Notes

High Molecular Weight PMMA by ATRP

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Introduction

High molecular weight polymers with controlled architecture are desirable for applications such as rheology modification,[1−3] control of crystallization characteristics, morphology development, and mechanical performance.[4−6] Potential application of atom transfer radical polymerization (ATRP) for such polymers would require high initiator efficiency, narrow polydispersity index (PDI), and a moderate reaction rate during the polymerization at high monomer-to-initiator ratio ($[M]_0/[I]_0$). Matyjaszewski[7,8] reviewed the past attempts at achieving high molecular weight; in general, the PDI increases rapidly beyond 1.2 when the number-average molecular weight (M_n) exceeds 100 000. Though methyl methacrylate (MMA) is among the most often studied monomers for ATRP, past kinetics investigations are limited to systems with attempted molecular weights less than 40 000 in a single step. However, kinetics in the high M_n systems is of interest because the persistent radical effect is predicted to diminish in systems with low initiator concentrations.[9,10] Grimaud and Matyjaszewski[11] reported MMA polymerizations in sealed tubes, yielding PDI = 1.18 up to M_n = 83 000, although the PDI increased to 1.4 at M_n = 169 000. Another possible route to high molecular weight polymers employs multiple steps of isolation and purification of the living polymer at intermediate stages and its use as a macroinitiator for further chain extension.[12−14] In the present work, we examine the ATRP kinetics in a high ($[M]_0/[I]_0$) system and thus evaluate the possibility of obtaining low PDI, high molecular weight PMMA by a one-pot synthesis.

Experimental Section

Materials. We used phenyl 2-bromo-2-methylpropionate (BMPE) as a model monofunctional initiator. It was synthesized according to the literature[15] and vacuum distillated before use. CuCl (Aldrich, 99.995%) was refluxed with glacial acetate acid, washed with absolute ethanol, and dried in a vacuum oven at 100 °C for 3 days. This initiator−catalyst combination should permit fast initiation, fast deactivation of the propagating radicals by Cu^{II} species, and reduced side reactions of the P_n−Cl growing chains formed by halogen exchange, thereby improving the control during ATRP.[16] MMA (Aldrich, 99%) was passed through a basic activated alumina column, extracted three times with 5 wt % NaOH (aqueous), washed with water and dried by using anhydrous $MgSO_4$, and finally distilled from CaH_2 just before use. Xylene (Biosolve, 99%) was distilled from CaH_2 before use. Three systems with different ligands (L) were used. *N,N,N′,N″,N″*-Pentamethyldiethyltriamine (PMDETA, Merck, >98%) was vacuum distilled before use. 2-Pyridinecarboxaldehyde pentylimine (PCPimine) was synthesized as described in ref 17 and vacuum distilled before use. 4,4′-*n*-Nonyl-2,2′-bipyridine (d*n*Nbpy, Aldrich, 97%) was recrystallized from absolute ethanol and dried in a vacuum oven at 40 °C overnight. While these ligands have previously been used for efficient polymerization of MMA to moderate molecular weights,[8,12,16,18,19] an alternative ligand, tris(2-dimethylaminoethyl)amine, was unsuitable due to poor solubility of the catalyst−ligand complex in MMA.[12]

Polymerization Procedure. For the polymerization system with d*n*Nbpy ligand and $[M]_0:[I]_0$ of 800:1, MMA (40.208 g, 0.402 mol), d*n*Nbpy (0.416 g, 1.02 mmol), and CuCl (0.0533 g, 0.54 mmol) were charged into a reaction flask and purged with dry argon for 1 h. BMPE (0.123 g, 0.51 mmol) was charged into another flask, diluted with xylene (10 mL), purged with dry argon for 1 h, and transferred dropwise over 3 min to the reaction flask. The reaction flask was immersed into an oil bath at 90 °C (time = 0). A magnetic bar in the reaction flask stirred the reaction mixture for 170 min. Samples were withdrawn with a syringe at desired time for kinetic study. Each sample was dissolved in THF, and the molecular weight distribution and monomer conversion were determined without further purification. For the polymerization system with $[M]_0:[I]_0$ of 6400:1, we used MMA (154.930 g, 1.55 mol), d*n*Nbpy (1.264 g, 3.10 mmol), CuCl (0.153 g, 1.54 mmol), BMPE (0.0615 g, 0.25 mmol), and xylene (10 mL) in the same way as mentioned above. With increasing viscosity, the stir bar did not rotate any more, and samples could not be withdrawn with syringe after 160 min. However, the reaction continued, and the last sample was collected at 500 min with a spatula.

Measurements. Molecular weight distributions were measured by size exclusion chromatography (SEC) using a Waters GPC equipped with a Waters 510 pump, a Waters 410 differential refractometer (40 °C), a Waters WISP 712 autoinjector (50 μL injection volume), a PLgel (5 μm particles) 50 × 7.5 mm guard column, and two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns (40 °C). Data acquisition and processing were performed using Waters Millennium 32 (v32) software. Tetrahydrofuran (THF, Biosolve, stabilized with BHT) was used as eluent at a flow rate of 1.0 mL/min. Calibration was done using polystyrene (PS) standards (Polymer Laboratories, 580−7.1 × 10^6 g mol^{-1}), and molecular weights were recalculated using the universal calibration principle and Mark−Houwink parameters (PS: $K = 1.14 \times 10^{-4}$ dL g^{-1}, $a = 0.716$; PMMA: $K = 0.944 \times 10^{-4}$ dL g^{-1}, $a = 0.719$). Monomer conversion was determined from concentration of the residual monomer by gas chromatography (GC) using Hewlett-Packard 5890 GC, equipped with AT-Wax capillary column (30 m × 0.53 mm × 10 μm), using xylene as an internal reference, and a 10 °C min^{-1} heating ramp.

Results and Discussion

Figure 1a shows that the semilogarithmic kinetics plots for ATRP of MMA with $[M]_0:[I]_0:[Cu^I]_0:[L]$ of 800:1:1:2, using the three different ligands. The linear plots demonstrate that the polymerization rate is pro-

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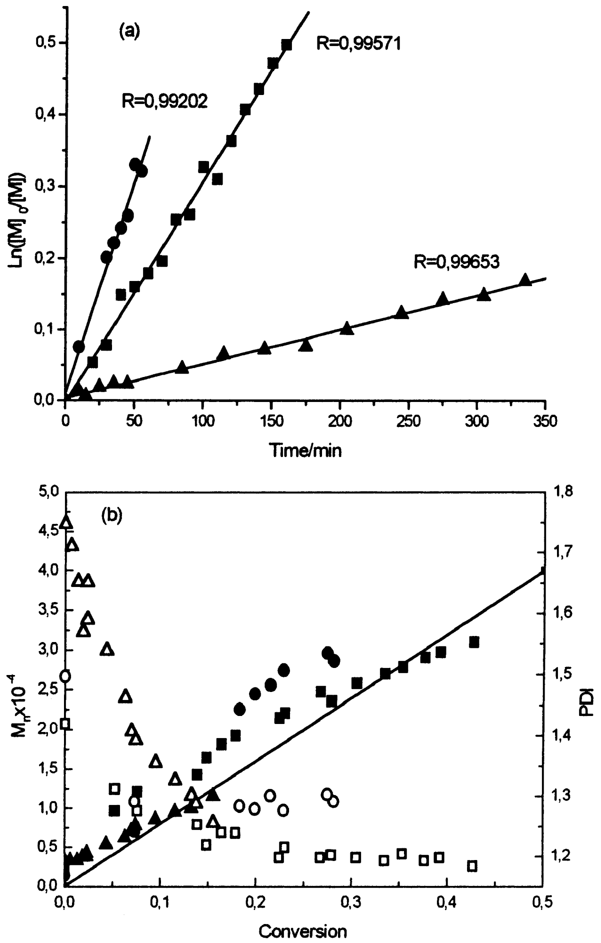


Figure 1. Comparison of ligands PMDETA (circle), d*n*Nbpy (square), and PCPimine (triangle) during ATRP of MMA at 90 °C with catalyst CuCl at $[M]_0$:$[I]_0$:$[CuCl]_0$:[L] = 800:1:1:2. (a) First-order kinetics plots. Lines represent best fits, and the regression coefficients are indicated. (b) Dependence of M_n (filled symbols) and PDI (open symbols) on monomer conversion. Line represents theoretical values for living polymerization.

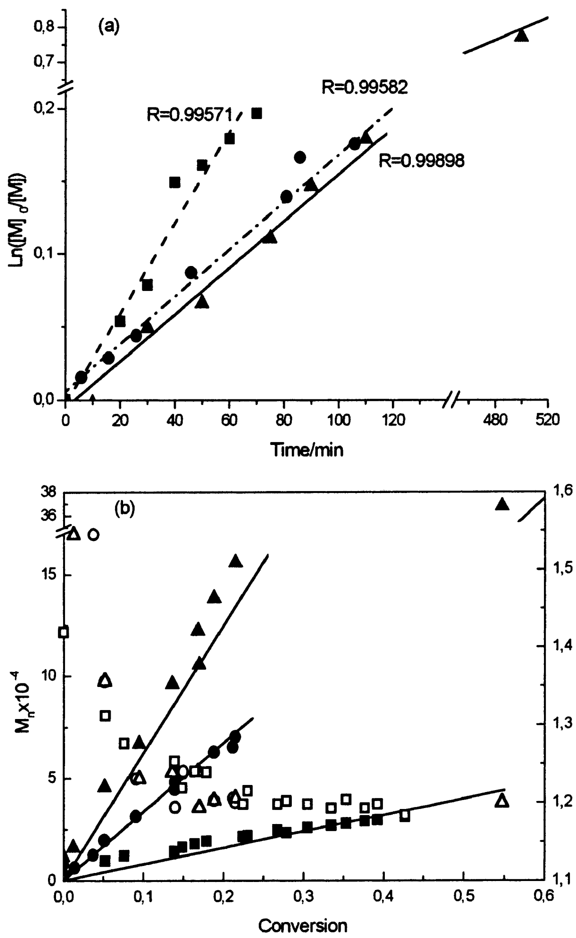


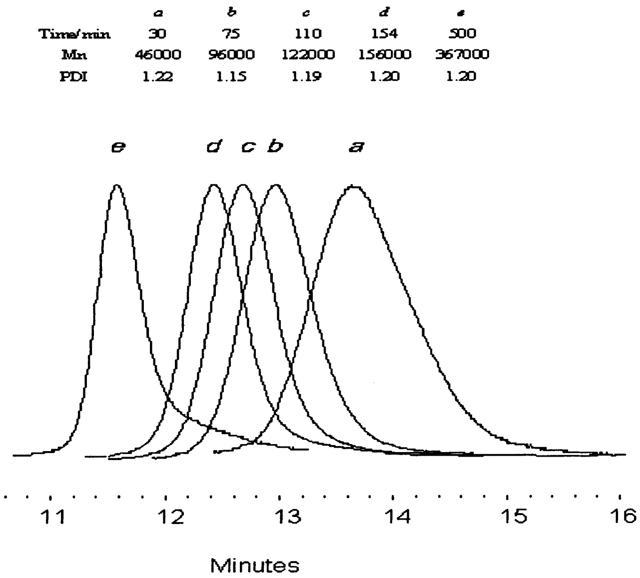
Figure 2. Effect of initial initiator concentration during ATRP of MMA at 90 °C with catalyst CuCl, ligand d*n*Nbpy, and initiator BMPE in xylene, using $[M]_0$:$[I]_0$:$[CuCl]_0$ = 800:1:1 (square), 3200:1:3 (circle), and 6400:1:6 (triangle) and keeping $[CuCl]_0$:[L] = 1:2. (a) First-order kinetics plots. Lines represent best fits, and the regression coefficients are indicated. (b) Dependence of M_n (filled symbols) and PDI (open symbols) on monomer conversion. Lines represent theoretical values for living polymerization.

portional to monomer concentration and indicate that the radical concentration is constant during the polymerization reactions.[8,9] The highest and lowest slope for the PMDETA and PCPimine ligands, respectively, are proportional to their apparent polymerization rate constants. Figure 1b shows that, at conversions greater than 0.1, M_n increases linearly with monomer conversion for the d*n*Nbpy and the PCPimine systems, in accordance with the theoretical prediction, thus indicating good control. The high M_n at conversion less than 0.1 is related to the rapid early growth of a small concentration of chains when the deactivator concentration is low.[20,21] The M_n increases with monomer conversion for the PMDETA system also but deviates from the theoretical prediction significantly under the reaction conditions used here. This may be due to the early termination by radical−radical coupling, caused by fast initiation and the large apparent polymerization rate. We suspect this because we used $[Cu^I]_0/[I]_0 = 1$, while a ratio as low as 0.2 was suitable for the PMDETA ligand system.[12] The PDI decreases with increasing monomer conversion (Figure 1b), reaching values of about 1.2 at about 0.15 conversion for the d*n*Nbpy and the PCPimine systems. Thus, the d*n*Nbpy-based system provides the desired characteristics of high initiation efficiency, low polydispersity, and a moderate apparent polymerization rate for PMMA of M_n up to 30 000 under the conditions examined. This indicates that this ligand could potentially be used for even higher molecular weight PMMA.

To examine this, we then used ($[M]_0/[I]_0 = 3200$ and 6400), with catalyst concentrations higher than initiator ($[CuCl]_0/[I]_0 = 3$ and 6, respectively) to enhance the apparent polymerization rate and thus avoid very long reaction times. The kinetics results presented in Figure 2a indicate that the apparent kinetics follows $\ln([M]_0/[M]) \sim t$, corresponding to a constant radical and Cu^{II} concentration during ATRP,[8,9] according to eq 1.

$$\frac{R}{[M]} = \frac{1}{t}\ln\left(\frac{[M]_0}{[M]}\right) = k_pK_{eq}\frac{[I]_0[Cu^I]}{[Cu^{II}]} = k_{app} \qquad (1)$$

If radical−radical termination is present during ATRP, the concentration of radical-deactivating Cu^{II} can build up (persistent radical effect), slowing down the apparent polymerization rate, leading to $\ln([M]_0/[M]) \sim t^{2/3}$.[21] However, the chain length dependence of radical−radical coupling[20] and the limited deactivator (Cu^{II}) solubility[10] may distort the persistent radical effect, with a $\ln([M]_0/[M]) \sim t$ relationship observed. Further, eq 1



	a	b	c	d	e
Time/min	30	75	110	154	500
Mn	46000	96000	122000	156000	367000
PDI	1.22	1.15	1.19	1.20	1.20

Figure 3. SEC traces of PMMA formed at different times during the $[M]_0$:$[I]_0$:$[CuCl]_0$ = 6400:1:6 polymerization of Figure 2.

assumes a low radical concentration or low termination rate and is thus valid at low $[Cu^I]$ and $[I]_0$.[22] Thus, conformity of our results with eq 1 may indicate reduced termination. Further, in the $[M]_0/[I]_0 = 800$, 3200, and 6400 experiments, the products $[I]_0[Cu^I]$ are (1.0, 0.26, 0.13) $\times 10^{-4}$ (mol $L^{-1})^2$, while the observed k_{app} are (1, 0.5, 0.52) $\times$ 0.0031 min^{-1}, respectively. This indicates that $[Cu^{II}]$ decreased to (1, 0.52, 0.25) $\times 0.032 \times k_pK_{eq}$ mol L^{-1} with dilution in the $[M]_0/[I]_0 = 800$, 3200, and 6400 experiments. This suggests reduced termination with initiator dilution,[9,10] since the $[Cu^{II}]$ buildup is attributed to initial termination of radicals.[23]

Figure 2b reveals that M_n is controlled with increasing conversion even in these systems with relatively few chains. The molecular weight distribution remains narrow, and PDI $\sim$ 1.20 can be achieved for M_n as large as 367 000 (Figure 3). A direct quantitative examination of livingness by block copolymer synthesis[24] from this as a macroinitiator was not attempted, because the required reliable separation of the SEC peak of this macroinitiator from the SEC peak of the copolymer would have required molecular weight growth to 10^6 or higher. However, the gradual shift of the narrow SEC peaks in Figure 3 to higher molecular weights further indicates that termination and chain transfer reactions are not high. In comparison, Grimaud and Matyjaszewski[11] observed higher polydispersities and distinct broadening of the SEC peak at $M_n = 183\,900$. Hovestad et al.[25] observed a high molecular weight tail, which they assigned to formation of high molecular weight species due to termination by combination. They also observed loss of PDI control for $[M]_0/[I]_0$ larger than 500. Since we observe little or no high molecular weight tail, this further indicates that termination by coupling during the polymerization is negligible. We do notice a low molecular weight tail in the otherwise narrowing peak at the highest $M_n = 367\,000$ (Figure 3), which can indicate slow propagation of a fraction of the chains.[26] This can be due to nonuniform concentrations at the gas−liquid interface, resulting from ineffective mixing in the highly viscous reaction system at these molecular weights. The decreasing fraction of low molecular weight chains (for example, compare weight fractions of components corresponding to elution time of 13.2 min in samples d and e in Figure 3) indicates that this low molecular weight tail cannot be attributed to dead chains.

Conclusions

We have compared the ATRP kinetics of MMA with three different ligands PMDETA, d*n*Nbpy and PCPimine, using a bromine functionalized initiator and CuCl catalyst at ($[M]_0/[I]_0 = 800$). The d*n*Nbpy ligand system provided very good control at a polymerization rate quite acceptable for obtaining high molecular weight PMMA, and we used this ligand at ($[M]_0/[I]_0 = 6400$). The observed kinetics follows a linear variation with monomer concentration and suggests that termination is negligible as expected at the high dilution of the initiator. As far as we are aware, this is the first successful attempt of a single-pot ATRP starting with high initiator dilution and leading to a degree of polymerization higher than 3500 with polydispersity as low as 1.2.

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References and Notes

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