Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 9227–9229 **9227**
DOI: 10.1021/ma101971z

Synthesis of Star Polymers Using ARGET ATRP

Joanna Burdyńska, Hong Y. Cho, Laura Mueller, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

Received August 25, 2010
Revised Manuscript Received October 13, 2010

Introduction. Star polymers are branched molecules containing multiple arms connected at a central core that have unique properties compared to their linear analogues.[1−3] Star polymers typically have lower viscosities than linear polymers and can also contain many end group functionalities within a single molecule, which is useful for various applications. The synthesis of star polymers has been successful by controlled radical polymerization (CRP).[4−6] Atom transfer radical polymerization (ATRP)[7−9] one of the most powerful CRP techniques, can provide star polymers by either polymerizing a monomer from a core,[10−14] attaching arms to a preformed multifunctional core,[15,16] or linking preformed arms together.[5,17−24] To synthesize stars by the latter method, often called the arm-first method, a macroinitiator or macromonomer is cross-linked in the presence of a di- or multivinyl cross-linking agent. Macroinitiators synthesized by ATRP have been successfully cross-linked under normal ATRP conditions. During normal ATRP, an alkyl halide initiator is activated through a reversible redox process by a transition metal catalyst in its lower oxidation state (most commonly Cu^I) to generate radicals and higher oxidation state catalyst (Cu^{II}).[25−27] The radical species continues propagation with monomer until it is again deactivated by Cu^{II}. Although normal ATRP is useful for synthesis of star polymers, it may lead to a relatively high amount of star−star termination reactions which limits arm conversion and broadens final molecular weight distribution.[28] This is due to a relatively high radical concentration during the polymerization process. In normal ATRP, the radical concentration can be controlled by controlling the ratio of Cu^I/Cu^{II} catalyst and the amount of alkyl halide initiator in the system. The alkyl halide concentration is fixed in the macroinitiator, and can only be diluted by solvent. A low Cu^I/Cu^{II} ratio could be employed, however the reaction would be much slower and would have difficulties in reaching higher conversions. Moreover, a high concentration of radicals inside the core favors termination and consumes Cu^I species more than under comparable homogeneous conditions.

A solution to these problems was developed for a normal ATRP process in that a macromonomer can be used in place of a macroinitiator. With this technique, the radical concentration can be independently controlled by using a small molecule alkyl halide initiator in conjunction with macromonomer arm.[29] A star polymer with improved molecular weight distribution could be obtained with this process. However, the reactions typically required repeated injections of alkyl halide initiator together with extra cross-linker to push toward higher arm conversion. Additionally, the reaction time was typically between 50 and 100 h and an extra synthetic step is typically required to convert a macroinitiator to macromonomer. Therefore, star synthesis by ATRP could still be improved.

Recently, a new ATRP initiation system was developed which allows for a significant decrease in the required Cu concentration. This system, known as activators regenerated by electron transfer (ARGET) ATRP utilizes a reducing agent to continuously regenerate the active Cu^I species which is otherwise lost through radical termination reactions.[30−36] During ARGET ATRP, the concentration of reducing agent determines the ratio of Cu^I/Cu^{II} catalyst, which in turn determines the radical concentration during polymerization. This technique for star synthesis is attractive because it is possible to control radical concentration during an ARGET ATRP. In controlled radical polymerization, radical concentration is highest at the beginning of the reaction and gradually decreases toward the end, due to the persistent radical effect.[37,38] If the radical concentration is too low during polymerization, the rate would be very slow. However, if it is too high, more termination reactions occur. Therefore, the use of ARGET ATRP can greatly improve star synthesis through the ability to adjust radical concentration during the polymerization process. At the beginning of the reaction, radical concentration can be kept low by using a lower concentration of reducing agent to prevent star−star termination. Radical concentration will steadily increase as reducing agent is introduced to the system. At later stages of the reaction, the star polymers become less susceptible toward coupling as they have grown in size and steric hindrance acts to prevent termination. Consequently, as the reaction progresses, more reducing agent can be fed into the system resulting in a faster polymerization rate without much termination. In this way, the synthesis of more uniform star (co)polymers can be achieved in a relatively short reaction time. In this communication, the synthesis of star polymers by normal and ARGET ATRP are compared.

Results and Discussion. A poly(*n*-butyl acrylate)−Br macroinitiator arm (PBA−Br) was synthesized using ARGET ATRP conditions to give a product with M_n = 10 300 and M_w/M_n = 1.11. This PBA−Br was used in the arm-first star synthesis under normal ATRP conditions (different ligands and different catalyst concentration) and under ARGET ATRP conditions (different reducing agent addition method) (Table 1). For normal ATRP star synthesis, CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and CuBr/tris(2-pyridylmethyl)amine (TPMA) were used (Table 1, entry 1−3). When CuBr/PMDETA was used as a catalyst (entry 1), 99% of the divinylbenzene (DVB) was consumed after 20 h. The GPC curves in Figure 1 A illustrate decreasing RI signal corresponding to the unreacted macroinitiators and increasing peak at higher molecular weight region corresponding to star polymers. Molecular weight ($M_{n,RI}$) was 39.6×10^3 determined by GPC with linear polySt standards. Area fraction of star polymers (A_{star}) in GPC curve was 84% at 20 h as calculated by deconvolution using Gaussian function. The absolute molecular weight measured by multiangle laser light scattering (MALLS) detector ($M_{w,MALLS}$) was 66.0×10^3. On the basis of DVB conversion, the d*n*/d*c* values in THF at 35 °C (a detailed calculation is described in the Supporting Information), and $M_{w,MALLS}$, the calculated number of arms per star core was 6. Similar results were observed when TPMA used as a ligand (Table 1, entry 2). A_{star} was 89% and $M_{w,MALLS}$ was 183×10^3.

---

*Corresponding author. E-mail: km3b@andrew.cmu.edu.

Table 1. Synthesis of (PolyBA)*n*-PolyDVB Star Polymers by ATRP and ARGET ATRP via the "Arm-First" Method[a]

entry	polymerization method	A_{star} [b]	$M_{\mathrm{n,RI}}$ [c] $\times 10^{-3}$	$M_{\mathrm{w,MALLS}}$ [d] $\times 10^{-3}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [e]	N_{arm} [f]	$N_{\mathrm{DVB,CORE}}$ [g]	d*n*/d*c* [h]
1	ATRP (PMDETA)[i]	0.84	39.6	66.0	1.18	6	46	0.079
2	ATRP (TPMA)[j]	0.89	66.9	183	1.19	15	250	0.076
3	ATRP (low [Cu])[k]	0	1.03	116	1.11	N/A	N/A	0.069
4	ARGET ATRP[l]	0.95	59.8	146	1.14	13	122	0.075
5	ARGET ATRP−CF[m]	0.98	78.0	254	1.19	22	263	0.073
6	ARGET ATRP−TF[n]	0.98	80.3	252	1.16	22	241	0.077

[a] Experimental conditions: $[\mathrm{PBA{-}Br}]_0 = 0.024$ M at 90 °C in anisole (75 vol %), stopped at 20 h. $M_{\mathrm{n,PBA}} = 10{,}300$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.11$. [b] Area fraction ratio of star polymers, determined by the multipeak splitting of the GPC curve using Gaussian function. [c] Number-average molecular weight, measure by THF GPC with RI detector, calibration with linear polySt standard. [d] Weight-average molecular weight, measured by THF GPC with MALLS detector. [e] Polydispersity, measured by THF GPC with RI detector, calibration with linear polySt standard. [f] Number-average value of the number of arms per star molecule, calculated based on equation in the Supporting Information. [g] Number-average value of DVB per star core, calculated by $M_{\mathrm{w,MALLS}} = (N_{\mathrm{arm}} \times M_{\mathrm{n,arm}}) + (N_{\mathrm{DVB,CORE}} \times M_{\mathrm{n,DVB}})$. [h] d*n*/d*c* values of star polymers, measured by THF GPC with MALLS detector. [i] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = 1/12/0.8/0.8$. [j] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr}]_0/[\mathrm{TPMA}]_0 = 1/12/0.8/0.8$. [k] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr}]_0/[\mathrm{TPMA}]_0 = 1/12/0.01/0.01$. [l] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{TPMA}]_0/[\mathrm{Sn(EH)_2}]_0 = 1/12/0.01/0.1/0.1$. [m] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{TPMA}]_0/[\mathrm{Sn(EH)_2}]_0 = 1/12/0.01/0.1/0$, continuous feeding $[\mathrm{Sn(EH)_2}]_{\mathrm{final}} = 0.2$. [n] Experimental conditions: $[\mathrm{PBA{-}Br}]_0/[\mathrm{DVB}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{TPMA}]_0/[\mathrm{Sn(EH)_2}]_0 = 1/12/0.01/0.1/0.01$, timed feeding $[\mathrm{Sn(EH)_2}]_{\mathrm{final}} = 0.2$.

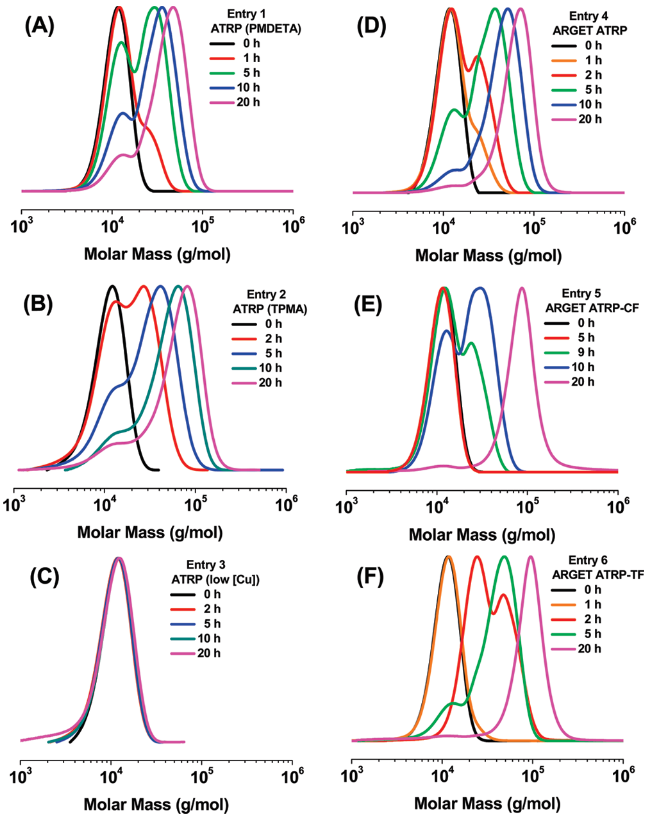

Figure 1. Molecular weight evolution by gel permeation chromatography during the star synthesis by (A) ATRP with CuBr/PMDETA (Table 1, entry 1), (B) ATRP with CuBr/TPMA (entry 2), (C) ATRP with low amount of CuBr/TPMA (entry 3), (D) ARGET ATRP (entry 4), (E) ARGET ATRP−CF (entry 5), and (F) ARGET ATRP−TF (entry 6), calibrated with linear polySt standard.

However, when a lower amount of the same, very active ATRP catalyst was used (1 mol % vs macroinitiator) no star polymer was formed within a 20 h time period (Table 1, entry 3 and Figure 1 C).

On the other hand, ARGET ATRP using the same concentration of catalyst, but in the presence of tin(II) 2-ethylhexanoate ($\mathrm{Sn(EH)_2}$) as reducing agent (Table 1, entries 4−6) showed much higher star yield (≥95%). First, the reaction was conducted with 0.1 eq. $\mathrm{Sn(EH)_2}$ (Table 1, entry 4 and Figure 1D). The obtained star polymer had the apparent molecular weight, $M_{\mathrm{n,RI}} = 59.8 \times 10^3$ and the absolute molecular weight $M_{\mathrm{w,MALLS}} = 146 \times 10^3$, indicating a larger number of arms incorporated to the star core than using normal ATRP with CuBr/PMDETA (Table 1, entry 1). Three different modes of $\mathrm{Sn(EH)_2}$ addition were studied. First, the entire reducing agent was added at the beginning of the reaction (Table 1, entry 4). Then, it was fed continuously during the reaction (ARGET ATRP−CF, Table 1, entry 5). The reaction was started without $\mathrm{Sn(EH)_2}$, then reducing agent was slowly and continuously added to the reaction system by a syringe pump during 20 h. No reaction occurred during the first 5 h, as the reducing agent was used to convert initially added $\mathrm{Cu^{II}}$ species and also remove the adventitious oxygen in the mixture. The reaction slowly started after enough $\mathrm{Sn(EH)_2}$ was introduced and resulted in a star with final $M_{\mathrm{w,MALLS}} = 254 \times 10^3$ and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.19$ in 98% yield. The third method for ARGET ATRP system is a timed-feeding system (ARGET ATRP−TF, Table 1, entry 6). At the beginning of polymerization, 0.01 eq. of $\mathrm{Sn(EH)_2}$ was added, after 1, 2.5, and 5 h an additional 0.03, 0.06, and 0.1 eq. of $\mathrm{Sn(EH)_2}$ was added, respectively (for a total of 0.2 eq. of $\mathrm{Sn(EH)_2}$ in the system). This reaction also showed high star yield ($A_{\mathrm{star}} = 98\%$) and high molecular weight $M_{\mathrm{w,MALLS}} = 252 \times 10^3$ and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.16$. For both stars the number of arms per star core was 22, indicating even higher molecular weight than for the traditional ARGET ATRP (Table 1, entry 4) as shown in Figure 1, parts E and F.

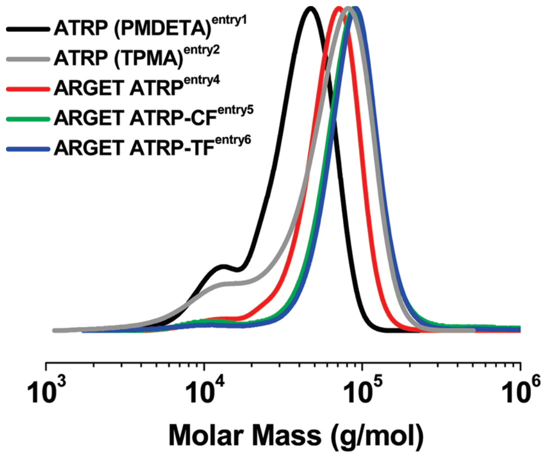

Figure 2. Comparison of final 20 h samples of the star polymers prepared by normal ATRP (PMDETA) (Table 1, entry 1, black line), ATRP (TPMA) (entry 2, gray line), ARGET ATRP (entry 4, red line), ARGET ATRP−CF (entry 5, green line), and ARGET ATRP−TF (entry 6, blue line).

All ATRP and ARGET ATRP reactions were stopped after 20 h. The synthesis using ARGET ATRP gives higher star yield than those for normal ATRP. Also, higher star molecular weight, higher star yield and higher number of arms per star core were obtained with ARGET ATRP as compared to normal ATRP. The polymerizations with feeding of reducing agent were quite slow at the beginning, but accelerated at the later stages. This observation confirms the benefits of using ARGET ATRP for star synthesis, in that polymerization rate (radical concentration) can be precisely controlled during polymerization. A comparison of the MWD of all star polymers prepared by ARGET ATRP and normal ATRP after 20 h is shown in Figure 2.

Conclusions. The arm-first star synthesis using a macroinitiator synthesized by ATRP could be significantly improved by using ARGET ATRP as compared to normal ATRP. Not only was less catalyst used, but stars were also prepared in essentially quantitative yield (98%) and with higher MW. Additional improvements can be obtained by applying slow feeding of the reducing agent to the reaction mixture. Additional studies are currently underway to further optimize the conditions for synthesis of various stars by ARGET ATRP.

Acknowledgment. The authors thank the National Science Foundation (DMR-10-26060) and acknowledge the Graduate Research Fellowship for L.M. and thank the members of the CRP Consortium at Carnegie Mellon University for their financial support.

Supporting Information Available: Text giving materials, characterization, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857–871.

(2) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068–1132.

(3) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.

(4) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384–6387.

(5) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350.

(6) (a) Goh, T. K.; Tan, J. F.; Guntari, S. N.; Satoh, K.; Blencowe, A.; Kamigaito, M.; Qiao, G. G. *Angew. Chem., Int. Ed.* **2009**, *48*, 8707–8711. (b) Pyun, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 217–220.

(7) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–15.

(8) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.

(9) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.

(10) Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nakagawa, Y. *Appl. Organomet. Chem.* **1998**, *12*, 667–673.

(11) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526–6535.

(12) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557–562.

(13) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218–7225.

(14) Matyjaszewski, K. *Polym. Int.* **2003**, *52*, 1559–1565.

(15) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960–4965.

(16) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 11360–11361.

(17) Abrol, S.; Kambouris, P. A.; Looney, M. G.; Solomon, D. H. *Macromol. Rapid Commun.* **1997**, *18*, 755–760.

(18) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482–4484.

(19) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340–2345.

(20) Du, J.; Chen, Y. *Macromolecules* **2004**, *37*, 3588–3594.

(21) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 7216–7223.

(22) Gao, H.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111–15113.

(23) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995–6004.

(24) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384–6387.

(25) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.

(26) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901–10.

(27) Matyjaszewski, K.; Tsarevsky, N. V. *Nat. Chem.* **2009**, *1*, 276–288.

(28) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 3154–3160.

(29) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 399–401.

(30) Jakubowski, W.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4482–4486.

(31) Jakubowski, W.; Min, K.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 39–45.

(32) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. *P. Natl. Acad. Sci.* **2006**, *103*, 15309–15314.

(33) di Lena, F.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 959–1021.

(34) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. *Langmuir* **2007**, *23*, 4528–4531.

(35) Min, K.; Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 1789–1791.

(36) Pietrasik, J.; Dong, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 6384–6390.

(37) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581–3610.

(38) Tang, W.; Tsarevsky, N. V.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 1598–1604.