Synthesis of High Molecular Weight Poly(styrene-*co*-acrylonitrile) Copolymers with Controlled Architecture

Joanna Pietrasik, Hongchen Dong, and Krzysztof Matyjaszewski*

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

Received May 1, 2006; Revised Manuscript Received July 6, 2006

ABSTRACT: High molecular weight styrene−acrylonitrile (SAN) copolymers were prepared under azeotropic conditions (60 mol % of styrene) by ARGET (activators regenerated by electron transfer) ATRP (atom transfer radical polymerization) at 80 °C in anisole. When a normal ATRP of styrene and acrylonitrile was conducted, the molecular weight of the resulting SAN copolymers was limited due to outer-sphere electron-transfer reactions. This was due to oxidation of polystyryl radicals to carbocations or reduction of polyacrylonitirile radicals to carbanions via reactions with Cu(II) and Cu(I) species, respectively. Since ARGET ATRP employs much lower concentrations of copper catalyst, the contributions of these side reactions are reduced, enabling formation of high molecular weight SAN copolymers ($M_n \sim 200\,000$) with low polydispersity ($M_w/M_n < 1.3$). Additionally, SAN copolymers with controlled chain architecture were prepared including block copolymers and starlike copolymers.

Introduction

Copolymers of styrene and acrylonitrile (SAN) possess outstanding chemical and mechanical properties leading to numerous applications.[1] They could be further enhanced by an additional control of molecular weights, polydispersities, and chain topology.

Properties of SAN copolymers depend on the overall copolymer composition and on the microstructure, primarily defined by the comonomer sequence distribution in the copolymer chain. The comonomer sequence distribution, initially modeled by the terminal model,[2] was subsequently described by the penultimate model[3] or, alternatively, by the complex participation model.[4]

SAN copolymers prepared by the conventional radical polymerization are characterized by broad molecular weight distribution. Controlled/living radical polymerization (CRP) provides a route to polymers with not only predetermined molecular weight and low polydispersities but also precisely controlled chain architecture.[5−10] The first successful attempts to apply CRP to the copolymerization of azeotropic mixtures of acrylonitrile and styrene were carried out in the presence of a stable free radical, TEMPO.[11] Although the homopolymerization of acrylonitrile with TEMPO as mediator was unsuccessful, the copolymerization reaction resulted in the preparation of SAN copolymers with low polydispersity. SAN copolymerization initiated from a polystyrene macroinitiator ($M_n \sim 20\,000$) led to the formation of a block copolymer with low polydispersity ($M_w/M_n < 1.3$) and molecular weight around 70 000. TEMPO-terminated polystyrene was also used to prepare SAN copolymers with variable ratios of styrene and acrylonitrile.[12] The highest polymerization rate was observed at ∼60 mol % of styrene. Other nitroxides were also reported to be suitable for controlled synthesis of SAN copolymers.[13,14]

RAFT was also successfully used to form SAN copolymers with molecular weight up to 50 000 and low polydispersity, $M_w/M_n < 1.1$.[15]

Copper-based atom transfer radical polymerization (ATRP) was previously applied to the synthesis of SAN copolymers using both low molecular weight and polymeric initiators.[16,17] However, only low molecular weight SAN copolymers were prepared. It was reported that during the homopolymerization of either styrene and acrylonitrile the catalytic species may participate in the outer-sphere electron-transfer (OSET) reactions by either oxidation of polystyryl radicals to carbocations or reduction of polyacrylonitirile radicals to carbanions via reactions with Cu(II) and Cu(I) species, respectively.[18] These processes limit the molecular weight of the resulting homopolymers.[19−24]

In the current study, we compared the copolymerization of styrene and acrylonitrile conducted under “normal” ATRP conditions, employing a “high” concentration of copper catalyst, and an ATRP conducted with a very low concentration of copper, using the recently developed method of the activators regenerated by electron transfer, ARGET ATRP.[25] Decreasing the absolute concentration of transition metal catalyst in an ARGET ATRP allowed the preparation of SAN copolymers with very high molecular weight and also the preparation of materials with controlled architecture.

Experimental Section

Materials. Styrene (S) (Aldrich, 99%) and acrylonitrile (AN) (Acros, 99%) were purified by passing through a column filled with neutral alumina. Tris(2-(dimethylamino)ethyl)amine (Me_6TREN),[26] ethylene glycol bis(2-bromoisobutyrate),[27] 1,1,1-tris(4-(2-bromoisobutyryloxy)phenyl)ethane,[27] and poly(ethylene oxide) monomethyl ether terminated with 2-bromoisobutyrate ($M_n = 5000$)[28] were synthesized following previously reported procedure. Copper(I) bromide (Aldrich, 98+%) was purified as described elsewhere.[29] Ethyl 2-bromoisobutyrate (EBiB) (Acros, 98%), 4,4-dinonyl-2,2-bipirydyne (dNbpy) (Aldrich, 97%), copper(II) bromide (Acros, 99%), copper(II) chloride (Acros, 99%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (Aldrich), and anisole (Aldrich, 99%) were used as received.

Synthetic Procedures. Copolymerization of Styrene and Acrylonitrile by Normal ATRP (Table 1, entry 1). A Schlenk flask was charged with Me_6TREN ligand (7.2 μL, 0.031 mmol) and copper(II) bromide (0.64 mg, 2.87 μmol), then anisole

---

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

10.1021/ma0611927 CCC: $33.50

Table 1. Experimental Conditions and Properties of SAN Copolymers Prepared by ATRP[a]

	molar ratio								
entry	Sty/AN	EBiB	CuBr	$CuBr_2$	ligand	time (h)	conv (%)	$M_n{}^b$ ($\times 10^{-3}$)	$M_w/M_n{}^b$
1	600/390	1	0.5	0.05	0.055 (Me_6TREN)	117.6	56.0	48.1	1.18
2	600/390	1	4		8 (dNbpy)	117.6	46.9	47.1	1.20

[a] The reactions were conducted in anisole at 80 °C. [Sty] = 3.17 M. [b] Determined by GPC in THF, based on polystyrene standard.

Table 2. Experimental Conditions and Properties of SAN Copolymers Prepared by ARGET ATRP[a]

	molar ratio									
entry	St/AN	EBiB	$CuCl_2$	$Me_6TREN/Sn(EH)_2$	Cu (ppm)	concn of Sty (M)	time (h)	conv (%)	$M_n{}^b$ ($\times 10^{-3}$)	$M_w/M_n{}^b$
3	600/390	1	0.01	0.5/0.5	10	3.17	164.0	76.5	88.5	1.19
4	600/390	1	0.03	0.5/0.5	30	3.17	67.0	80.6	70.9	1.18
5	600/390	1	0.05	0.5/0.5	50	3.17	21.7	71.1	99.3	1.22
6	1000/650	1	0.05	0.5/0.5	30	3.17	116.0	58.0	78.1	1.23
7	2000/1300	1	0.165	1.0/1.0	50	3.17	91.3	48.5	126.1	1.23
8	2000/1300	1	0.10	1.0/1.0	30	3.17	69.4	41.7	100.3	1.23
9	2000/1300	1	0.10	1.0/1.0	30	5.07	46.4	69.6	211.8	1.42
10	2000/1300	1	0.03	0.5/0.5	10	5.07	92.2	60.0	166.2	1.26
11	600/390	0.5 (di-)	0.03	0.5/0.5	30	3.17	18.7	77.5	157.0	1.28
12	600/390	0.33 (tri-)	0.03	0.5/0.5	30	3.17	18.3	63.9	188.8	1.25
13	2000/1300	1 ($PEO_{5,000}$-)	0.10	1.0/1.0	30	3.17	23.9	24.7	100.8	1.19

[a] The reactions were conducted in anisole at 80 °C. [b] Determined by GPC in THF, based on polystyrene standard.

(5.52 mL) was added, and the contents were stirred until a homogeneous solution formed. Then styrene (4.0 mL, 0.0349 mmol), acrylonitrile (1.52 mL, 0.0231 mmol), and ethyl 2-bromoisobutyrate (8.12 μL, 0.0553 mmol) were added to the flask. After three freeze−pump−thaw cycles, the flask was filled with nitrogen, and then while the mixture was immersed in liquid nitrogen, 4.11 mg (0.0287 mmol) of CuBr was added. The flask was sealed with a glass stopper, evacuated, and backfilled four times with nitrogen. After melting the reaction mixture and warming to the room temperature, the initial sample was taken and the sealed flask was placed in thermostated oil bath at 80 °C. Samples were taken at timed intervals and analyzed by gas chromatography (GC) and gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

Copolymerization of Styrene and Acrylonitrile by ARGET ATRP (Table 2, entry 4). Styrene (4.0 mL, 0.0349 mmol), acrylonitrile (1.52 mL, 0.0231 mmol), and anisole (4.22 mL) were added to a dry Schlenk flask. Then, an initiator EBiB (8.12 μL, 0.0533 mmol) and a solution of $CuCl_2$ complex (0.223 mg, 1.66 μmol)/Me_6TREN (0.38 μL, 1.66 μmol) in anisole (0.8 mL) were added. The resulting mixture was degassed by four freeze−pump−thaw cycles. After melting the mixture, a solution of $Sn(EH)_2$ (8.95 μL, 0.0278 mmol) and Me_6TREN (6.36 μL, 0.0278 mmol) in anisole (0.5 mL) was added. An initial sample was taken, and the sealed flask was placed in thermostated oil bath at 80 °C. Samples were taken at timed intervals and analyzed by gas chromatography (GC) and gel permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

Analyses. Molecular weight and molecular weight distribution were determined by GPC, conducted with a Waters 515 pump and a Waters 2414 differential refractometer using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) in THF as an eluent (35 °C, flow rate of 1 mL/min). Linear polystyrene standards were used for calibration. Absolute molecular weight was measured on GPC (Waters Microstyragel columns (guard, 10^5, 10^3, and 10^2 Å) with THF as eluent at 35 °C (flow rate = 1.00 mL/min). The detectors consisted of a differential refractometer (Waters 410, $\lambda = 930$ nm), differential viscometer (ViscoStar, Wyatt Technology), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology DAWN EOS, 30 mW, $\lambda = 690$ nm). Absolute molecular weights were determined with the d*n*/d*c* values of (0.157 mL/g) using Wyatt ASTRA software. Conversion of styrene and acrylonitrile was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column with anisole as an internal standard. Because of the high volatility of AN, the samples were immediately injected into the GC after dilution with THF. Injector and detector temperatures were kept constant at 250 °C. Analysis was carried out isothermally at 40 °C for 2 min followed by an increase of temperature to 160 °C at a heating rate of 20 °C/min and holding at 160 °C for 2 min. Conversion was calculated by detecting the decrease of the monomer peak area relative to the peak areas of the standards.

Results and Discussion

Synthesis of SAN Copolymers by Normal ATRP. The azeotropic feed ratio of styrene and acrylonitrile (60/40 molar ratio) was used for all experiments. To examine the effects of catalyst complexes displaying different activity on the reaction, two catalytic systems were used for the synthesis of SAN copolymers by ATRP: CuBr complexes formed with dNbpy and Me_6TREN. Cu(I) complexes with dNbpy are ∼10 000 times less active ATRP catalyst than complexes based on Me_6TREN.[26,30,31] Consequently, to provide a sufficiently fast polymerization rate, a larger amount of dNbpy/Cu(I) catalyst was used (entry 2) than that of Me_6TREN-based complex (entry 1). Furthermore, in the case of Me_6TREN, 10% of deactivator was added to the reaction medium in order to reduce contribution of termination reactions, according to the persistent radical effect.[6,32]

An ATRP catalyst may not only participate in a reversible atom transfer process but also can induce some side reactions. The catalysts may complex with monomer, may form organometallic species, may participate in catalytic chain transfer, may disproportionate, may lose halogen atoms, and additionally may also get involved in the outer-sphere electron-transfer (OSET) reactions by either oxidation of growing radicals to carbocations or reduction of radicals to carbanions.[18,19,33,34] Carbocations rapidly eliminate HX, which results in a loss of chain functionality and consequently loss of control over the reaction.[19] Studies with model compounds and macromolecular polystyrene species demonstrated that the elimination reaction was accelerated in the presence of the copper(II) complex. This process was faster for bromine-mediated ATRP than for chlorine-based systems and was more noticeable in polar solvents.[19,21]

The OSET process may also reduce the radicals to carbanions. Carbanions rapidly react with protic impurities, such as water, and form R−H terminated chains.[20] This reduction process should be preferred for the highly electrophilic polyacrylonitrile

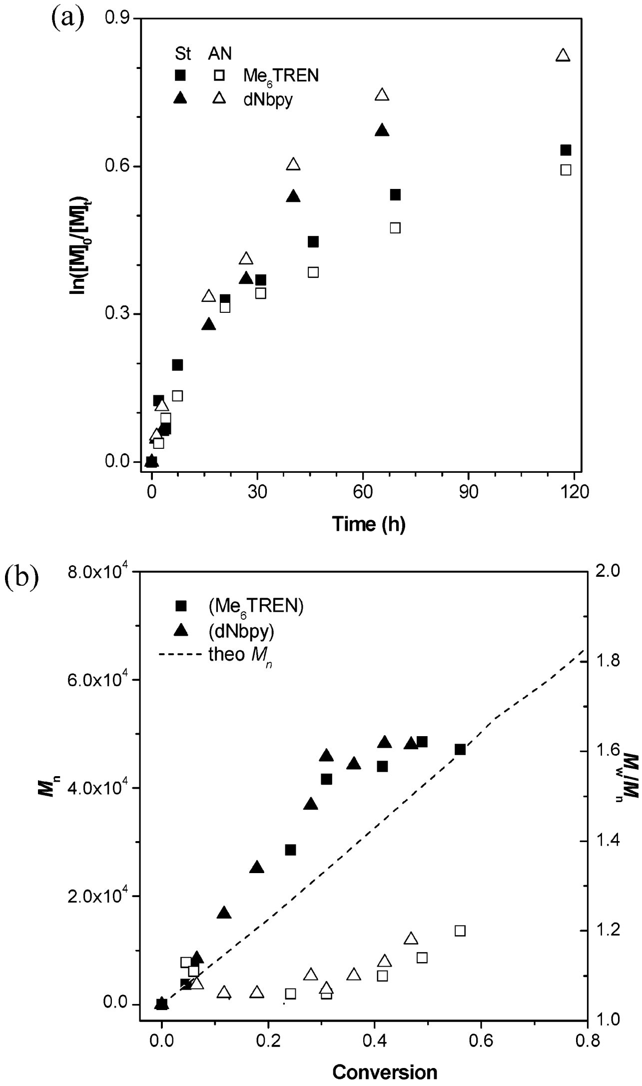

Figure 1. Semilogarithmic kinetic plots (a) and dependence of molecular weights (filled symbols) and molecular weight distributions (open symbols) (b) for ATRP of styrene and acrylonitrile (Table 1, entries 1 and 2).

radicals. Although this reaction was also proposed for polystyryl radicals,[35] it should be less likely, since polystyryl radicals have reduction potential by >500 mV more negative than polyacrylonitrile radicals. Both OSET processes reduce attainable molecular weights of polymers synthesized by ATRP, but since the OSET is a bimolecular process, the rate of these side reactions should depend on the catalyst selection and concentration of catalysts.

Therefore, the proper catalyst selection is very important. If a catalyst is too reducing, Cu(I) could be rapidly oxidized to Cu(II), simultaneously reducing radicals to carbanions by OSET. If catalysts are not reactive enough, then Cu(II) species could be reduced to Cu(I) and radicals oxidized to carbocations. Additionally, very active catalysts generate more radicals and may lead to more significant radical termination.[26,32]

Results of the optimized normal ATRP for SAN copolymerization with less active CuBr/dNbpy and more active CuBr/Me_6TREN catalysts are shown in Table 1 and also in Figures 1 and 2.

Figure 1 presents the semilogarithmic kinetic plots for polymerization of SAN with dNbpy and Me_6TREN/Cu(I) catalysts. The former catalyst was used at an 8 times higher concentration in order to attain a similar polymerization rate. Neither dNbpy nor Me_6TREN provides a constant number of growing radicals during the ATRP process, as shown by a progressive curvature of kinetic plots (Figure 1). Monomer conversion stopped at around 50% and 60%, respectively. Molecular weights reached nearly 50 000. The polydispersity of the copolymers start to increase above 50% monomer conversion. This can be due to involvement of chain breaking reactions.

The deactivation of active species for both catalytic systems is confirmed by the progressive tailing of the peaks in SEC traces (Figure 2). Attempts to continue the reaction by introducing an additional amount of Me_6TREN/Cu(I) were not successful.

Synthesis of SAN Copolymers by ARGET ATRP. The recently introduced concept of ARGET (activators regenerated by electron transfer) ATRP enables conducting an ATRP process with a significantly lower concentration of catalysts which is continuously regenerated by various reducing agents.[25] Furthermore, ARGET ATRP can be started with a very low concentration of the oxidatively stable Cu(II) species, which additionally alleviates problems of catalyst dissolution and purification of the reaction mixture. Moreover, because of a lower catalyst concentration, side reactions originated from the catalyst should be significantly suppressed.

ARGET ATRP was conducted with ethyl 2-bromoisobutyrate (EBiB) as an initiator and Me_6TREN/Cu as the catalyst. Experimental conditions and properties of SAN copolymers prepared by ARGET ATRP are shown in Table 2. To optimize the amount of copper, three different amounts of a catalytic system were used: 10, 30, and 50 ppm vs monomer (Table 2,

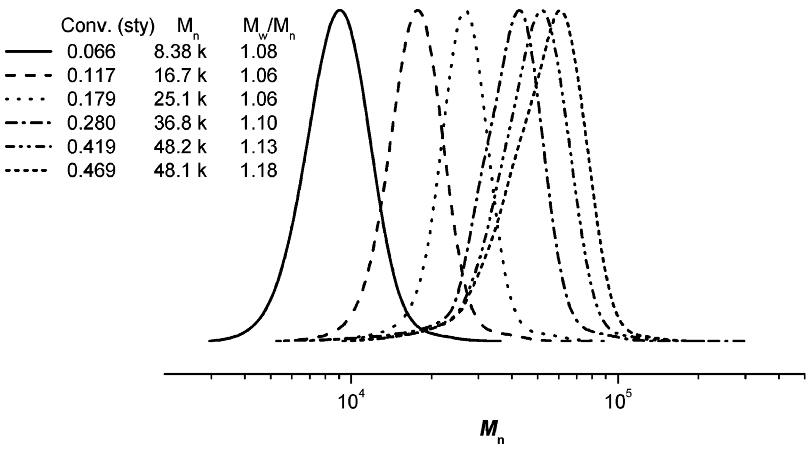

Figure 2. Evolution of SEC traces for ATRP of styrene and acrylonitrile with Me_6TREN as a ligand (Table 1, entry 1).

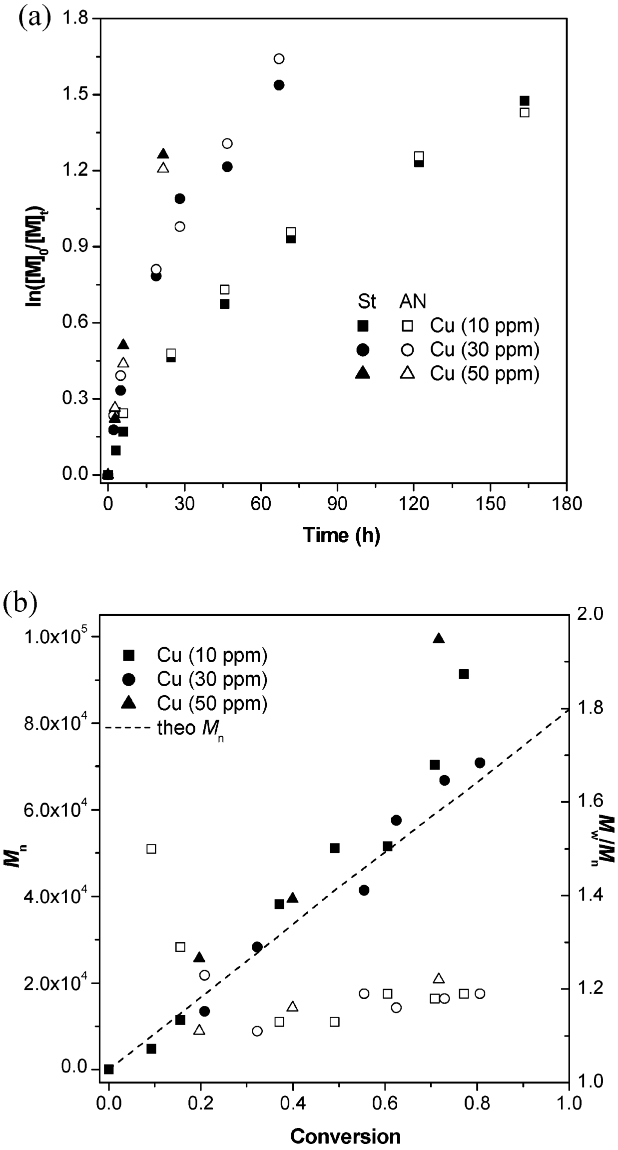

Figure 3. Kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion in ARGET ATRP of styrene and acrylonitrile with 10, 30, and 50 ppm of copper (Table 2, entries 3−5), St/AN/EBiB/Me_6TREN/Sn(EH)$_2$ = 600/390/1/0.5/0.5, in anisole at 80 °C.

entries 3−5). The amount of the reducing agent, Sn(EH)$_2$, was kept constant at 50 mol % vs the initiator. Kinetic plots for the aforementioned reactions with different copper concentrations are presented in Figure 3.

The polymerization rate increased with the copper concentration. A slight curvature of semilogarithmic kinetic plots indicates that the number of growing radicals decreased. The experimental molecular weight obtained from GPC analyses using linear polystyrene standards were close to theoretical values. Overall higher polydispersities can be ascribed to very small amount of Cu(II) species and relatively slow deactivation.

Figure 4 shows a smooth shift of the entire molecular weight distribution toward higher molecular weight without any tailing for the system containing 30 ppm of catalyst.

When a higher DP was targeted (DP$_n$ = 1650), polymerization was slower and the level of control over polymerization was reduced when compared with the experiments targeting a DP$_n$ = 990 (Table 2, entries 4 and 6). Figure 5 presents the kinetic plots for the copolymerization of styrene and acrylonitrile with 30 ppm of copper vs monomer as well as molecular weight and polydispersities of the polymers prepared in this system.

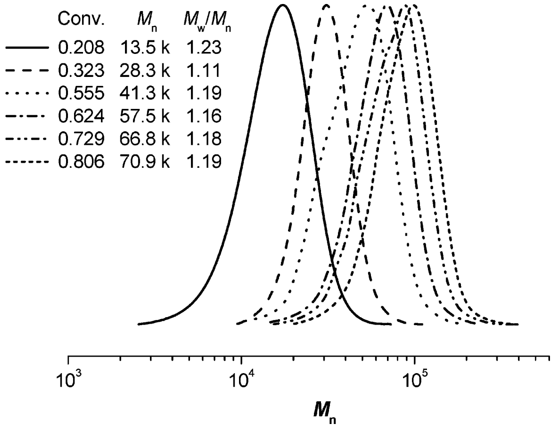

Figure 4. Evolution of molecular weight distribution during ARGET ATRP of styrene and acrylonitrile with 30 ppm of copper (Table 2, entry 4). St/AN/EBiB/CuCl$_2$/Me_6TREN/Sn(EH)$_2$ = 600/390/1/0.03/0.5/0.5, in anisole at 80 °C.

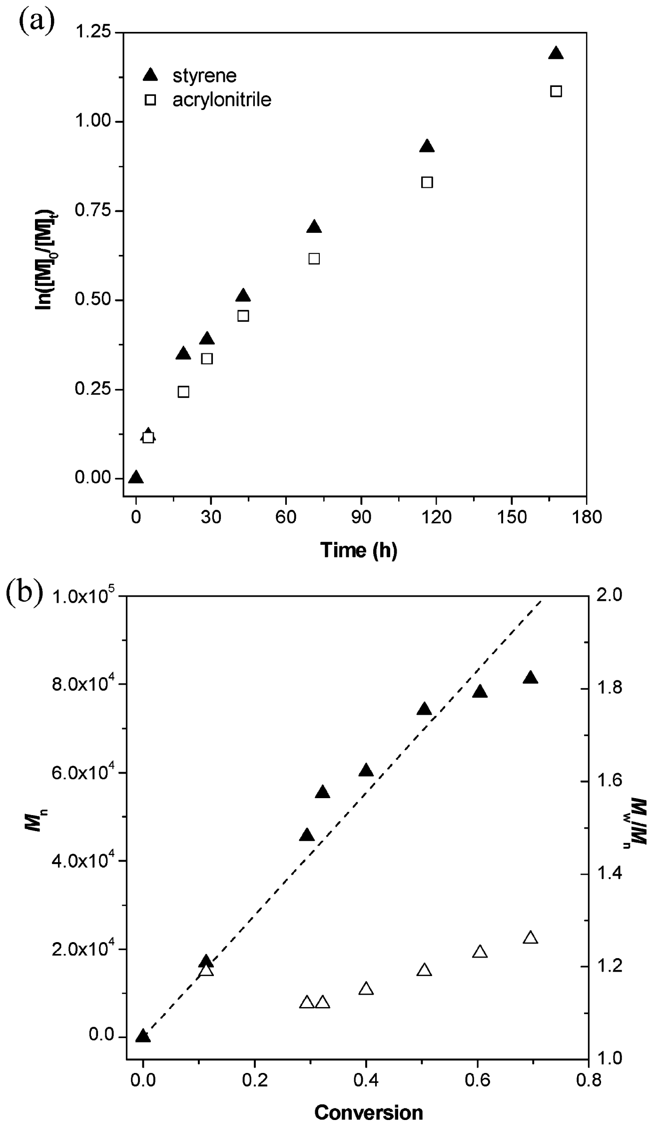

Figure 5. Kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion for ARGET ATRP of styrene and acrylonitrile with 30 ppm of copper (Table 2, entry 6), St/AN/EBiB/CuCl$_2$/Me_6TREN/Sn(EH)$_2$ = 1000/650/1/0.05/0.5/0.5, in anisole at 80 °C.

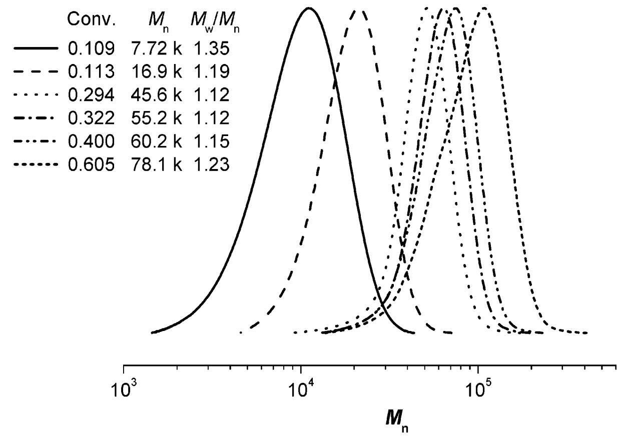

Figure 6. Evolution of molecular weight distribution during ARGET ATRP of styrene and acrylonitrile with 30 ppm of copper (Table 2, entry 6). St/AN/EBiB/CuCl$_2$/Me$_6$TREN/Sn(EH)$_2$ = 1000/650/1/0.05/0.5/0.5, in anisole.

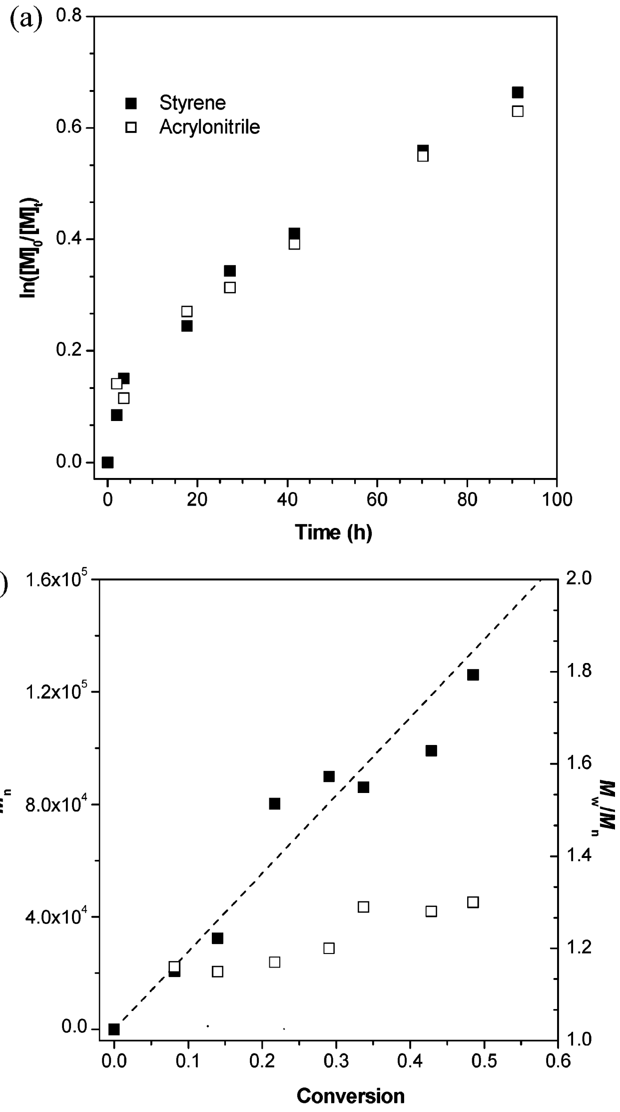

Figure 7. Kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion for ARGET ATRP of styrene and acrylonitrile with 50 ppm of copper (Table 2, entry 7), St/AN/EBiB/CuCl$_2$/Me$_6$TREN/Sn(EH)$_2$ = 2000/1300/1/0.165/1/1, in anisole at 80 °C.

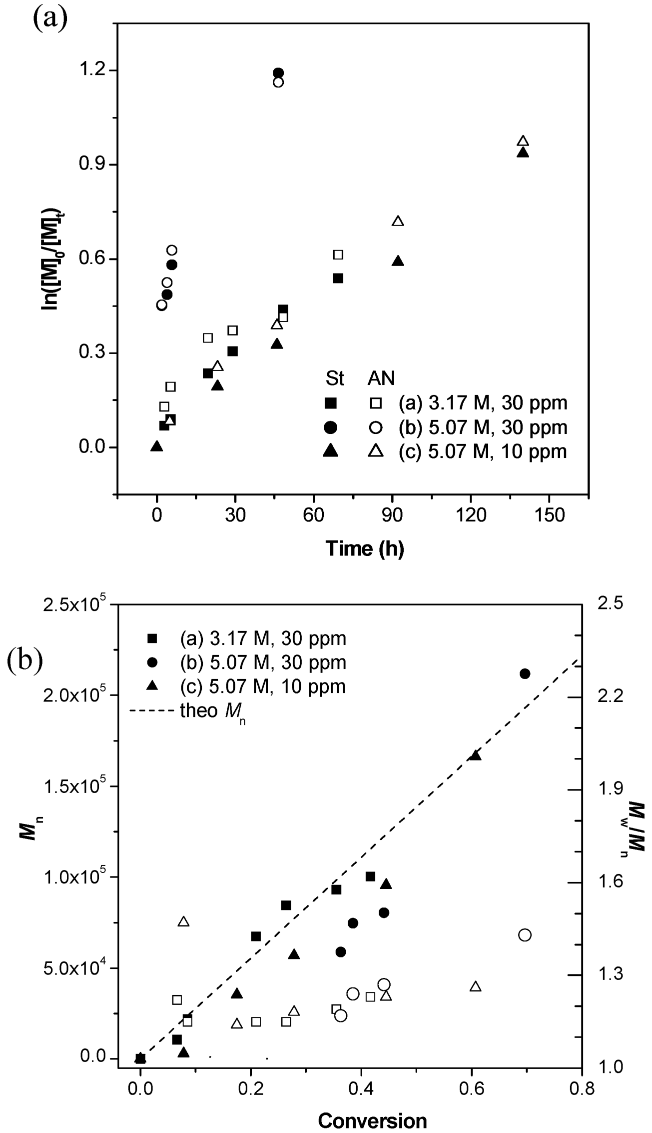

Figure 8. Kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion for ARGET ATRP of styrene and acrylonitrile with 30 and 10 ppm of copper (Table 2, entries 8−10), St/AN/EBiB/CuCl$_2$/Me$_6$TREN/Sn(EH)$_2$ = 2000/1300/1/0.1/1.0/1.0 (30 ppm), 2000/1300/1/0.03/0.5/0.5 (10 ppm), in anisole at 80 °C.

The increase in polydispersity is accompanied by a tailing in SEC traces and eventual appearance of a shoulder (Figure 6). This could indicate formation of dead chains by termination reactions. Therefore, high monomer conversion cannot be attained with a sufficient control over polymerization under these conditions.

Similar behavior was observed for the reaction targeting even higher molecular weight, DP$_n$ = 3300. In this system, higher concentrations of copper catalyst (50 ppm vs monomer) and reducing agent were used. A curvature of the semilogarithmic kinetic plots was observed, and an increase of polydispersity with monomer conversion was found, but experimental molecular weights were above 100 000 and close to those theoretically predicted (Figure 7).

The amount of solvent was reduced in order to increase the rate of monomer conversion and retain control over the reaction, (Table 2, entries 8−10). The initial concentrations of comonomers were increased from 3.17 to 5.07 M. The catalyst concentration was 10 and 30 ppm vs comonomers. Figure 8 presents kinetic plots for the polymerizations. Significant differences in the reactions rate were observed. At higher comonomers concentration, 5.07 M, monomer conversion reached 70% and M_n = 211 800; however, the molecular weight distribution was relatively broad, M_w/M_n > 1.4. When the

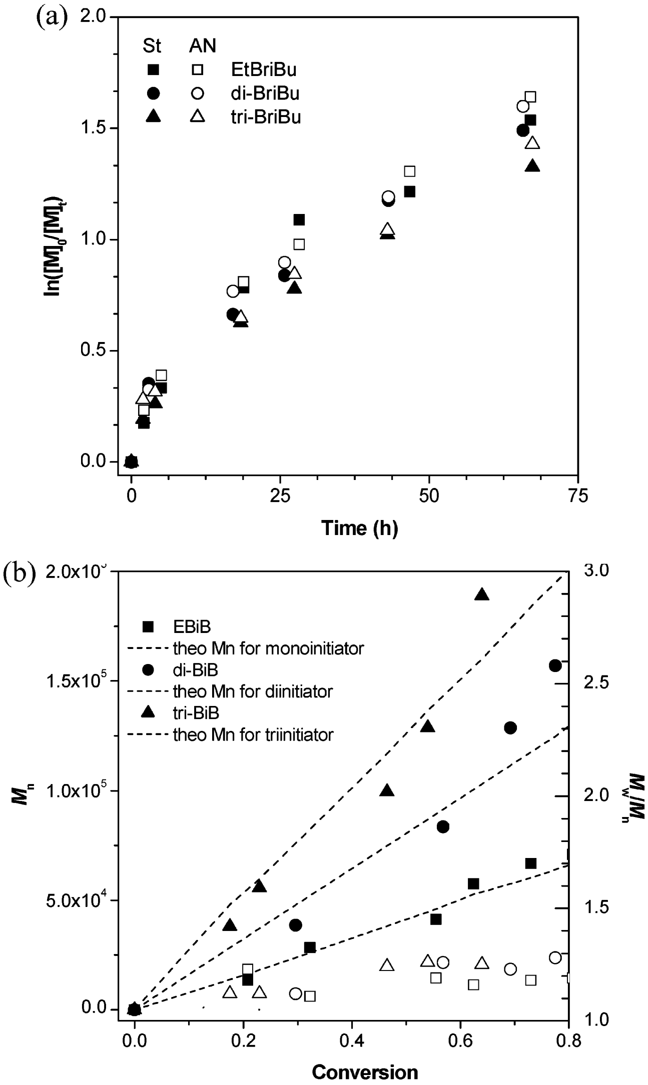

Figure 9. First-order kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion for ARGET ATRP of SAN initiated by mono-, di-, and trifunctional initiators with 30 ppm of copper (Table 2, entries 4, 11 and 12), St/AN/RX/$CuCl_2$/Me_6TREN/Sn(EH)$_2$ = 600/390/1/0.03/0.5/0.5, in anisole at 80 °C.

Table 3. Relative and Absolute Molecular Weight Data for SAN Copolymers Prepared from Mono-, Di-, and Trifunctional Initiators as Well as PEO-Based Macroinitiator

	M_n		
functionality	GPC[a]	3D-GPC[b]	$[\eta]_n$[c] (dL/g)
EBiB	100 100	116 900	0.633
EBiB	211 000	216 600	1.013
di-BiB	98 100	92 100	0.569
di-BiB	157 000	160 400	0.846
tri-BiB	98 400	126 000	0.602
tri-BiB	188 800	203 700	0.790

[a] Measured by GPC with linear polystyrene standards. [b] Measured by triple detection GPC; the d*n*/d*c* value of SAN copolymer (60% styrene) was determined as 0.157 mL/g. [c] Number-average intrinsic viscosity determined by 3D-GPC.

amount of copper was decreased to 10 ppm, keeping comonomers concentration at the same level, 5.07 M, the kinetic plot was linear, molecular weight very close to theoretical value, M_n = 166 200, and polydispersity was low, M_w/M_n = 1.26. (Table 2, entry 10). Thus, lower catalyst concentration reduced side reactions between the growing radicals and copper species leading to well-defined SAN copolymers.

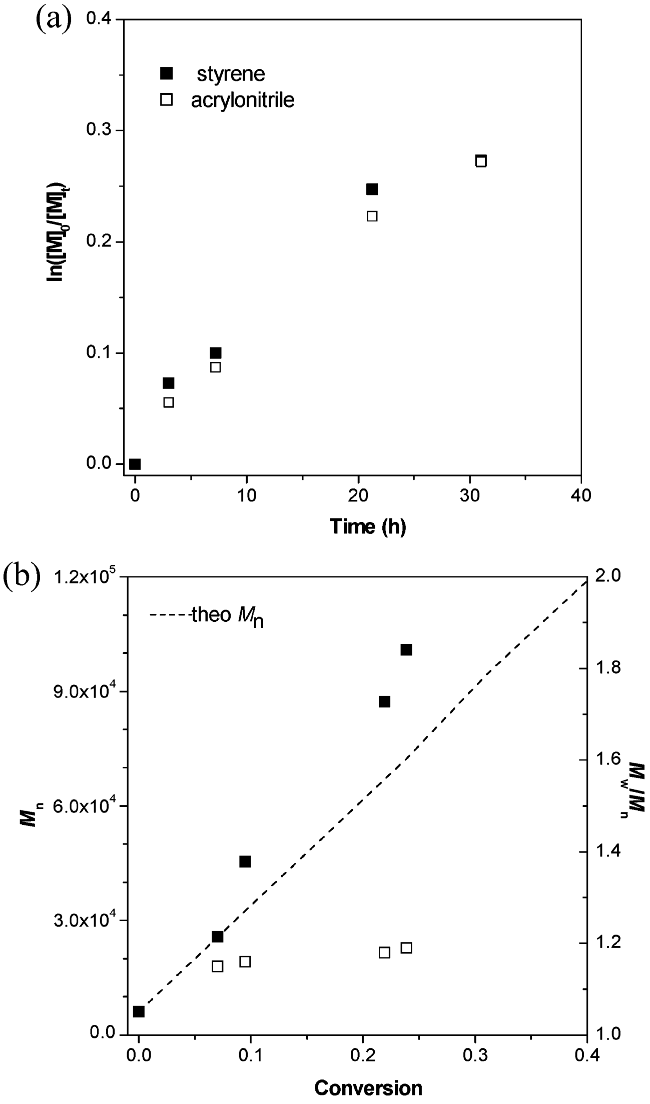

Figure 10. First-order kinetic plots (a) and molecular weight and molecular weight distribution (b) as a function of conversion for ARGET ATRP of SAN initiated from macroinitiator with 30 ppm of copper (Table 2, entry 13), St/AN/RX/$CuCl_2$/Me_6TREN/Sn(EH)$_2$ = 2000/1300/1/0.1/1.0/1.0, in anisole at 80 °C.

Synthesis of SAN from Di- and Trifunctional Initiators. ARGET ATRP can be used not only for synthesis of linear chains growing in one direction but also for multifunctional initiators. Figure 9 shows kinetic plots and evolution of molecular weight with conversion for systems containing initiators with variable functionality. The overall concentration of alkyl halide moieties was kept constant. Since the values of f*[I], where f is the number of alkyl halide species per molecule, and [Cu] were constant, monomer was consumed at the same rate. However, the overall molecular weight grew faster during polymerization conducted with higher functionality initiators, although the concentration of active species was constant. Figure 9 illustrates the evolution of molecular weights and molecular weight distributions with conversion using linear polystyrene calibration. The polydispersity remained low throughout the reaction, indicating good control, M_w/M_n < 1.3.

Triple-detector GPC (with viscometry and light scattering detectors) was used to determine the absolute molecular weight of SAN synthesized from mono-, di-, and trifunctional initiators. The absolute molecular weights and those based on calibration using linear polystyrene standards are compared in Table 3. They were in a good agreement, although some differences were observed for star copolymers due to their more compact structure. Star copolymers, as expected, had lower viscosity.

SAN Copolymers Initiated from a Macroinitiator. A poly(ethylene oxide) macroinitiator containing the 2-bromoisobutyrate group was used for the copolymerization of styrene and acrylonitrile. The reaction conditions are shown in Table 2, entry 13. Figure 10 presents a kinetic plot for the copolymerization as well as evolution of molecular weight and molecular weight distribution with time. Small discrepancies between the molecular weight determined by GPC and theoretical values were observed at the early stages of the polymerization. The polydispersity remained low during the entire process.

Conclusions

Normal ATRP has limitations in the synthesis of high molecular weight SAN copolymers due to the plausible participation of OSET reactions. ARGET ATRP allows both: a significant reduction of a catalyst used (down to 10 ppm) and a suppression of side reactions, enabling better polymerization control of SAN copolymers with molecular weights in the range of $M_n \sim 200\,000$ and low polydispersities ($M_w/M_n < 1.3$). Initiation by mono-, di-, and trifunctional initiators and a poly(ethylene oxide) macroinitiator resulted in the formation of well-defined SAN copolymers with controlled architecture.

Acknowledgment. The authors acknowledge the financial support by the National Science Foundation (DMR 05-49353), members of the ATRP/CRP Consortia at Carnegie Mellon University, and Kosciuszko Foundation. J. Spanswick and W. Jakubowski are acknowledged for helpful discussions as well as J. K. Oh for providing a macroinitiator.

References and Notes

(1) Ziemba, G. P. *Encycl. Polym. Sci. Technol.* **1964**, *1*, 425−435.
(2) Alfrey, T., Jr.; Goldfinger, G. *J. Chem. Phys.* **1944**, *12*, 205−209.
(3) Merz, E.; Alfrey, T.; Goldfinger, G. *J. Polym. Sci.* **1946**, *1*, 75−82.
(4) Cais, R. E.; Farmer, R. G.; Hill, D. J. T.; O'Donnell, J. H. *Macromolecules* **1979**, *12*, 835−839.
(5) Matyjaszewski, K., Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, NJ, 2002.
(6) Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329−385.
(7) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2−166.
(8) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337−377.
(9) Matyjaszewski, K. *Polym. Int.* **2003**, *52*, 1559−1565.
(10) Matyjaszewski, K.; Ziegler, M. J.; Arehart, S. V.; Greszta, D.; Pakula, T. *J. Phys. Org. Chem.* **2000**, *13*, 775−786.
(11) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. *Macromolecules* **1996**, *29*, 6393−6398.
(12) Baumann, M.; Roland, A.-I.; Schmidt-Naake, G.; Fischer, H. *Macromol. Mater. Eng.* **2000**, *280/281*, 1−6.
(13) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.
(14) Detrembleur, C.; Sciannamea, V.; Koulic, C.; Claes, M.; Hoebeke, M.; Jerome, R. *Macromolecules* **2002**, *35*, 7214−7223.
(15) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(16) Tsarevsky, N. V.; Sarbu, T.; Goebelt, B.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 6142−6148.
(17) Tsarevsky, N. V.; Bernaerts, K. V.; Dufour, B.; Du Prez, F. E.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 9308−9313.
(18) Matyjaszewski, K. *Macromol. Symp.* **1998**, *134*, 105−118.
(19) Matyjaszewski, K.; Davis, K.; Patten, T. E.; Wei, M. *Tetrahedron* **1997**, *53*, 15321−15329.
(20) Matyjaszewski, K.; Jo, S. M.; Paik, H.-j.; Shipp, D. A. *Macromolecules* **1999**, *32*, 6431−6438.
(21) Lutz, J.-F.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 897−910.
(22) Lutz, J.-F.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2002**, *203*, 1385−1395.
(23) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710−4717.
(24) Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1785−1801.
(25) (a) Jakubowski, W.; Min, K.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 39−45. (b) Jakubowski, W.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4482−4486.
(26) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958−5959.
(27) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526−6535.
(28) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475−4478.
(29) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, 1−4.
(30) Qiu, J.; Matyjaszewski, K.; Thouin, L.; Amatore, C. *Macromol. Chem. Phys.* **2000**, *201*, 1625−1631.
(31) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629−8639.
(32) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(33) Braunecker, W. A.; Pintauer, T.; Tsarevsky, N. V.; Kickelbick, G.; Matyjaszewski, K. *J. Organomet. Chem.* **2005**, *690*, 916−924.
(34) Braunecker, W. A.; Tsarevsky, N. V.; Pintauer, T.; Gil, R. R.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4081−4088.
(35) Lazzari, M.; Chiantore, O.; Mendichi, R.; Lopez-Quintela, M. A. *Macromol. Chem. Phys.* **2005**, *206*, 1382−1388.

MA0611927