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Transformation of the Cationic Growing Center of Poly(tetrahydrofuran) into Samarium Amide. Block Copolymerization of Tetrahydrofuran with Methyl Methacrylate

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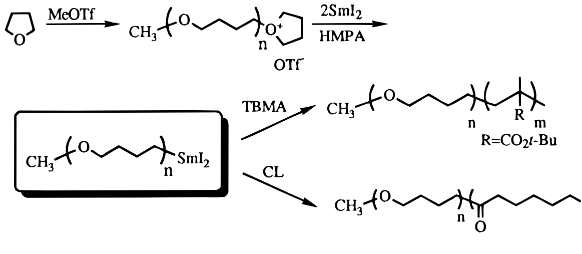
ABSTRACT: Two-electron reduction of *N*-*tert*-butyl-*N*-methylaziridinium trifluoromethanesulfonate with samarium(II) iodide in the presence of hexamethylphosphoramide gave the corresponding samarium amides in an excellent yield through the reductive cleavage of a carbon−nitrogen bond of the ring followed by the elimination of ethylene. The produced samarium amide could polymerize methyl methacrylate (MMA) in high initiation efficiency (80%), leading to the formation of highly syndiotactic poly(MMA) (85%) with narrow molecular weight distribution ($<$1.19). End capping of living poly(THF) with *N*-*tert*-butylaziridine and sequential reduction by samarium(II) iodide resulted in the corresponding poly(THF) with samarium amide moiety at the polymer end at functionality of 48%. The polymerization of MMA with the terminal samarium amide produced the block copolymer of THF with MMA.

Introduction

Transformation of growing centers enables it to produce block copolymers consisting of different types of monomers in polymerization mechanism.[1] Copolymers obtained through the transformation process is expected to show unique properties which are not attainable by the usual methods. The transformation is possible to be achieved by two-electron reduction or oxidation of growing centers, theoretically. Although many efforts have been made to switch the mechanism of polymerization, direct reduction or oxidation of the growing centers by electron transfer has not been achieved. In the traditional way, complicated multistep paths have been required to transform the character of growing centers.[2]

We have recently demonstrated the novel transformation reaction of cationic polymerization into an anionic one by samarium(II) iodide (SmI_2).[3] In brief, the reduction of the growing center of living poly(THF) by SmI_2 quantitatively provided a terminal carbanion,[3a] which was active for the polymerization of some electrophilic monomers such as *tert*-butyl methacrylate (TBMA)[3b−d] and ϵ-caprolactone (CL),[3e,f] leading to unimodal block copolymers of THF with TBMA or CL (Scheme 1).

Scheme 1



However, the transformed macroanion could not polymerize methacrylates with a small substituent on an ester group such as methyl methacrylate (MMA) due to the hard character of alkylsamariums.[4] Considering the facile modification of the nature of poly(methacrylate)s by varying the ester moiety, this restriction is expected to decrease the synthetic utility of the SmI_2-induced transformation. It is of importance to control the reactivity of transformed terminal nucleophiles which are suitable for the second monomer polymerization.

In contrast to the affinity of alkylsamariums toward a carbonyl group, lanthanide amides such as $La[N(TMS)_2]_3$ have been reported to be active for the polymerization of MMA.[5] Therefore, the transformation of the cationic growing center of poly(THF) into a terminal samarium amide and sequential addition of

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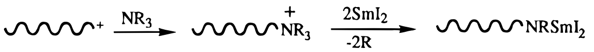
Scheme 2



Scheme 3

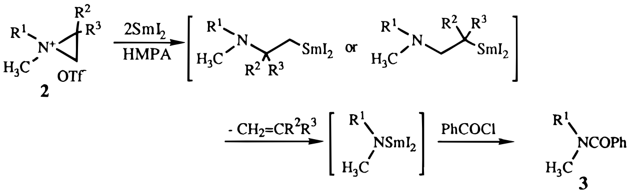


Table 1. Reductive Coupling of Aziridinium Triflate with Benzoyl Chloride

run		R^1	R^2	R^3	yield[a] (%)
1	**2a**	*tert*-Bu	H	H	92
2	**2b**	*tert*-Bu	H	Me	62
3	**2c**	Bn	H	H	53
4	**2d**	Bn	Me	Me	21

[a] Isolated yields.

MMA would enable the block copolymerization of THF with MMA.

We establish here the transformation of a cationic growing center into a terminal samarium amide, which includes an end capping of the cationic growing center with a tertiary amine to produce terminal ammonium salts followed by the reductive cleavage of two carbon–nitrogen bonds (Scheme 2). The polymerization of MMA by poly(THF) with a terminal samarium amide would provide the block copolymer of THF with MMA. In this paper, the reduction of ammonium salts which are the model compounds of amine-terminated poly(THF) together with the polymerization of MMA by the resulting samarium amide are described. We also make attempts to transform the growing center of poly(THF) into samarium amide and copolymerize MMA with the macroanion.[6]

Results and Discussion

Acyclic ammonium salts are generally resistant toward reduction by common reducing agents, which allows their use as supporting salts in electrolysis. We chose three-membered cyclic ammonium salts, i.e., aziridinium salts, because of the following reasons: (1) The high ring-opening ability of aziridinium salts in their cationic polymerizations[7] would permit them to undergo reductive cleavage of the ring by SmI_2. (2) The resulting carbanion with a heteroatom at the β-position would cause spontaneous elimination of ethylene derivative, providing samarium amide (Scheme 3).

Reduction of Aziridinium Salts. The reduction of various N-substituted aziridinium trifluoromethanesulfonates (**2a**–**d**) by SmI_2 was first examined. The reduction was carried out by the addition of a 0.1 M THF solution of SmI_2 into the reaction mixture of **2** in THF in the presence of hexamethylphosphoramide (HMPA) at room temperature. The reduction completed within 20 min, which could be monitored by the change of the reaction mixture in color from purple to yellow. The formation of the corresponding samarium amides was confirmed by the isolation of N-substituted *N*-methylbenzamide (**3**) after a treatment of the product with benzoyl chloride (Scheme 3). Table 1 summarizes the effects of substituents on the reduction of aziridinium salts. The corresponding benzamide **3a** was obtained in good yield (92%) in the case of employing **2a**. This result means that the reductive cleavage of the aziridine ring followed by spontaneous elimination of ethylene successfully occurred, producing samarium amide species without serious side reaction.[8] Introduction of methyl groups onto the aziridine ring decreased the yield of the benzamides (runs 2 and 4). In these cases, a complete consumption of SmI_2 was not observed, indicating the existence of radical reactions. There are two reaction pathways in the reductive cleavage of the ring; giving primary or secondary (tertiary, in the case of **2d**) radicals by one-electron reduction of **2b**–**d**. The slower reduction of the secondary or tertiary radical than that of primary one[9] might induce radical reactions such as disproportionation and dimerization, which contributed the decrease in the yield. The lower yield in the reductive coupling of **2c** with benzoyl chloride might be contributed by abstraction of proton from **2c** or reductive cleavage of benzyl group.

Scheme 4

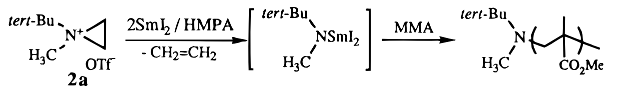


Table 2. Polymerization of MMA with Samarium *N-tert*-Butyl-*N*-methylamide[a]

run	MMA (mmol)	yield[b] (%)	$\bar{M}_n{}^{b,c}$	$\bar{M}_w/\bar{M}_n{}^{b,c}$	tacticity[d] rr:rm:mm
1	2.0	89	1500	1.15	78:19:3
2	3.8	87	2400	1.19	84:14:2
3	5.8	89	4100	1.18	84:15:1
4	8.1	87	4300	1.13	85:14:1

[a] Polymerization conditions: **2a** (0.2 mmol), 0 °C. [b] 3% HCl (aq) insoluble parts. [c] Estimated by GPC (THF, poly(MMA) standards). [d] Determined by ^{13}C NMR spectra.

Polymerization of Alkyl Methacrylates by the Samarium Amide. The polymerization of MMA was next examined by using **2a** as an aziridinium salt, which gave the best result in the reductive coupling with benzoyl chloride (Scheme 4).

The polymerization was performed by adding MMA into the reaction mixture of the samarium amide at 0 °C. Gas chromatographic analyses showed that the polymerization completed within 30 min under the reaction conditions. Table 2 summarizes the results of the MMA polymerization varying the feed ratio of **2a** to MMA. Poly(MMA) with relatively narrow molecular weight distribution (<1.19) was obtained in high yield in each experiment. These results are in contrast to the polymerization of MMA with lanthanide amides in which the molecular weight distribution of the poly(MMA) was broad, probably due to the slow initiation.[5] Relatively high syndiotacticities were attainable in the present polymerization system.[10] A plot of the molecular weight of poly(MMA) versus the ratio of monomer to **2a** is illustrated in Figure 1. The molecular weight of the produced poly(MMA) (GPC, based on poly(MMA) standards) was proportional to the ratio of MMA to **2a** and close to the calculated value. The initiation efficiencies were calculated to be up to 80% from the slopes in Figure 1. The samarium amide was also active for the polymerization for various methacrylates such as ethyl, isopropyl, and benzyl methacrylates, which were not able to be polymerized by alkylsamarium (Table 3). The corresponding polymers were obtained in good yield in every case.

Block Copolymerization of THF with MMA. As mentioned above, samarium amide derived from the

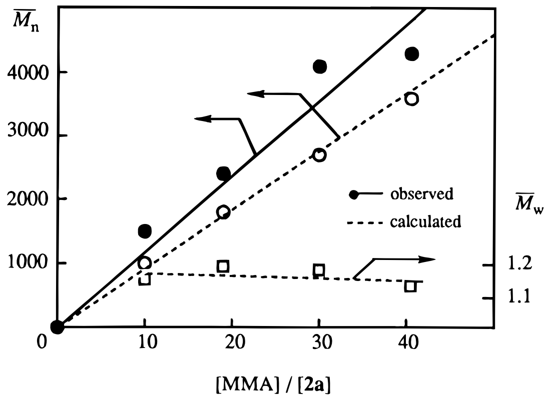


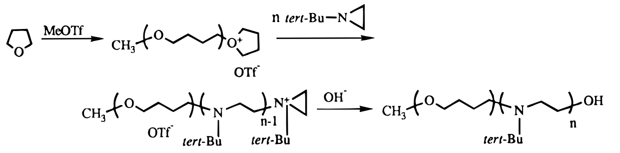
Figure 1. M_n vs monomer/initiator ratio for the polymerization of MMA.

Table 3. Polymerization of Methacrylates with Samarium *N*-*tert*-Butyl-*N*-methylamide

run	methacrylate (mmol)	condition (°C, h)	yield[a] (%)	$\bar{M}_n$[a,b]	$\bar{M}_w/\bar{M}_n$[a,b]
1	EtMA (2.1)	0 °C, 6 h	78	2800	1.27
2	i-PrMA (1.8)	0 °C, 6 h	87	2900	1.22
3	TBMA (1.9)	rt, 24 h	80	2100	1.16
4	BnMA (2.0)	0 °C, 24 h	81	3200	1.22

[a] 3% HCl (aq), insoluble parts. [b] Estimated by GPC (THF, poly(MMA) standards).

Scheme 5



reduction of an aziridinium salt was active for the polymerization of various methacrylates. Since the reaction of living poly(THF) with tertiary amines provides poly(THF) with the structure of ammonium salts at the polymer end,[11] the reduction of the terminalaziridinium salt would result in the formation of a terminal samarium amide.

Poly(THF) was synthesized by using methyl trifluoromethanesulfonate (MeOTf) as an initiator at room temperature. End capping of living poly(THF) with *N*-*tert*-butylaziridine (**1a**) was carried out by the addition of 2 equiv of **1a** to the solution of living poly(THF) at 0 °C (Scheme 5).[12] ^{1}H NMR spectra of hydroxy-terminated poly(THF) (**4a**) and poly(THF) (**4b**) obtained after the end capping followed by an alkaline hydrolysis are illustrated in Figure 2.

The peak attributed to the terminal methylene protons (a) could be observed at 3.65 ppm in the ^{1}H NMR spectrum of **4a**. On the other hand, this peak completely disappeared, while the peaks due to the *tert*-butyl (a′) and methylene protons derived from **1a** (d′) were formed at 1.12 and 2.45−2.67 ppm, respectively, as observed in the ^{1}H NMR of **4b**. The absorption at 3.55 ppm could be assigned as the methylene group adjacent to terminal hydroxy group (g′). From these results, it can be concluded that the propagating center of living poly(THF) quantitatively reacted with **1a** to produce the aziridine-terminated poly(THF). The integrated ratio of the peaks (e′) and (*tert*-Bu) (3:18.9) indicates that the average number of reacted aziridine was 2.1 ($n = 2.1$).

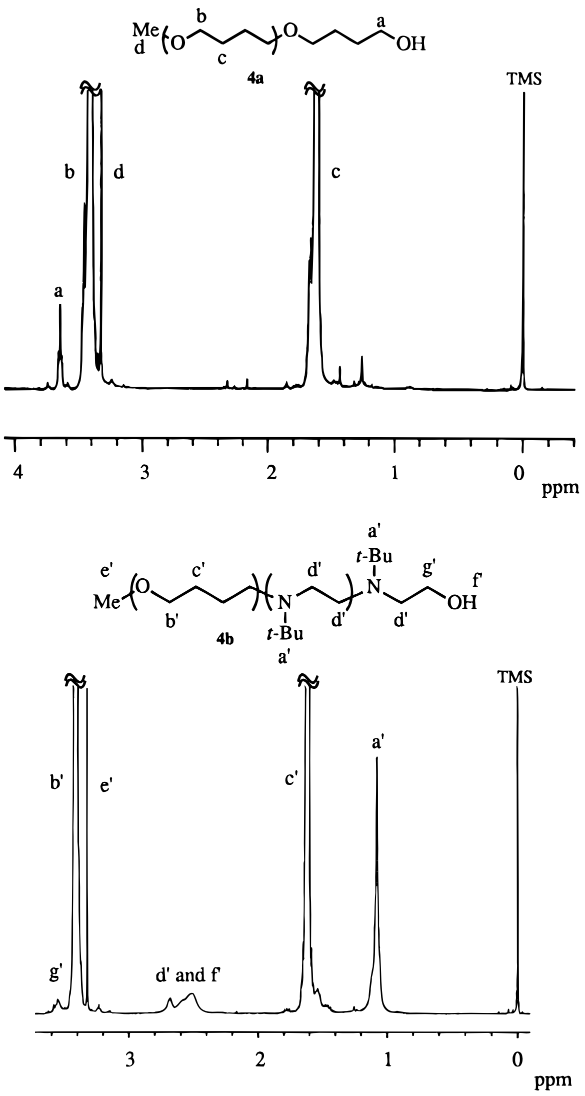
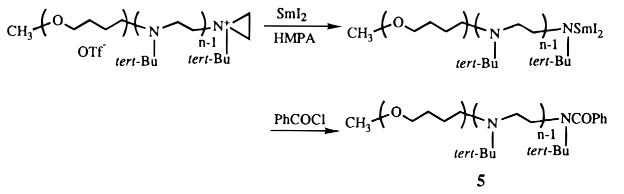
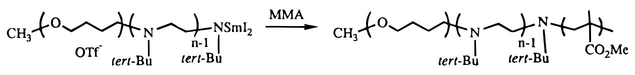


Figure 2. ^{1}H NMR spectra of (a) hydroxy-terminated poly(THF) and (b) poly(THF) end capped with **1a** followed by an alkaline hydrolysis (in $CDCl_3$, 27 °C).

Scheme 6



Scheme 7



The reduction of the aziridine-terminated poly(THF) with SmI_2 was conducted by the addition of a 0.1 M THF solution of SmI_2 to the polymerization solution in the presence of HMPA (Scheme 6).

The color change of reaction mixture from purple to yellow was observed within 20 min after charging SmI_2 solution, meaning that the reduction completely proceeded. ^{1}H NMR spectrum of the poly(THF) (**5**) obtained after the treatment of the product with benzoyl chloride is illustrated in Figure 3. The peaks at 7.28, 1.55, and 3.18 ppm were assignable as the protons of phenyl, *tert*-butyl, and methylene (f) groups of structure **5**, respectively. This result supports the formation of poly(THF) with a terminal samarium amide. However, the low functionality of the terminal benzamide moiety

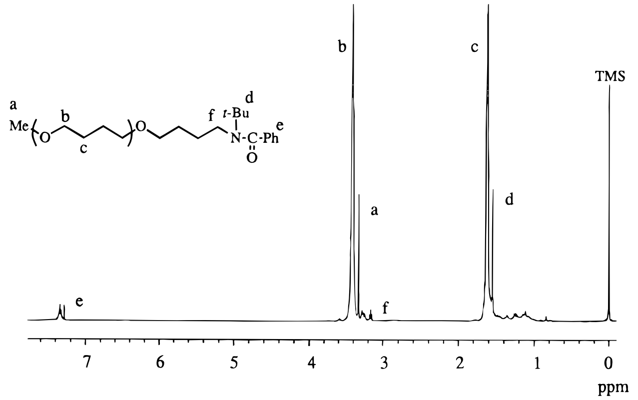


Figure 3. ^{1}H NMR spectra of poly(THF) obtained by the reaction of the terminal samarium amide with benzoyl chloride (in $CDCl_3$, 27 °C).

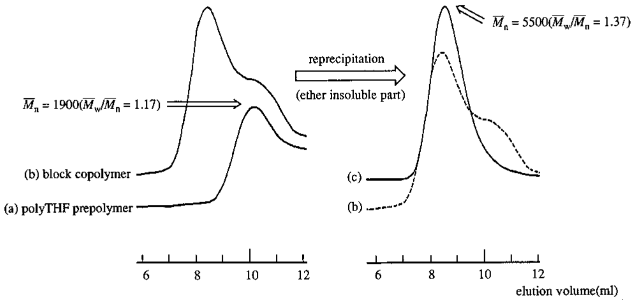


Figure 4. GPC measurements of the block copolymerization. (a) Poly(THF) prepolymer; (b) after block copolymerization; (c) block copolymer after precipitation into ether.

(0.48) which was calculated from the integrated intensity of peaks a and e indicates that some side reactions occurred during the reduction. The possible side reactions represent the elimination of isobutylene or aziridine moiety from the terminal group. The successful results in the reductive coupling of *N-tert*-butyl-*N*-methylaziridine with benzoyl chloride can exclude the elimination of isobutylene. The absence of olefinic peak in the ^{1}H NMR spectrum of **5** also supports that the elimination of aziridine moiety did not proceed during the reduction. The reason of the low functionality in this procedure could not be made clear at this present. Goethals et al. have reported that the back-biting reaction of the propagation end occurs in the polymerization of **1a**, although it was much slower than the propagation in the presence of **1a**.[7] The possibility of a back-biting reaction taking place is present since **1a** was completely consumed in the present polymerization system. Therefore, one of the reasons of the low functionality might be the "temporarily living" nature of the polymerization of **1a** which might lead to the formation of terminal cyclic ammonium structure. The presence of β-protons of the aziridine ring is also likely to cause the side reaction, which might be supported by the result in which the reductive coupling of *N-tert*-butyl-*N*-ethylaziridine with benzoyl chloride gave a trace amount of the coupled product.

The produced terminal samarium amide was found to be active for the polymerization of MMA to give the block copolymer of THF with MMA (Scheme 7). The results of GPC measurement of the block copolymerization are illustrated in Figure 4.

The increase in molecular weight of polymer was observed after charging MMA as shown in Figure 4, which indicates the formation of block copolymer. The GPC trace attributed to the prepolymer of THF was detected in the GPC curve of the block copolymer, which was derived from the low transformation efficiency in this procedure. However, the block copolymer (high molecular polymer) could be isolated selectively by the reprecipitation into ether as shown in Figure 4. The formation of the block copolymer of THF with MMA was confirmed by its ^{1}H NMR analysis, in which the signals attributed to both THF and MMA units could be observed (Figure 5). The low conversion of MMA (23%) means the presence of a termination reaction, which led to the increase in the molecular weight distribution during the block copolymerization. The block efficiency calculated by the gravity of the block copolymer and ^{1}H NMR analyses was within 20%, resulting from the low transformation efficiency as described above.

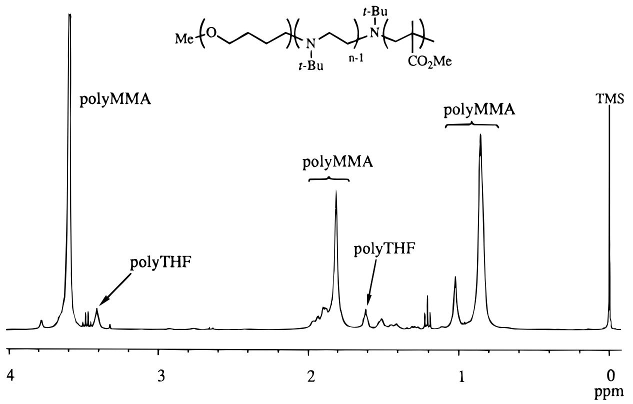


Figure 5. ^{1}H NMR spectrum of the block copolymer of THF with MMA (in $CDCl_3$, 27 °C).

Summary

In this paper, we have shown a novel method for the preparation of samarium amide by the reduction of aziridinium salts under the SmI_2/HMPA system. The produced samarium amide was active for the polymerization of various alkyl methacrylates to give a highly syndiotactic polymer. It should be noted that a relatively narrow molecular weight distribution was attainable by the present polymerization system compared with the MMA polymerization with lanthanide amides. The transformation of the cationic growing center of living poly(THF) into a terminal samarium amide could be achieved in 48% efficiency by end capping of living poly(THF) with aziridine followed by the reduction by SmI_2. Although the formation of THF homopolymer was observed due to the low transformation efficiency, a block copolymer of THF with MMA which was not attainable by the previous direct reduction method[3] could be obtained.

Experimental Section

Materials and Instruments. A THF solution of SmI_2 was prepared according to the reported manner.[13] THF was distilled prior to use from sodium/benzophenone under nitrogen. HMPA was distilled from CaH_2 under reduced pressure. Methyl trifluoromethanesulfonate was distilled from P_2O_5 under a nitrogen atmosphere. *N-tert*-Butylaziridine (**1a**) was synthesized by the reported manner.[14a] The yield of **1a** was greatly improved when the chlorosulfonation of *N-tert*-butylethanolamine hydrochloride was carried out in CH_2Cl_2, and the resulted ester was isolated by filtration. **1b**,[14b] **1c**,[14c] and **1d**[14c] were prepared by the reported manner. **2a** and **2d** were prepared by the reaction of the corresponding aziridines with a small excess of MeOTf in ether at −20 °C and isolated by recrystallization.[14d] **2b** and **2c** were prepared in situ and used without isolation. All methacrylates and benzoyl chloride were distilled in the usual way.

^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX-90 and JNM-EX-400 spectrometers. Gel permeation chromatographic analysis was carried out on a Toyo Soda (CCP&8000, TSK gel G3000, THF) after calibration with standard polystyrenes.

Reduction of Aziridinium Salts. A typical procedure is as follows: a 0.1 M THF solution of SmI_2 was added to the reaction mixture of **2a** (117 mg, 0.446 mmol) and HMPA (670 μL) in THF (3 mL) at room temperature, and the solution was stirred for 20 min (until the color of the reaction mixture changed from purple to yellow). After the addition of benzoyl chloride (123 mg, 0.876 mmol), additional stirring was carried out for 12 h. After addition of aqueous 3% HCl (ca. 10 mL) the reaction mixture was extracted with ether for several times. The organic layer was collected, washed with brine, dried with $MgSO_4$, and concentrated. **3a** (78.5 mg, 92%) was obtained after the SiO_2 chromatography (eluent: hexane–ethyl acetate).

Polymerization of Alkyl Methacrylates by Samarium Amide. A general procedure is as follows: to the mixture of samarium amide (see above) in THF was added MMA at 0 °C, and the reaction mixture was stirred for 30 min at 0 °C. Purification was carried out by the reprecipitation of the product with aqueous 3% HCl containing methanol.

Block Copolymerization of THF with MMA. Methyl trifluoromethansulfonate (0.25 mmol) was added to dry THF (3 mL), and the solution was stirred for 5 min at room temperature. After charging 2 equiv of **1a** to the solution at 0 °C, HMPA (380 μL), and then a 0.1 M THF solution of SmI_2 (5 mL, 0.5 mmol), the reaction temperature was raised to room temperature for ca. 20 min. After the complete change of the reaction mixture (from purple to yellow-brown), methyl methacrylate was added at 0 °C, and the reaction mixture was stirred for 4 h. The products were obtained by the extraction with toluene. The isolation of the block copolymer was carried out by the reprecipitation into ether.

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