig. 8). From Fig. 9, it can be seen that M_n values for three concentrations of ligand increase with conversion and PDIs are less than 1.4. Figure 10 shows the apparent rate constant of polymerization as a function of the ratio of PMDETA:Cu(II). The maximum rate constant is observed at a 1:1 ratio of PMDETA:Cu(II). This may be concerned with the structure of complex. However, the ratio with maximum rate constant is very complicated due to ligand may participate in side reactions;^[35] therefore, many factors (i.e. solvent, initiator and even monomer) can change the ratio. Wootthikanokkan's results of ATRP of MMA in toluene using ethyl bromopropionate (EBP)/CuBr/PMDETA as the initiating system showed that monomer

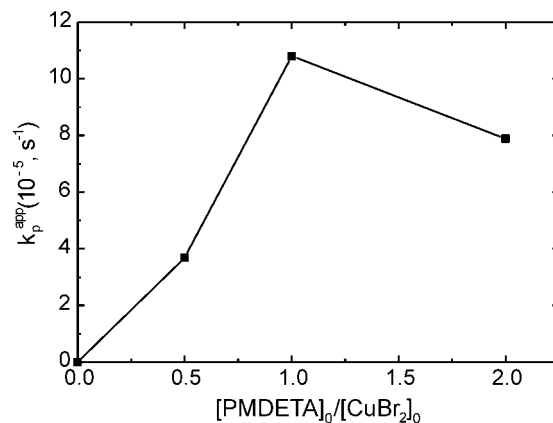


Figure 10. Plot of k_p^{app} vs. $[PMDETA]_0/[CuBr_2]_0$ in solution RATRP of MMA in DMF at $69^\circ C$. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/1/n$ ($n = 0.5, 1, 2$); $MMA/DMF = 3/1$ (v/v); $69^\circ C$.

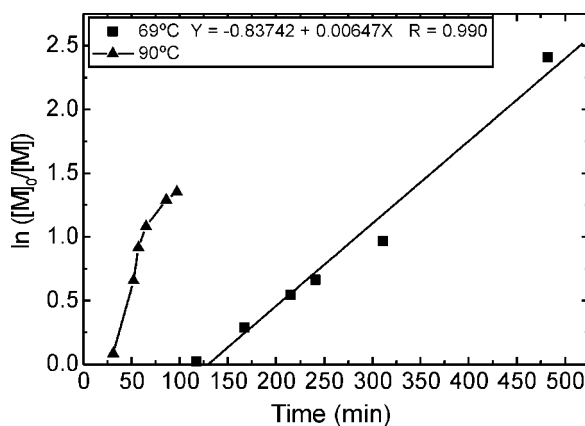


Figure 11. Kinetics of solution RATRP of MMA in DMF at different temperatures. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/1/1$; $MMA/DMF = 3/1(v/v)$.

conversion had a maximum value with the increasing of $[PMDETA]_0/[CuBr]_0$, but the maximum conversion was not always corresponding to the point at which the mole ratio of $[PMDETA]_0/[CuBr]_0$ was equal.^[27]

Effect of Polymerization Temperature on RATRP of MMA

The kinetic plots of the homogeneous RATRP of MMA in DMF at different polymerization temperatures are displayed in Fig. 11. At 90°C, curvature of the kinetic plot is observed, indicating a possible termination reaction. At this temperature, the deactivation of propagating PMMA chains was not fast enough compared with the PMMA propagation, especially at higher conversion (i.e., after 50%), under this RATAP

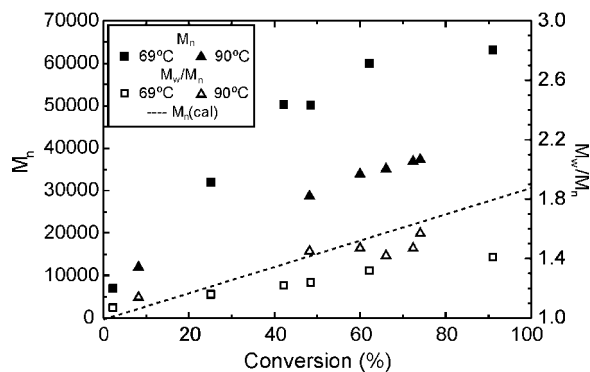


Figure 12. Dependence of molecular weights and molecular weight distributions on monomer conversion in solution RATRP of MMA in DMF at different temperatures. Conditions: $[MMA]_0/[AIBN]_0/[CuBr_2]_0/[PMDETA]_0 = 600/1/1/1$; $MMA/DMF = 3/1(v/v)$.

RATRP of MMA

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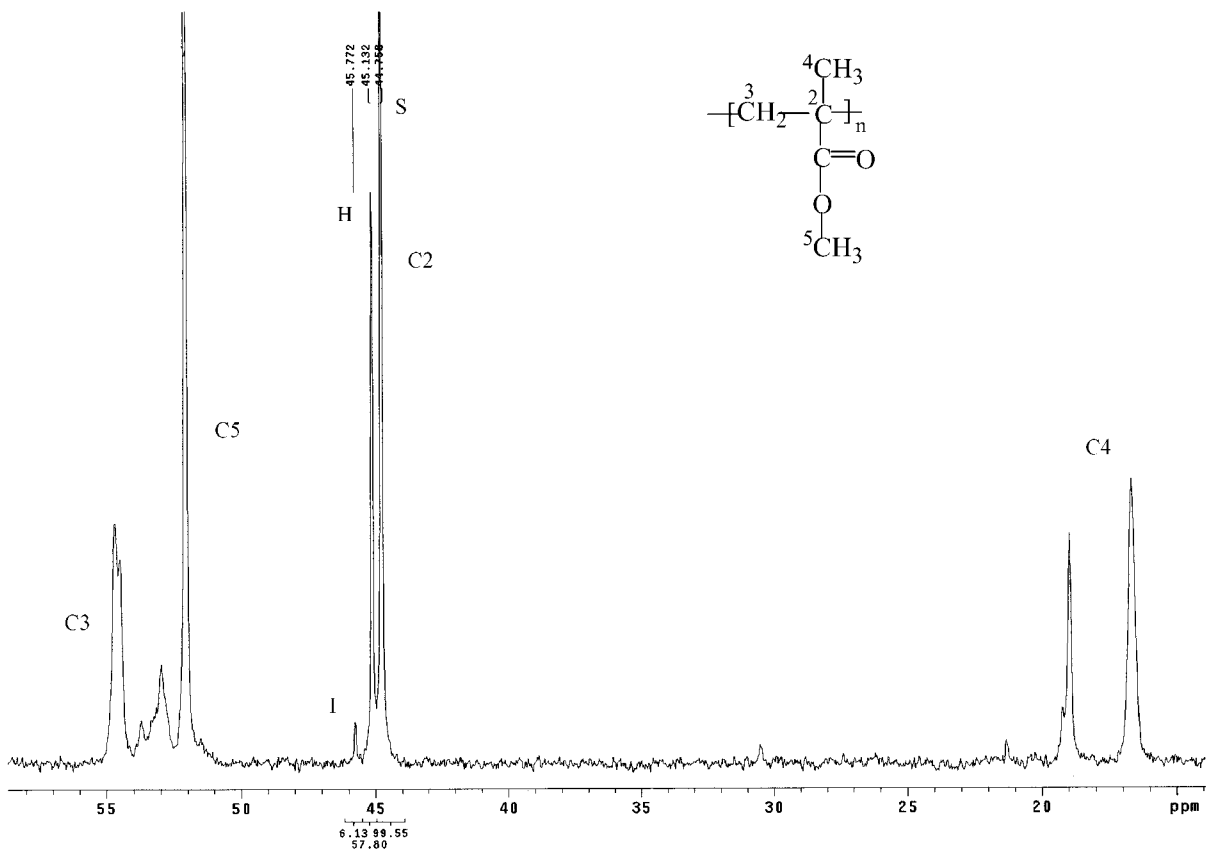


Figure 13. ^{13}C NMR spectrum of PMMA prepared with AIBN/CuBr₂/PMDETA as the initiating system in DMF at 69°C.

conditions. This can also result in the increase of PDIs (the PDIs at this polymerization temperature were higher than that at 69°C) (Fig. 12). When the homogeneous RATRP of MMA was conducted at 69°C, a higher conversion (91%) was obtained, and the linear semilogarithmic plot of $\ln([M]_0/[M])$ vs. time indicates constant concentration of growing species. Figure 12 shows the number-average molecular weights and polydispersities vs. conversion. In both cases, molecular weights increase with conversion; however, these are higher than the calculated values, indicating low apparent initiator efficiency. The initiator efficiency increasing with temperature can be observed. This is contributed to the fact that AIBN decomposed slower at a lower temperature (69°C), resulting in the incomplete initiation under this conditions. Increasing temperature, the rate of decomposition of AIBN should be increased, leading to the increase of initiator efficiency.

Stereochemistry of RATRP of MMA

To better understand the mechanism of RATRP, the stereochemistry of PMMA was investigated. Figure 13 shows the ^{13}C NMR spectra of PMMA prepared using AIBN/CuBr₂/PMDETA as an initiation system. The tacticity of PMMA was calculated from ^{13}C NMR of the quaternary carbon group (C2).^[2,36]

According to the integral area of peaks of I, S and H in C2, the stereoregularity of PMMA can be calculated as shown in Table 1. From Table 1, it can be seen that PMMA synthesized by RATRP are predominately syndiotactic (S, 60.9%), next to the heterotactic (H, 35.4%) and isotactic (I, 3.7%). As compared with the results (listed in Table 1) by conventional free radical polymerization (RP),^[37] PMMA prepared using AIBN/CuBr₂/PMDETA as an initiation system and by RP has the same composition within experimental error, indicating that the same type of active species is presented in RATRP and RP.

End Group Characterizations

An additional method toward verifying the functionality of a polymer prepared by ATRP is its use as a macroinitiator for the same or other monomers. A chain extension of MMA with PMMA ($M_{n(\text{GPC})} = 26,800$, $M_w/M_n = 1.15$) as the macroinitiator was performed. The polymerization was carried out in DMF using CuCl/PMDETA as the catalyst (polymerization conditions: $[MMA]_0/[macroinitiator]_0/[CuCl]_0/[PMDETA]_0 = 300/1/2/4$; MMA/DMF = 1/1 (v/v); T = 110°C; t = 30.5 h). The M_n for 48.8%

Table 1. Stereoregularity of PMMA under different polymerization processes.

Polymerization process	I(%)	A(%)	S(%)
RATRP	3.70	35.40	60.90
RP	3.00	34.00	63.00

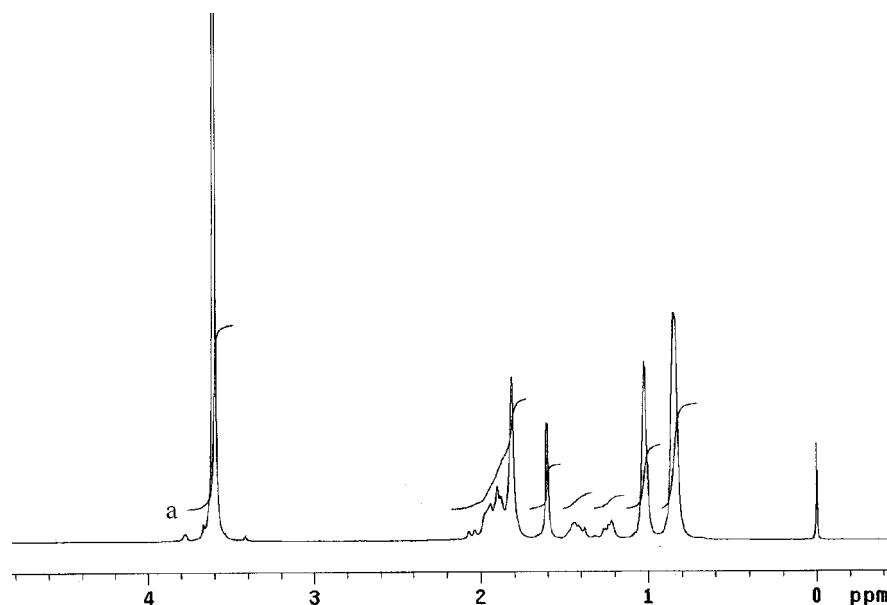


Figure 14. ^1H NMR spectrum of PMMA prepared with AIBN/CuBr₂/PMDETA as the initiating system in DMF at 69°C.

conversion of the chain-extended PMMA increased to 34,600 and the polydispersity index (1.49) was higher than that of the macroinitiator ($M_w/M_n = 1.15$). A small part of the macroinitiator probably remained unreacted or some side reactions occurred. Furthermore, Fig. 14 shows ^1H NMR spectrum of PMMA prepared using AIBN/CuBr₂/PMDETA as an initiation system. The signal at 3.77 ppm corresponds to the methyl ester group at the chain end as mentioned by Sawamoto,^[38] which deviating the chemical shift (3.60 ppm) of other methyl ester group in PMMA due to the electron-attracting function of ω -halogen(Br). These thus prove the fact that the PMMA synthesized using AIBN/CuBr₂/PMDETA as an initiation system is the product of RATRP.

CONCLUSION

The homogeneous RATRP of MMA, using AIBN/CuBr₂/PMDETA as initiation system, can be easily carried out in DMF (25%, v/v) at 69°C lower temperature. Plots of $\ln([M]_0/[M])$ vs. time and molecular weight evolution vs. conversion showed a linear dependence. The molecular weight distributions kept quite narrow (1.07 ~ 1.5), but the initiator efficiencies were very low (generally below 0.5), indicative of a poor control of molecular weight. RATRP exhibited inverse first-order kinetics with respect to the initial copper(II) concentration, however, the polymerization kinetics were not first-order with respect to the initial initiator concentration.

ACKNOWLEDGEMENTS

We gratefully acknowledge National Nature Science Foundation of China (No. 20176033) and Nature Science Foundation of Jiangsu Province (No. BK2001141) for support for this work.

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Received September 2002

Revision received November 2002