Macromolecules **2005,** *38,* 1041−1043 **1041**

Atom Transfer Radical Polymerization of Methyl Methacrylate in Fluoroalcohol: Simultaneous Control of Molecular Weight and Tacticity

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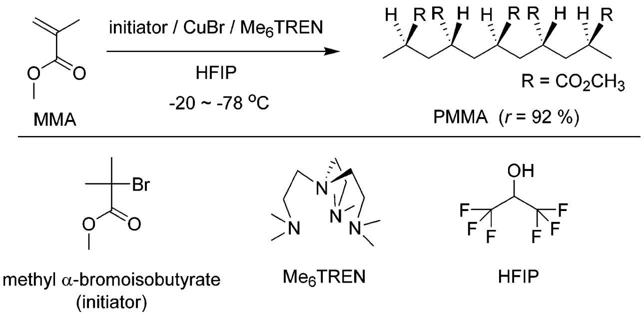
Received November 14, 2004
Revised Manuscript Received January 9, 2005

Introduction. In radical polymerization, continuous interest and effort are focused on controlling the molecular weight and stereoregularity of synthesized polymers. Recently, the controlled/living radical polymerization (CRP),[1−3] which provides polymers with targeted molecular weight and narrow polydispersity, has been developed that can control the stereochemistry.[4−6] Matyjaszewski et al. reported that the atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) polymerization of (meth)acrylamides in the presence of yttrium trifluoromethanesulfonate ($\mathrm{Y(OTf)_3}$) and ytterbium trifluoromethanesulfonate as complexing agents produced well-defined isotactic polymers, such as poly(*N*,*N*-dimethylacrylamide), poly(*N*-methylmethacrylamide), and stereoblock poly(*N*,*N*-dimethylacrylamide).[4,6] Sawamoto et al. reported with us the RAFT polymerization of *N*-isopropylacrylamide with $\mathrm{Y(OTf)_3}$ leading to well-defined stereoblock polymers.[5] The simultaneous control of molecular weight and stereoregularity based on the CRP technique was limited to (meth)acrylamide monomers; therefore, it is of interest to expand the applicable monomers, such as to methyl methacrylate (MMA).[6]

In addition, there was an excellent hint for the control of the stereoregularity by conventional radical polymerization; i.e., one of our groups reported that fluoroalcohols were effective solvents for producing highly syndiotactic PMMA, rr = ca. 90%.[7,8] Thus, the CRP technique along with the solvent effect of fluoroalcohols should be a suitable candidate for the simultaneous control of both molecular weight and stereochemistry of PMMA. In general, the selected solvent significantly affected the polymerization tendency of ATRP;[9,10] e.g., the more polar the solvent was, the faster the polymerization rate.[9] Hence, we focused on the design of stereocontrolled ATRP, which promises simultaneous control of the molecular weight and stereoregularity. Here we report the synthesis of highly syndiotactic PMMA with a very narrow polydsipersity on the basis of the ATRP initiating system of $\mathrm{Cu^I}$/tris(2-(dimethylamino)ethyl)amine ($\mathrm{Me_6TREN}$) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the highly polar solvent, as shown in Scheme 1.

Scheme 1



Results and Discussion. The polymerization of MMA in toluene, THF, methanol, and HFIP was carried out using the methyl α-bromoisobutyrate/copper(I) bromide (CuBr)/$\mathrm{Me_6TREN}$ initiating system under the condition of $\mathrm{[MMA]_0/[initiator]_0/[CuBr]_0/[Me_6TREN]_0}$ = 200/1/2/4.[11] The polymerization results are summarized in Table 1. There was a significant difference in the polymerization behavior among the solvents used. The reaction system was homogeneous with a slightly green color in toluene, THF, and methanol, while white suspension in HFIP. In addition, for toluene, THF, and methanol, the control of the molecular weight and polydipersity of the produced polymers was not successful (runs 1−4), which agreed with the previous result for the polymerization of MMA using the ATRP initiating system of $\mathrm{Cu^I/Me_6TREN}$.[12] In contrast, the polymerization in HFIP at low temperature was relatively successful and produced PMMAs with narrow polydispersities (runs 5 and 6). These results indicate that the ATRP of MMA using methyl α-bromoisobutyrate/CuBr/$\mathrm{Me_6TREN}$ in HFIP should be an attractive candidate for the stereocontrolled ATRP of MMA.

Thus, to establish a suitable condition for the living polymerization of MMA using the methyl α-bromoisobutyrate/CuBr/$\mathrm{Me_6TREN}$ initiating system, we carried out the polymerization in HFIP as the highly polar solvent. At −78 °C, the polymerization with MMA/HFIP at 1/1 (v/v) proceeded smoothly, while that with MMA/HFIP at 1/3 (v/v) did not occur because the polymerization system was frozen.[8] When the $\mathrm{[MMA]_0/[initiator]_0/[CuBr]_0/[Me_6TREN]_0}$ condition of 200/1/1/1 was employed, the polymerization rate was extremely slow, the monomer conversion was ca. 10%, and the polymer with $M_n = 4000$ and $M_w/M_n = 1.3$ was obtained after 500 h. In contrast, for the $\mathrm{[MMA]_0/[initiator]_0/[CuBr]_0/[Me_6TREN]_0}$ = 200/1/2/4 condition, the polymerization proceeded smoothly. Although the M_n values of the obtained polymers increased with the increasing monomer conversion, the measured molecular weights were much higher than calculated ones, and the M_w/M_n values of the obtained polymers were relatively narrow in the range of 1.29−1.44.

In addition, the polymerization in HFIP at −20 °C was examined for $\mathrm{[MMA]_0/[initiator]_0/[CuBr]_0/[Me_6TREN]_0}$ = 200/1/1/1. The molecular weights for the different amount of HFIP (MMA/HFIP = 1/1, 1/2, 1/3, and 1/4 (v/v)) are shown in Figure 1A. For the polymers obtained using the MMA/HFIP ratios of 1/1, 1/2, and 1/3, the M_n values of the obtained polymers increased

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10.1021/ma047656n CCC: $30.25

Table 1. Polymerization of Methyl Methacrylate (MMA) Using Methyl α-Bromoisobutyrate/CuBr/Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) as the Initiating System in Various Solvents[a]

run	solvent	temp (°C)	time (h)	conv[c] (%)	M_n[d]	$M_{n,th}$[e]	M_w/M_n[d]
1	toluene	30	20	6.1	105 000	1240	1.83
2	toluene	−20	20	21	42 200	4260	3.52
3	THF	−20	90	13	8 400	2640	2.10
4	MeOH	−20	145	15	14 700	3040	1.82
5	HFIP[f]	−20	24	42	13 100	8520	1.17
6[b]	HFIP[f]	−78	30	25	13 400	5070	1.31

[a] MMA/solvent = 1/3 (v/v). [b] MMA/solvent = 1/1 (v/v). [c] Determined by GC from the concentration of residual monomer with THF or toluene as the internal standard. [d] Determined by SEC using polystyrene standards. [e] $M_{n,th} = M_{MMA}[MMA]_0\text{conv}/(100[\text{initiator}]_0)$; M_{MMA} is the molar mass of MMA. [f] HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

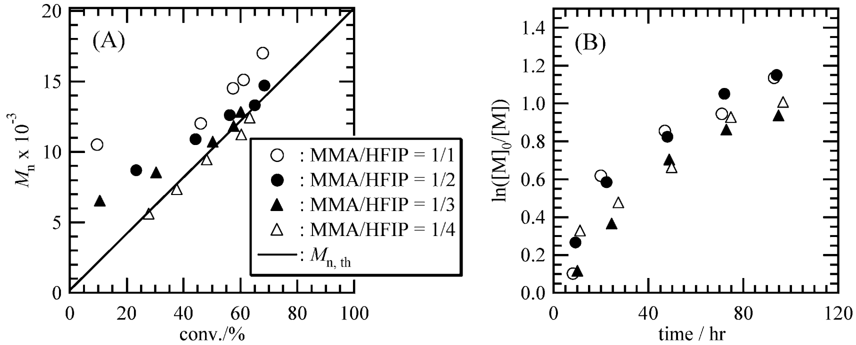

Figure 1. (A) Dependence of M_n and M_w/M_n on monomer conversion and (B) kinetic plots for the polymerization of MMA at −20 °C in HFIP with $[MMA]_0/[\text{initiator}]_0/[CuBr]_0/[Me_6TREN]_0$ = 200/1/1/1. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

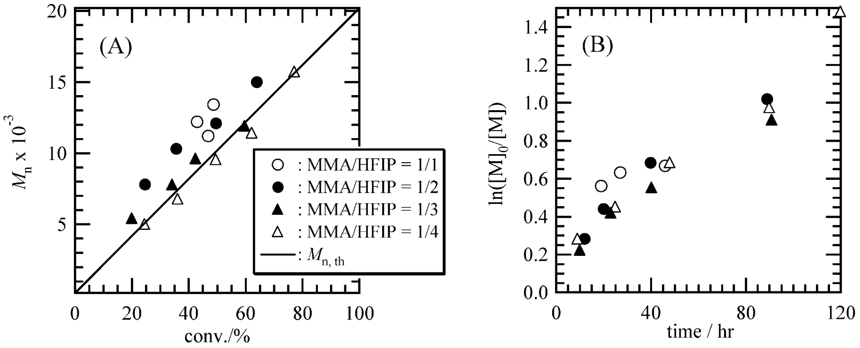

Figure 2. (A) Dependence of M_n and M_w/M_n on monomer conversion and (B) kinetic plots for the polymerization of MMA at −20 °C in HFIP with $[MMA]_0/[\text{initiator}]_0/[CuBr]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 200/1/1/0.2/1.2. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

with increasing monomer conversion, though the measured molecular weights were slightly higher than the calculated ones. In contrast, the theoretical linearity was observed when the MMA/HFIP ratio was 1/4. The M_w/M_n values of the obtained polymers were relatively narrow; i.e., 1.50−1.51 for MMA/HFIP of 1/1, 1.23−1.30 for 1/2, 1.22−1.25 for 1/3, and 1.18−1.26 for 1/4. Figure 1B shows the kinetic plots for the different MMA/HFIPs. The polymerization with MMA/HFIP of 1/1, 1/2, 1/3, and 1/4 exhibited nonlinear increases with a fast polymerization during the early stage of the reaction. These results indicate that some termination of growing chains should occur due to a high radical concentration.[12]

To more precisely control the early stages of the polymerization, the polymerization of MMA using the Cu^I/Me_6TREN initiating system was carried out in the presence of Cu^{II}. For $[MMA]_0/[\text{initiator}]_0/[CuBr]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 200/1/1/0.2/1.2 at −20 °C, the polymerization system was a white heterogeneous mixture. These results are shown in Figure 2. The addition of Cu^{II} to the system was effective for the early stage of polymerization. In addition, a well-controlled polymerization was observed up to a conversion as high as ~77% (Figure 2A), except for MMA/HFIP of 1/1, and the kinetic plots displayed a nonlinear increase with the monomer conversion, as shown in Figure 2B. In particular, the experimental and theoretical M_ns were nearly identical for the MMA/HFIP ratios of 1/3 and 1/4. The M_w/M_n values of the obtained polymers were narrower than those of the produced polymers using the ATRP initiating system in the absence of copper(II) bromide ($CuBr_2$): 1.39−1.59 for the MMA/HFIP ratio of 1/1, 1.18−1.27 for 1/2, 1.17−1.21 for 1/3, and 1.19−1.24 for 1/4. These results indicate that the addition of $CuBr_2$ affected the early stage of the polymerization.

The microstructure of the obtained polymers was determined by the 44−46 ppm region in the ^{13}C NMR spectrum, corresponding to the quaternary backbone carbons.[13,14] PMMA with a high degree of syndiotacticity was obtained as triad tacticity *rr* = 75−84%. The polymer obtained at −20 °C (run 5) had an *rr* of 75% and persistence ratio $\rho = 0.936$,[15] and the triad tacticity at −78 °C (run 6) was the highest with *rr* = 84% and $\rho = 0.974$. These ρ values indicated that the polymerization proceeded through a Bernouillian statistical process, and the stereochemistry was determined only by the last monomer unit, i.e., a typical radical polymerization process. This efficient stereocontrol should be caused by both the solvent effect of HFIP and the low-temperature effect.[7,8,16] Further studies, such as the nature of the catalyst in HFIP and the polymerization mechanism, are now in progress.

Conclusions. The simultaneous control of the molecular weight and stereochemistry of PMMA has been accomplished for the ATRP using the Cu^I/Me_6TREN initiating system in HFIP at low temperature, which is the first report of the synthesis of a well-defined and stereoregulated PMMA based on radical polymerization. The addition of $CuBr_2$ has an effect on the early stage of the polymerization, and the M_w/M_n values of PMMA were lower than those produced by the ATRP without $CuBr_2$. The polymerization even proceeds at −78 °C with narrow M_w/M_ns. The obtained polymer has a high degree of syndiotacticity such as $r = \sim 92\%$.

Acknowledgment. The authors thank Mitsubishi Chemical Co. for providing tris(2-(dimethylamino)ethyl)amine. The authors also thank Central Class Co. for providing 1,1,1,3,3,3-hexafluoro-2-propanol.

References and Notes

(1) (a) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (c) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (d) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(2) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.

(3) (a) Chief, J.; Chong, Y. K.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijis, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. (b) Chiefari, J.; Rizzardo, E. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: Hoboken, NJ, 2002; p 629.

(4) Lutz, J. F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986.

(5) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702.

(6) Lutz, J. F.; Jakubowski, W.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2004**, *25*, 486.

(7) Isobe, Y.; Yamada, K.; Nakano, T.; Okamoto, Y. *Macromolecules* **1999**, *32*, 5979.

(8) Isobe, Y.; Yamada, K.; Nakano, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4693.

(9) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* **1998**, *31*, 1535.

(10) (a) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674. (b) Wang, X.-S.; Luo, N.; Ying, S.-K. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1255. (c) Wang, X.-S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640.

(11) A typical procedure for polymerization. MMA (972 mg, 9.71 mmol), CuBr (13.8 mg, 0.0960 mmol), and Me_6TREN (44.2 mg, 0.192 mmol) were added to a dry Schlenk flask equipped with a magnetic stirring bar in an Mbraum glovebox. The flask was attached to a high-vacuum line. Degassed HFIP (3.0 mL) was added to the flask at −20 °C and then stirred for 1 h. Finally, methyl α-bromoisobutyrate (8.69 mg, 0.0480 mmol) was added to the mixture. The polymerization was quenched by exposure to air. The reaction mixture was diluted with chloroform and passed through aluminum oxide to remove the catalyst. The chloroform solution was concentrated under vacuum to give PMMA (conversion, 42%; M_n, 13 100; M_w/M_n, 1.17; *rr*, 75%).

(12) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629.

(13) (a) Peat, I. R.; Reynolds, W. P. *Tetrahedron Lett.* **1972**, *14*, 1359. (b) Wang, J. S.; Jerome, R.; Warin, R.; Teyssie, P. *Macromolecules* **1993**, *26*, 5984. (c) Baumgarten, J. L.; Muller, A. H. E.; Hogen-Esch, T. E. *Macromolecules* **1991**, *24*, 353.

(14) The microstructure of the purified polymers was analyzed by ^{13}C NMR (100 MHz) spectrometer (a JEOL JNM-A400II instrument). The quantitative spectra were obtained using 20% (w/v) sample in chloroform-d_1 at 55 °C, 45° pulse angle, inverse gated decoupling with a 7.0 s delay, 10 000 scans.

(15) The persistence ratio $\rho = 2(r)(m)/(mr)$.

(16) Haddleton, D. M.; Kukulj, D.; Duncalf, D. J.; Heming, A. M.; Shooter, A. J. *Macromolecules* **1998**, *31*, 5201.

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