

Synthesis of High Molecular Weight 3-Arm Star PMMA by ARGET ATRP

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Abstract: High molecular weight (MW), 3-arm star poly(methyl methacrylate) (PMMA) with a narrow MW distribution ($M_n=570,000$ g/mol, PDI=1.36) was successfully synthesized by activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP). The polymerization was carried out with a trifunctional initiator/CuBr₂/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) initiator/catalyst system in the presence of a tin(II) 2-ethylhexanoate [Sn(EH)₂] reducing agent at 90 °C. The concentration of the copper catalyst was as low as 30 ppm, and a high initiation efficiency of the initiating sites was obtained. The chain-end functionality of the high MW, 3-arm star PMMA was confirmed by a chain extension experiment with styrene via ARGET ATRP, using the same catalyst system.

Keywords: activators regenerated by electron transfer (ARGET), atom transfer radical polymerization (ATRP), star polymer, poly(methyl methacrylate), high molecular weight.

Introduction

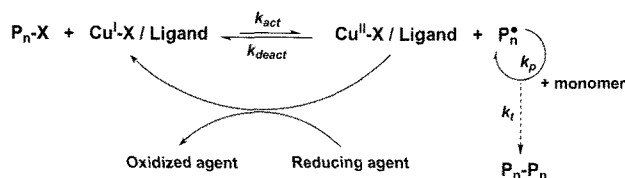
Atom transfer radical polymerization (ATRP) is one of the most successful controlled radical polymerization techniques for the preparation of polymers having controlled molecular weights (MWs) and MW distributions, and well-defined architectures.¹ Recently, activators regenerated by electron transfer (ARGET) ATRP has been developed. This new system improves the ATRP process by using environmentally acceptable reducing agents to constantly regenerate the Cu(I) activator species (Scheme I). This consequently allows a significant reduction in the amount of copper species required (from typically 1,000 ppm down to ~10 ppm).²⁻⁸ Therefore, the removal of the residual copper catalyst may not be necessary for some applications.

The synthesis of high MW polymers via ATRP is still a challenge because termination and other side reactions also occur during ATRP. In fact, these reactions become more prominent as higher MW polymers are targeted.¹ When synthesizing high MW polymers, high initiator efficiency and low extents of chain transfer and termination reactions are required, while maintaining a moderate reaction rate. There

are several reports on the use of ATRP to synthesis high MW polymers, such as poly(methyl methacrylate) (PMMA) and poly[2-(dimethylamino)ethyl methacrylate].⁹⁻¹² Interestingly, it was recently reported that high MW of polymers that cannot be produced via ATRP, can be effectively synthesized via ARGET ATRP.⁵⁻⁸ This is because the extent of the main side reaction, which limits the formation of these polymers via ATRP, is reduced when using ARGET ATRP, due to the drastically smaller amounts of Cu(II) species required. Pietrasik *et al.*⁷ have synthesized high MW poly(styrene-co-acrylonitrile) (SAN) copolymers via ARGET ATRP. By comparison, only low MW SAN copolymers have been obtained by normal ATRP. The high MW SAN copolymers were obtained by reducing the side reactions between the growing radicals and the copper catalyst.

In this study, the synthesis of high MW 3-arm star PMMA with a narrow MW distribution via ARGET ATRP was investigated. The polymerization was carried out by using a new copper(II) bromide (CuBr₂)/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) catalyst system in the presence of a tin(II) 2-ethylhexanoate [Sn(EH)₂] reducing agent. The amount of copper could be reduced down to ~30 ppm. The chain-end functionality of the resulting high MW star PMMA was also demonstrated by its successful block

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Scheme I. Mechanism of ARGET ATRP.

copolymerization of styrene via ARGET ATRP. It is known that high MW star polymers will be particularly useful in rheological applications because they have low melt and solution viscosities when compared to linear analogues with the same MWs.^{13,14} It is expected that the high MW 3-arm star PMMA synthesized in this research can be used in similar applications without the need to remove the residual copper catalyst.

Experimental

Materials. MMA (Duksan, Korea, 99%) was washed with an aqueous NaOH solution and water, stirred over calcium hydride (CaH₂), and distilled under reduced pressure. Styrene (Aldrich, 99%) was passed through a column filled with neutral alumina, dried over CaH₂, and then distilled under reduced pressure. Anisole (Acros, 99%) was distilled under vacuum. Tetrahydrofuran (THF, Duksan, Korea) was dried over Na and benzophenone. PMDETA (Acros, 99%), CuBr₂ (Aldrich, 99%), Sn(EH)₂ (Aldrich, ~95%), phloroglucinol dihydrate (Acros, 99%), 2-bromoisobutryl bromide (Aldrich, 98%), and triethylamine (TEA, Acros, 99%) were all used as received.

Synthesis of 1,3,5-Tris(2-bromoisobutyryloxy)benzene (TBIB). The trifunctional initiator was synthesized according to a previously reported method.¹⁵ Phloroglucinol dihydrate (4.0 g, 24.6 mmol) and triethylamine (10.2 mL, 73.8 mmol) were dissolved in 250 mL of anhydrous THF. Under a N₂ atmosphere, 2-bromoisobutryl bromide (10.5 mL, 73.8 mol) was added dropwise to the solution at 0 °C. The mixture was stirred at room temperature for 24 h. When the reaction was completed, triethylammonium bromide was removed by filtration and the solvent was removed by rotary evaporation. The product was dissolved in 50 mL of ethyl acetate, and then washed with water and an aqueous NaHCO₃ solution. The organic layer was separated and dried with anhydrous MgSO₄. After the solvent was removed, the product was further purified by recrystallization from petroleum ether (11.2 g, 80 % yield). ¹H NMR (CDCl₃): δ [7.16 (s, 3H), 2.05 (s, 18H)].

General Procedure for ARGET ATRP of MMA. Anisole (10 mL), TBIB (17.78 mg, 0.03 mmol), CuBr₂ (0.69 mg, 0.003 mmol), and PMDETA (9.6 μL, 0.46 mmol) were charged into a 50 mL reaction flask, and the mixture was bubbled with N₂ for 10 min. Degassed MMA (10 mL, 93.5 mmol) was added with stirring, and the mixture was again

bubbled with N₂ for 10 min. Finally, Sn(EH)₂ (15.1 μL, 0.046 mmol) was added to the reaction mixture. The flask was immersed into an oil bath at 90 °C.

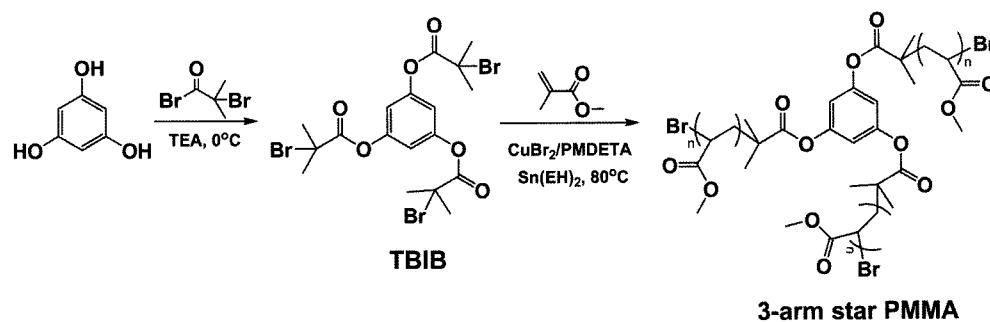
Extension of PMMA 3-Arm Star Macroinitiator with Styrene via ARGET ATRP. The synthesized 3-arm star PMMA having the number-average MW (*M_n*) of 128,000 g/mol and a polydispersity index (PDI) of 1.15 was used as a macroinitiator (MI). Anisole (15 mL), the 3-arm star PMMA MI (1 g, 0.0078 mmol), CuBr₂ (0.17 mg, 0.0007 mmol), and PMDETA (1.6 μL, 0.077 mmol) were charged into a 50 mL reaction flask. The resulting mixture was bubbled with N₂ for 10 min. Degassed styrene (0.89 mL, 7.8 mmol) was added with stirring, and the mixture was again bubbled with N₂ for 10 min. Finally, Sn(EH)₂ (2.5 μL, 0.0076 mmol) was added to the reaction mixture. The overall polymerization conditions were styrene/MI/CuBr₂/PMDETA/Sn(EH)₂ = 1000/1.0/0.1/1.0/1.0. The flask was sealed and immersed into an oil bath at 110 °C.

Cleavage of the Arm of the 3-Arm Star PMMA. The 3-arm star PMMA (*M_n* = 128,000 g/mol, PDI = 1.15) (10 mg) was dissolved in THF (10 mL). Isopropyl alcohol (2 mL) and NaOH (1 mg) were added, and the solution was refluxed overnight at 80 °C in order to hydrolyze the ester groups at the core of the star PMMA.

Analysis. The MW and polydispersity of the resulting polymers were determined by a gel permeation chromatography (GPC) system (Young Lin SP930D solvent delivery pump) coupled with an RI detector (RI 750F) and two columns (PLGel 20 μm Mixed-A and PLGel 10 μm 10⁴ Å; Agilent technologies). The eluent used was THF at 40 °C with a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration. ¹H NMR spectroscopy was performed using a Varian VXR-Unity NMR spectrometer (400 MHz) with CDCl₃ as the solvent.

Results and Discussion

In this study, high MW 3-arm star PMMA was synthesized via ARGET ATRP. Scheme II outlines the synthesis of a trifunctional initiator, TBIB, and its use in the preparation of high MW 3-arm star PMMA. The Br-containing ATRP-initiating groups were linked to each of the hydroxyl groups of the phloroglucinol dehydrate by an esterification reaction. The ARGET ATRP was performed by employing a CuBr₂/PMDETA catalyst system with TBIB as the core initiator in the presence of Sn(EH)₂, all under homogeneous conditions (in anisole). A tiny amount of Cu(II) species is used with a sufficiently large excess of the reducing agent, Sn(EH)₂. This not only reduces Cu(II) to Cu(I) to start the ATRP but it is also responsible for scavenging oxygen and radical inhibitors. Table I lists the reaction conditions and results of the ARGET ATRP of 3-arm star PMMA. High MW of 3-arm star PMMA was successfully synthesized using a copper concentration as low as 30 ppm. The MWs were close to



Scheme II. Synthesis of the trifunctional initiator, TBIB, and ARGET ATRP of high MW 3-arm star PMMA.

Table I. Polymerization Results of High MW 3-Arm Star PMMA by ARGET ATRP

Entry	Molar Ratios					Cu (ppm)	Time (min)	Conv. (%)	$M_{n,Theo.}$ ($\times 10^{-3}$)	$M_{n,GPC}$ ($\times 10^{-3}$)	M_w/M_n
	MMA	TBIB	CuBr ₂	PMDETA	Sn(EH) ₂						
1	3,000	1	0.1	1.5	1.5	30	120	45	134	128	1.15
2	3,000	1	0.2	1.5	1.5	50	240	25	75	40	1.16
3	3,000	1	0.3	1.5	1.5	100	720	22	66	49	1.13
4	4,000	1	0.13	1.9	1.9	30	100	55	219	230	1.24
5	6,000	1	0.20	3.0	3.0	30	120	52	312	320	1.22
6	8,000	1	0.26	3.8	3.8	30	160	44	352	455	1.30
7	10,000	1	0.34	5.0	5.0	30	250	50	502	508	1.34
8	12,000	1	0.43	6.0	6.0	30	270	53	636	570	1.36

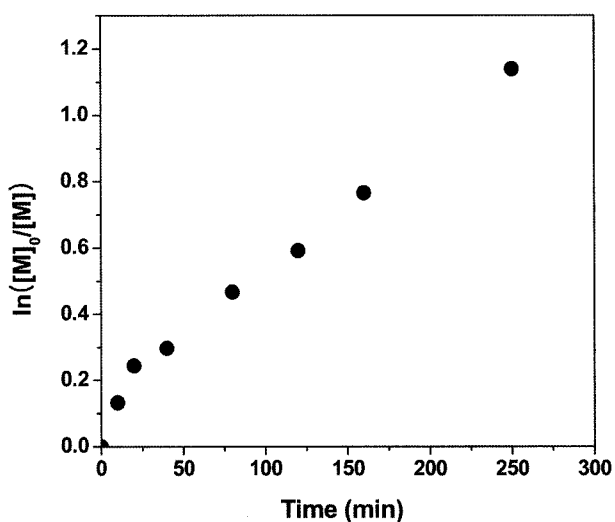


Figure 1. Kinetic plot for the ARGET ATRP of MMA with 30 ppm of copper. Experimental conditions: MMA/TBIB/CuBr₂/PMDETA/Sn(EH)₂=3000/1/0.1/1.5/1.5; [MMA]₀=4.675 M, $T=90^\circ\text{C}$, in anisole (1 vol equiv vs monomer).

theoretical values, and the MW distributions were very narrow. The catalyst ratio of CuBr₂/PMDETA/Sn(EH)₂ = 0.1/1.5/1.5 was suitable for the synthesis of the high MW star PMMA. At a monomer-to-initiating ratio of 12,000/1, 3-arm star PMMA with $M_n = 570,000$ g/mol and PDI = 1.36 was obtained.

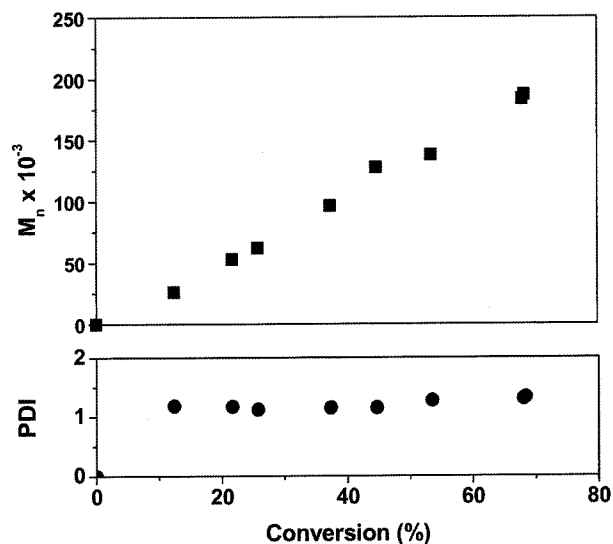


Figure 2. PMMA molecular weight and polydispersity as a function of conversion in the ARGET ATRP of MMA with 30 ppm of copper. Experimental conditions: MMA/TBIB/CuBr₂/PMDETA/Sn(EH)₂=3000/1/0.1/1.5/1.5; [MMA]₀=4.675 M, $T=90^\circ\text{C}$, in anisole (1 vol equiv vs monomer).

Figure 1 presents the kinetic plot for the ARGET ATRP of MMA (Table I, entry 1), and Figure 2 shows the excellent control over the MW and polydispersity in this system. Figure 3 shows a smooth shift of the entire polydispersity

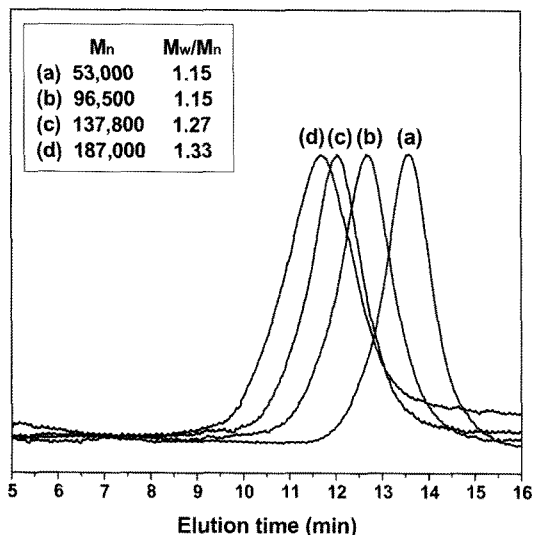


Figure 3. GPC traces during the ARGET ATRP of 3-arm star PMMA: (a) 20 min, (b) 80 min, (c) 160, and (d) 300 min. Experimental conditions: MMA/TBIB/CuBr₂/PMDETA/Sn(EH)₂=3000/1/0.1/1.5/1.5; [MMA]₀=4.675 M, T=90 °C, in anisole (1 vol equiv vs monomer).

toward higher MWs with increasing reaction time. All of the GPC traces were monomodal without any tailing caused by linear PMMA chains formed by chain transfer reactions. These results indicate that the ARGET ATRP of MMA has controlled/living characteristics. Xue *et al.*¹⁰ synthesized high MW 6-arm star PMMA ($M_n \approx 1,010,000$ g/mol, PDI ≈ 1.30) using a hexafunctional initiator via ATRP at 90 °C. However, this MW was determined after the removal of the linear PMMA chains formed by chain transfer reactions during the ATRP process.

In this study, the 3-arm star structure of the high MW PMMA was also confirmed by the cleavage of its arms (hydrolysis). Figure 4 shows the GPC curves before and after

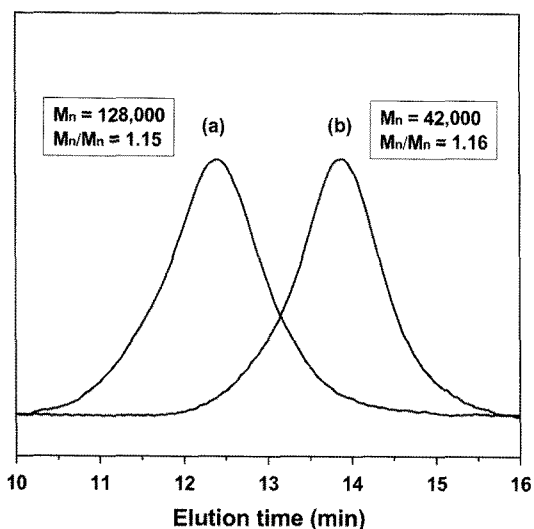


Figure 4. GPC traces (a) before and (b) after the arm cleavage of the high MW 3-arm star PMMA.

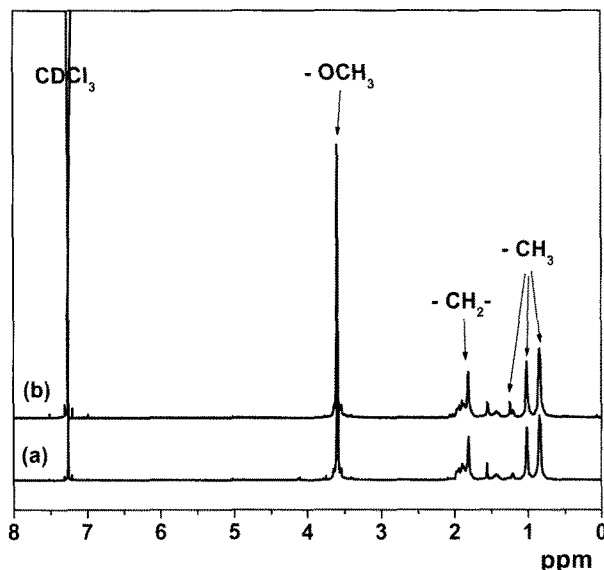


Figure 5. ¹H NMR spectra of (a) the 3-arm star PMMA and (b) the cleaved arms.

the arm cleavage of the 3-arm star PMMA (Table 1, entry 1). After the arm cleavage, the M_n of the linear PMMA was determined by GPC to be 42,000 g/mol (PDI=1.16) (the expected M_n is 42,700 g/mol). This suggests that the high-MW PMMA had a well-controlled 3-arm star architecture, as was intended. Figure 5 shows ¹H NMR spectra of the original 3-arm star PMMA and the cleaved arms. It is clear that the materials exhibited the same chemical shifts and area ratios for all of their different types of protons.

The chain-end functionality of the high MW 3-arm star PMMA was investigated by a chain extension experiment with styrene via ARGET ATRP. The high MW 3-arm star PMMA (Table I, entry 1) was used as a macroinitiator (MI) for the ARGET ATRP of styrene in anisole at 110 °C, using a CuBr₂/PMDETA catalyst system in the presence of the reducing agent, Sn(EH)₂. The overall polymerization conditions were styrene/MI/CuBr₂/PMDETA/Sn(EH)₂ = 1000/1.0/0.1/1.0/1.0. Figure 6 shows the GPC trace of the high MW 3-arm star PMMA-*block*-polystyrene (PMMA-*b*-PSt). The GPC curve is monomodal and symmetrical in nature with no traces of residual MI, indicating a high efficiency of the star PMMA MI. The clean and clear shift toward the higher molar mass region with the polymerization indicates the successful formation of the high MW 3-arm star PMMA-*b*-PSt ($M_n = 177,000$ g/mol, PDI=1.24). Jakubowski *et al.*⁸ recently reported that high MW PSt could be synthesized by ARGET ATRP using a CuBr/tris[2-(dimethylamino)ethyl]amine catalyst and a Sn(EH)₂ reducing agent at 90 °C. This was achieved by reducing the extent of the side reactions between the growing radicals and the copper catalyst. 87% of chain-end functionality was maintained at a 92% monomer conversion, whereas only 48% of chains retained chain-end functionality in normal

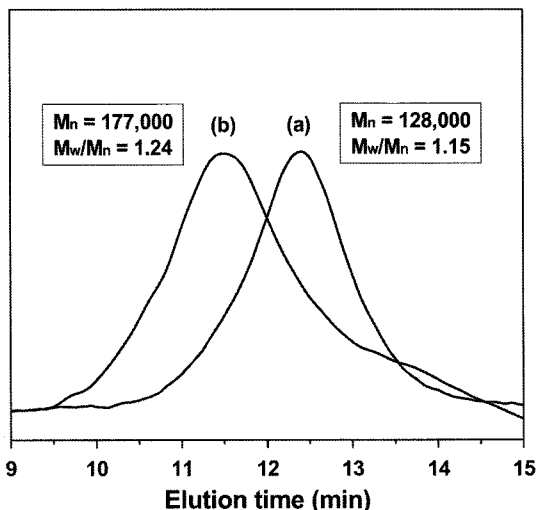


Figure 6. GPC traces of (a) the 3-arm star PMMA and (b) the 3-arm star PMMA-*b*-PSt. Experimental conditions: Styrene/MI/CuBr₂/PMDETA/Sn(EH)₂ = 1000/1.0/0.1/1.0/1.0; [St]₀ = 0.5178 M, *T* = 110 °C, in anisole.

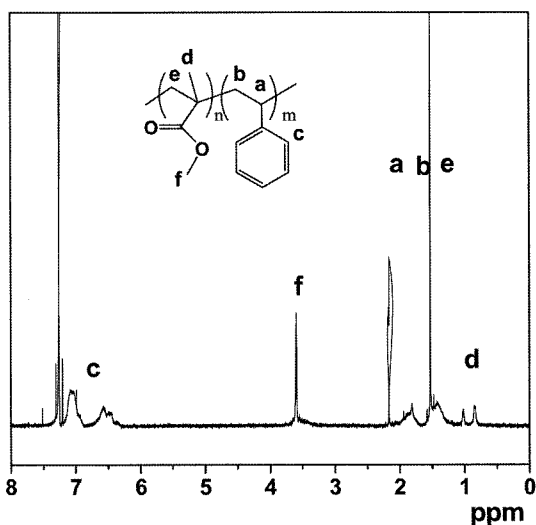


Figure 7. ¹H NMR spectrum of the 3-arm star PMMA-*b*-PSt. Experimental conditions: Styrene/MI/CuBr₂/PMDETA/Sn(EH)₂ = 1000/1.0/0.1/1.0/1.0; [St]₀ = 0.5178 M, *T* = 110 °C, in anisole.

ATRP. The composition of the 3-arm star PMMA-*b*-PSt was elucidated by ¹H NMR spectroscopy (Figure 7). The molar compositions were determined by comparing the relative intensities of the resonance signals at 3.6 ppm (attributed to the methoxy (-OCH₃) protons of the MMA unit) and those between 6.4 and 7.2 ppm (due to the phenyl protons from the styrene unit). On the basis of the molar fraction composition, the *M_n* of the PMMA-*b*-PSt copolymer was 189,000 g/mol, which is in good agreement with the *M_n* determined by GPC. As is clear from Figures 6 and 7, the polymerization of the second block was also well controlled when using ARGET ATRP.

Conclusions

High MW 3-arm star PMMA with a narrow MW distribution was synthesized by a “core-first” method with a CuBr₂/PMDETA catalyst system in the presence of a [Sn(EH)₂] reducing agent in anisole at 90 °C. The catalyst ratio of CuBr₂/PMDETA/Sn(EH)₂ = 0.1/1.5/1.5 was suitable for the synthesis of very high MW star PMMA. The chain-end functionality of the high MW 3-arm star PMMA was investigated by a chain extension experiment with styrene via ARGET ATRP. The overall polymerization conditions were styrene/MI/CuBr₂/PMDETA/Sn(EH)₂ = 1000/1.0/0.1/1.0/1.0.

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