

## Controlled/"Living" Radical Polymerization of Methyl Methacrylate by Atom Transfer Radical Polymerization

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Received December 6, 1996

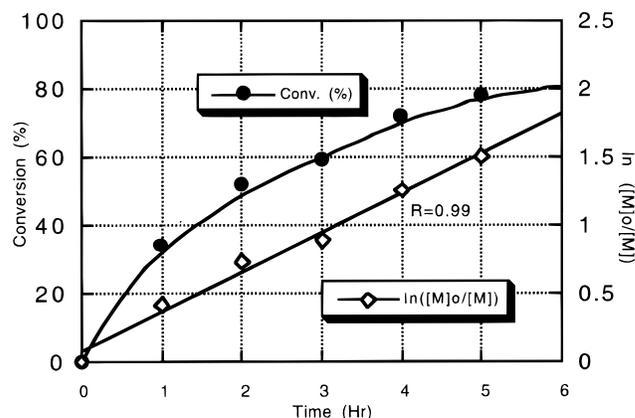
Revised Manuscript Received February 3, 1997

One of the most important goals of synthetic polymer chemistry is to gain control not only over the molecular weights and polydispersities of polymer chains, but also their architecture and end-groups. Living polymerizations, in which neither transfer nor termination takes place, appeared to be the best technique to reach this target.<sup>1</sup> Mainly performed by anionic,<sup>2</sup> cationic,<sup>3</sup> or group transfer polymerization,<sup>4</sup> living polymerizations require specific experimental conditions that often make their industrial application difficult. Recently, controlled/"living" approaches to radical polymerizations were reported.<sup>5–11</sup> In these processes, the contribution of termination and transfer reactions remains very low,<sup>7</sup> although they cannot be completely eliminated. One of the most successful controlled/"living" radical polymerization methods developed is atom transfer radical polymerization<sup>9</sup> (ATRP). It has its roots in organic chemistry's atom transfer radical addition<sup>12,13</sup> (ATRA), which is sometimes called Kharasch addition.<sup>14</sup> ATRP has been proven to be effective for a wide range of monomers<sup>15</sup> and appears to be a powerful tool for the polymer chemist, providing new possibilities in structural and architectural design<sup>16</sup> and allowing the development of new materials with monomers currently available.<sup>17,18</sup>

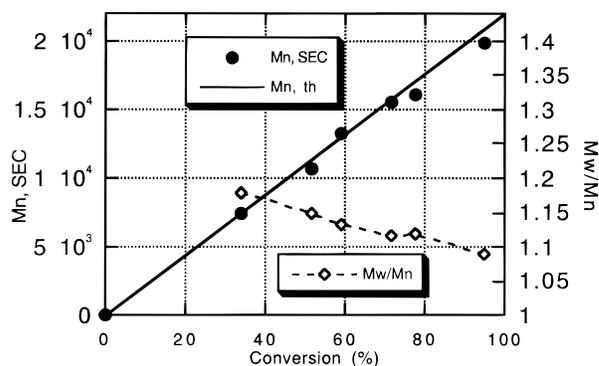
This communication reports that atom transfer radical polymerization can be used successfully to control the polymerization of methyl methacrylate (MMA) over a broad range of molecular weights, reaching very low polydispersities, with easy reaction conditions and relatively rapid kinetics. As reported by Sawamoto,<sup>10,19</sup> ATRP based on ruthenium catalytic systems allows for control of the polymerization of MMA until  $M_n = 20\,000$  with slow reaction rates (typically 80% conversion in 20–30 h). By using a homogeneous ATRP catalytic system based on copper bromide and a substituted bipyridine, we were able to synthesize poly(MMA) with polydispersities as low as 1.1 ( $M_n = 20\,000$ ) in a few hours while controlling molecular weights until  $M_n = 180\,000$ .

MMA was polymerized with *p*-toluenesulfonyl chloride (*p*-TSCl) in conjunction with copper(I) bromide (CuBr) and 4,4'-bis(5-nonyl)-2,2'-bipyridine (dNbipy)<sup>20</sup> in diphenyl ether (DPE) at 90 °C.<sup>21</sup> *p*-Toluenesulfonyl chloride was used as an initiator for styrene polymerization<sup>22,23</sup> and in metal-catalyzed ATRA. When aiming at PMMA of  $M_n = 20\,000$  at 100% conversion (Figures 1 and 2), 1/2 equiv of catalyst to initiator was used in order to reduce the amount of radicals in the medium. Complexation of copper by 4,4'-bis(5-nonyl)-2,2'-bipyridine allowed the reaction mixture to be homogeneous. As shown in Figure 1, 80% conversion was reached in 5 h, and semilogarithmic kinetic plots are linear, indicating that the radical concentration is constant during the polymerization.

A linear increase of number average molecular weight,  $M_{n,SEC}$ , vs monomer conversions up to 95% was found

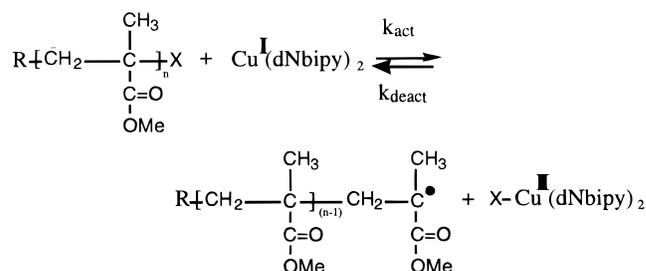


**Figure 1.** Conversion and  $\ln([M]_0/[M])$  plots vs time in solution polymerization (50% vol) of MMA in diphenyl ether at 90 °C with  $[p\text{-TSCl}]_0 = 0.021$  mol/L,  $[\text{CuBr}]_0 = 0.0105$  mol/L,  $[\text{dNbipy}]_0 = 0.021$  mol/L.



**Figure 2.** Dependence of molecular weights and polydispersities on conversion in solution polymerization (50% vol) of MMA in diphenyl ether at 90 °C with  $[p\text{-TSCl}]_0 = 0.021$  mol/L,  $[\text{CuBr}]_0 = 0.0105$  mol/L,  $[\text{dNbipy}]_0 = 0.021$  mol/L.

### Scheme 1



(Figure 2). The  $M_{n,SEC}$  is very close to the theoretical one,  $M_{n,th}$ , defined by eq 1,<sup>24</sup> which assumes that one molecule of initiator generates one growing polymer chain:

$$M_{n,th} = ([\text{MMA}]_0 / [p\text{-TSCl}]_0) \times (MW)_0 \times p \quad (1)$$

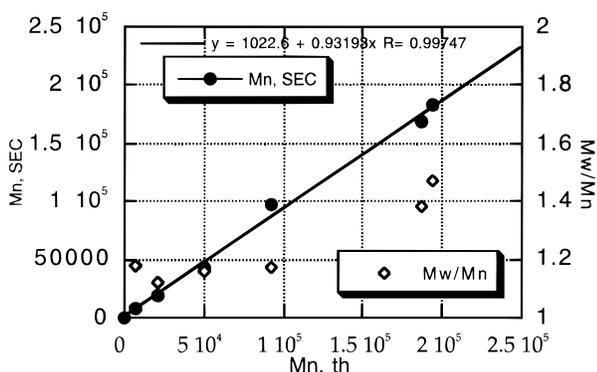
Together with the straight kinetic plot  $\ln([M]_0/[M])$  vs time, this confirms that the polymerization process is controlled/"living" with a negligible amount of transfer and termination. Polydispersities decreased from 1.18 to 1.09, and remained very low, indicating a fast exchange between active and dormant species (see Scheme 1).

An additional series of experiments was carried out in sealed tubes (see Table 1), with different  $[\text{MMA}]_0/[p\text{-TSCl}]_0$  ratios. The concentration of copper and ligand was kept constant at  $[\text{CuBr}]_0 = 0.0105$  mol/L and

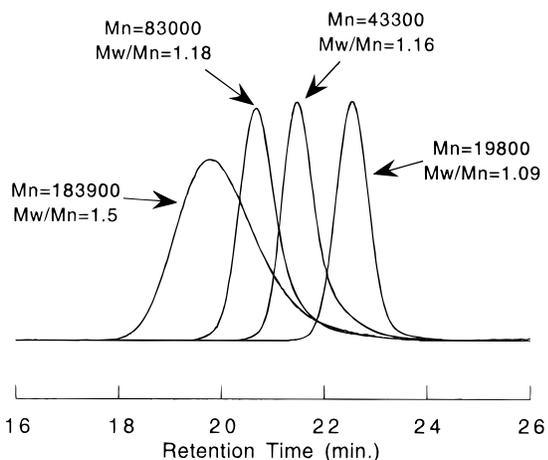
**Table 1. Results of Methyl Methacrylate Solution Polymerization in Diphenyl Ether (50% vol) at 90 °C**

conv (%)	$10^3[p\text{-TSCl}]_0$ (mol/L)	$\ln([M]_0/[M])$	time (h)	$M_{n,th}$	$M_{n,SEC}$	$M_w/M_n$
52 <sup>a</sup>	21.25	0.73	2	11 400	10 600	1.15
95 <sup>a</sup>	21.25	2.99	20	20 900	19 800	1.09
98 <sup>a</sup>	9.35	3.91	15	49 000	43 300	1.16
92 <sup>b</sup>	4.675	2.52	20	92 100	83 000	1.18
82 <sup>b</sup>	2.05	1.71	24	186 900	169 000	1.4
85 <sup>b</sup>	2.05	1.89	48	194 000	183 900	1.5

<sup>a</sup> Schlenk flask, 5 mL of MMA + 5 mL of DPE, conversion = 52% after 2 h and conversion = 95% after 20 h (80% conversion reached after 6 h). <sup>b</sup> Sealed tube, 2 mL solution.



**Figure 3.** Correlation of experimental and theoretical molecular weights and polydispersities in solution polymerization (50% vol) of MMA in diphenyl ether at 90 °C.  $[CuBr]_0 = 0.0105$  mol/L,  $[dNbipy]_0 = 0.021$  mol/L.



**Figure 4.** GPC traces (RI detection) of poly(MMA) obtained with *p*-TSCl/CuBr/dNbpy in diphenyl ether at 90 °C.  $[p\text{-TSCl}]_0 = 0.021, 0.00935, 0.004675,$  and  $0.00205$  mol/L, respectively (from low MWs to high MWs);  $[CuBr]_0 = 0.0105$  mol/L,  $[dNbipy]_0 = 0.021$  mol/L.

$[dNbipy]_0 = 0.021$  mol/L respectively. Figure 3 compares  $M_{n,SEC}$  vs  $M_{n,th}$  as calculated by the means of eq 1.

A linear plot is observed until  $M_n = 180\,000$ . This indicates a high efficiency of the *p*-toluenesulfonyl chloride initiator<sup>25</sup> and a constant number of chains. The polydispersities were much lower than in a conventional radical polymerization until  $M_n = 80\,000$ .

Table 1 summarizes the results of methyl methacrylate polymerization under various experimental conditions.

Figure 4 shows the GPC traces of some polymers synthesized in this study. The polymers with  $M_n = 20\,000$  were prepared in a Schlenk flask while the

higher molecular weight polymers were prepared in sealed tubes.

ATRP is known to proceed *via* the establishment of a rapid equilibrium between active and dormant species<sup>11</sup> according to Scheme 1.

To reduce the termination process, which is second order with respect to the concentration of radicals (propagation is first order), the concentration of radicals has to be lowered, which means the equilibrium should be shifted towards the dormant species. In the case of MMA, where propagation is faster than in the case of styrene,<sup>26–28</sup> this requirement becomes even more stringent. Only  $1/2$  equiv of metal catalyst to initiator was used in solution polymerizations (for molecular weights higher than  $M_n = 50\,000$ , where the amount of initiator is very low, a higher ratio was used) to reduce the radical concentration and the rate of the polymerization. Using unsubstituted bipyridine as a ligand, the system was heterogeneous and the polymerization less controlled. 4,4'-Bis(5-nonyl)-2,2'-bipyridine efficiently solubilizes both copper(I) and copper(II) species with two equivalents of ligand to each metal. The rate of deactivation is therefore enhanced in comparison to heterogeneous system. The use of copper bromide, instead of copper chloride, showed more rapidly decreasing polydispersities (*p*-TSCl/CuCl, conversion = 25%,  $M_n = 8500$ ,  $M_w/M_n = 2$  while with *p*-TSCl/CuBr for the same conversion,  $M_n = 7800$ ,  $M_w/M_n = 1.18$ ). This is due to the better efficiency of bromide in the deactivation step, as also observed by Bengouh in a series of studies of the inhibition of MMA polymerization in DMF.<sup>29,30</sup>

In summary, we demonstrated that atom transfer radical polymerization can be successfully adapted to the synthesis of poly(methyl methacrylate) with controlled molecular weights up to  $M_n = 180\,000$  and very narrow polydispersities up to  $M_n = 90\,000$ . This was achieved by using a substituted bipyridine ligand on the catalyst, which created a homogeneous system, coupled with an efficient initiator for this polymerization, *p*-toluenesulfonyl chloride or benzhydryl chloride,<sup>25</sup> and adapting the reaction conditions to the reactivity of the methyl methacrylate monomer.

**Acknowledgment.** Support from the Industrial sponsors of the ATRP Consortium is gratefully acknowledged. T.G. acknowledges additional support from Elf Aquitaine.

## References and Notes

- (1) Webster, O. *Science* **1991**, *251*, 887.
- (2) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience Publishers: New York, 1968.
- (3) Matyjaszewski, K. *Cationic Polymerizations*; Marcel Dekker: New York, 1996.
- (4) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
- (5) Solomon, D. H.; Rizzardo, E.; Cacioli, P. *Eur. Pat. Appl., EP 135280*, 1985.
- (6) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
- (7) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638.
- (8) Wayland, B. B.; Pszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
- (9) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
- (10) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
- (11) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

- (12) Curran, D. P. *Synthesis* **1988**, 489.
- (13) Bellus, D. *Pure Appl. Chem.* **1985**, 57, 1827.
- (14) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *Science* **1944**, 102, 128.
- (15) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, 28, 7901.
- (16) Gaynor, S. G.; Edelman, S. Z.; Matyjaszewski, K. *Macromolecules* **1996**, 29, 1079.
- (17) Greszta, D.; Matyjaszewski, K. *ACS Polym. Prepr.* **1996**, 37 (1), 569.
- (18) Nakagawa, Y.; Matyjaszewski, K. *ACS Polym. Prepr.* **1996**, 37 (2), 270.
- (19) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, 29, 1070.
- (20) 4,4'-Bis(5-nonyl)-2,2'-bipyridine was synthesized as follows: 250 mL of 4-(1-butyl-pentyl)pyridine and 10 g of Pd/C were placed in a 500 mL flask, and heated to 210 °C in an oil bath under Ar(g) with reflux and rapid stirring. After 1 week, the reaction mixture was cooled, filtered first through filter paper (Pd/C was rinsed with Et<sub>2</sub>O), then filtered over celite. The ether was removed by rotoevaporation, and the remaining yellow/beige liquid was vacuum distilled to remove the unreacted pyridine. The residue was then distilled under high vacuum; 41 g of ~99% pure dinonylbipyridine were collected at 180 °C under 10<sup>-7</sup> Torr, which slowly started to crystallize upon cooling. <sup>1</sup>H NMR: 8.55 ppm (d), 8.2 (d), 7.0 (d), 2.6 (d), 1.5–1.7 (m), 1–1.35 (m), 0.8 (t).
- (21) The polymerizations were carried out in Schlenk flasks ( $M_n < 30\,000$ ) under dry argon or in sealed tubes under vacuum for higher molecular weights. Methyl methacrylate was filtered through an alumina column and then dried over molecular sieves, degassed by argon bubbling, and stored under argon. Diphenyl ether was dried over molecular sieves, degassed and stored in the same way. Copper bromide was purified with glacial acetic acid and washed with pure ethanol, then stored under argon. *p*-Toluenesulfonyl chloride was used as received. When using a Schlenk flask, all reagents were added except initiator, and the mixture was degassed three times by freeze–pump–thaw cycles. The mixture was heated at reaction temperature (90 °C) until homogeneous (about 2 min) and then initiator was added. When using sealed tubes, a single solution (5 mL of MMA + 5 mL of DPE + catalyst and ligand) was prepared for all the tubes. Then 2 mL of the reaction mixture was distributed to each tube, initiator was added, and the reaction mixture was degassed three times before sealing under vacuum. The resulting polymer solutions were cooled down after sampling, dissolved in THF and analyzed by gas chromatography (residual concentration of monomer is determined with dodecane as an internal standard). Prior to injection on to the SEC, samples were passed through a neutral alumina column in order to remove catalyst. SEC calibration curves were calculated with poly(methyl methacrylate) standards from Polymer Laboratories.
- (22) Percec, V.; Barboiu, B. *Macromolecules* **1995**, 28, 7970.
- (23) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, 29, 3665.
- (24) [MMA]<sub>0</sub> and [p-TSCl]<sub>0</sub> represent the initial concentrations of MMA and p-TSCl, respectively; (MW)<sub>0</sub> is the molecular weight of monomer and *p* is the conversion.
- (25) Among other efficient initiators for MMA polymerization, benzhydryl chloride leads to polydispersities as low as 1.05 ( $M_n = 16\,000$ ) with molecular weights controlled until  $M_n = 210\,000$  ( $M_w/M_n = 1.5$ ). At  $M_n = 120\,000$ , polydispersities are still very low ( $M_w/M_n = 1.13$ ).
- (26) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, 196, 3267.
- (27) Gilbert, R. G. *Pure Appl. Chem.* **1996**, 68, 1491. Propagation constants for bulk polymerization of styrene (<sup>sty</sup>*k<sub>p</sub>*) and methyl methacrylate (<sup>MMA</sup>*k<sub>p</sub>*) at 90 °C calculated according to  $k_p = 10^{7.630} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp(-32.51 \text{ kJ mol}^{-1}/RT)$  for styrene and  $k_p = 10^{6.423} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \exp(-22.34 \text{ kJ mol}^{-1}/RT)$  for MMA lead to <sup>sty</sup>*k<sub>p</sub>* = 895.4 L mol<sup>-1</sup> s<sup>-1</sup> and <sup>MMA</sup>*k<sub>p</sub>* = 1615.9 L mol<sup>-1</sup> s<sup>-1</sup> respectively.
- (28) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, 30, 851.
- (29) Bengough, W. I.; Fairservice, W. H. *Trans. Faraday Soc.* **1965**, 61, 1206.
- (30) Bengough, W. I.; Fairservice, W. H. *Trans. Faraday Soc.* **1971**, 67, 414.

MA961796I