Novel Pyrrole End-Functional Macromonomers Prepared by Ring-Opening and Atom-Transfer Radical Polymerizations

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ABSTRACT: New α-pyrrole macromonomers have been prepared using functional initiators by ring-opening polymerization (ROP) of ϵ-caprolactone and atom-transfer radical polymerization (ATRP) of different vinyl monomers. In the first case, the ROP of ϵ-caprolactone was initiated by 2-pyrrolylethan-1-ol at 110 °C using stannous octanoate as a catalyst. The functionalization of the polymers was quantitative, and the molecular weight was well controlled by adjusting the monomer to initiator molar ratio. Alternatively, ATRP of different monomers was carried out using 2-pyrrolylethyl 2-bromo-2-methylpropionate as the initiator in the presence of a CuBr/2-bipyridine or $NiBr_2(PPh_3)_2$ as the catalyst at temperatures ranging from 70 to 110 °C. Using this controlled radical polymerization method, α-pyrrole homopolymers and copolymers of styrene, methyl and *tert*-butyl methacrylate, *n*-butyl acrylate, poly(ethylene oxide methacrylate), (dimethylamino)ethyl methacrylate, and methyloxyethylethyl methacrylate have been prepared with controlled molecular weights and narrow polydispersities.

Introduction

The macromonomer technique is the simplest way to prepare graft copolymers. Macromonomers are polymers end-capped with a polymerizable group able to copolymerize with low molecular weight monomers. Macromonomers can be prepared by modifying polymer end groups or, most conveniently, by using functional initiators for controlled/living polymerizations. To date, a wide variety of macromonomers have been prepared bearing styrene, (meth)acrylate, norbornene, epoxide, and lactone functionalities. Therefore, graft copolymers can be prepared using this technique by most types of polymerization mechanisms.[1] However, further advances in this field need new types of macromonomers to be designed supported by a close understanding in the corresponding copolymerization mechanism.

The field of electrically conductive polymers offers great opportunities for graft copolymers because of their unique nanoscopic morphologies and mechanical properties. Polypyrrole is one of the most popular conductive polymers due to its electroactivity, low density, high electrical conductivity, and environmental stability.[2] Unfortunately, polypyrrole is an amorphous, insoluble, and powdery product, which must be modified to be processable. One approach to improve its processability is copolymerization and more in particular the preparation of graft copolymers (Scheme 1). Although there are several examples in the literature about graft copolymers based on conductive polymers,[3−6] polypyrrole graft copolymers have not been deeply investigated. One reason is the synthetic limitations due to the lack of properly functionalized macromonomers that may offer a variety of chemical−physical properties. The aim of this paper is to report the synthesis of a variety of α-pyrrole macromonomers prepared by ring-opening or atom-transfer radical polymerizations. Because of the versatility of both polymerization methods, we have prepared macromonomers from amorphous polymers with relatively high glass transition temperature, poly(methyl methacrylate) and polystyrene, low-T_g amorphous polymers, poly(*n*-butyl acrylate), and semicrystalline derivatives poly(ϵ-caprolactone).

Experimental Section

Materials. ϵ-Caprolactone (ϵ-CL) (99+%) was dried over CaH_2 and distilled under reduced pressure. The samples were stored under dry nitrogen atmosphere until use. Monomers for ATRP were passed through an alumina column in order to remove the stabilizer. All other chemicals, ethanolamine (99+%), 2,5-dimethoxyetrahydrofuran (98%), 2-bromoisobutyryl bromide (98%), methyl methacrylate (99%), styrene (99%), *tert*-butyl methacrylate (99%), 2-(dimethylamino)ethyl methacrylate (98%), and 2-(2-methoxyethoxy)ethyl methacrylate (98%), were purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of 2-Pyrrolylethan-1-ol, 1. Ethanolamine (200 g, 3.26 mmol) was added with efficient agitation to ice-cooled glacial acetic acid (HOAC) (360 mL) at a rate such that the temperature was maintained at 15−25 °C. When the addition was complete, 2,5-dimethoxytetrahydrofuran (100 g, 0.75 mmol) was added in one portion. The reaction flask was placed in an oil bath, and the temperature was raised to 110−120 °C, at which point distillation of a liquid commenced. After ca. 1.5 h at that temperature about 125 mL of a distillate had been collected. The residual liquid in the reaction vessel was cooled to room temperature, diluted with H_2O, and extracted with CH_2Cl_2. The extract was washed successively with saturated aqueous solutions of NaCl and Na_2CO_3. It was dried over $MgSO_4$, and the solvent was removed by evaporation. The residue was then dissolved in MeOH (200 mL), 20 wt % NaOH (100 mL) was added, and the solution was left at room temperature for 1 h. The solution was poured into saturated aqueous NaCl solution, the product was extracted into CH_2Cl_2, and the extract was dried. The solvent was removed in a vacuum leaving a dark oil (57 g, 70%). ^1H NMR ($CDCl_3$): δ 2.21 (s, 1H, O*H*), 3.75 (t, 2H, CH_2−OH), 3.95 (t, 2H, NCH_2−CH$_2$), 6.15 (s, 2H, C*H* 3,4), and 6.68 (s, 2H, C*H* 2,5). ^{13}C NMR ($CDCl_3$): 51.95, 62.85, 108.52, and 120.93 ppm.

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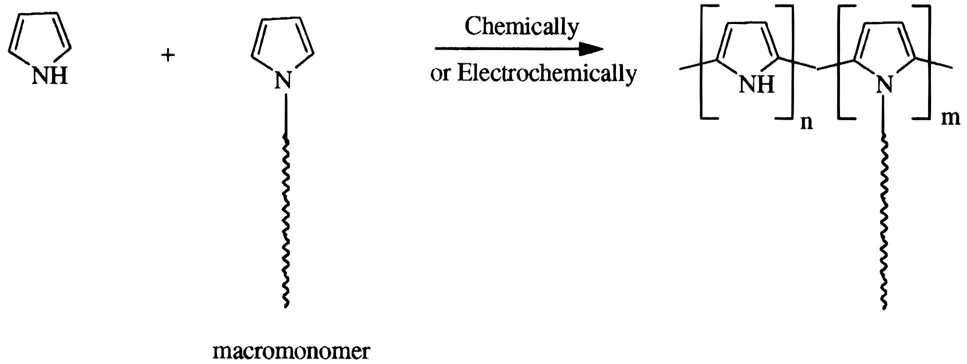
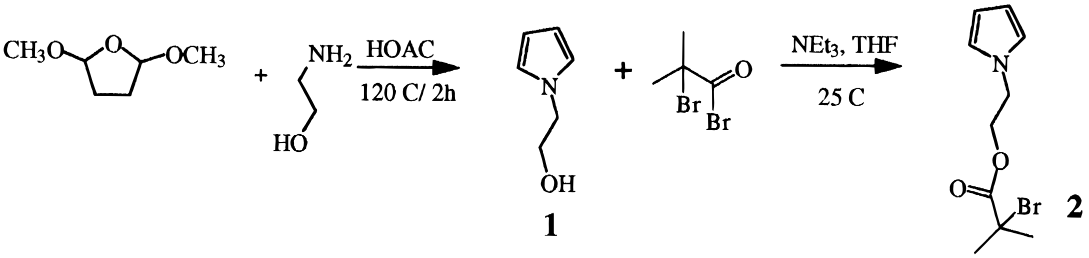
Scheme 1



Scheme 2



Synthesis of 2-Pyrrolylethyl 2-Bromo-2-methylpropanoate, 2. 2-Pyrrolylethan-1-ol (6.27 g, 56 mmol) was dissolved in 100 mL of CH_2Cl_2. Triethylamine (8.80 g, 62 mmol) was added, and the flask was placed in an ice—water mixture. Then, 2-bromoisobutyryl bromide (14.16 g, 62 mmol) was added dropwise over a period of 0.5 h. The reaction was stopped after 5 h. The white precipitate was filtered, and the solution was washed three times with 1 M HCl and twice with H_2O. Finally, the solution was dried with $MgSO_4$, and the solvent was removed in a vacuum leaving a dark oil (15 g, 85%). ^1H NMR ($CDCl_3$): δ 1.86 (s, 6H, C(CH_3)$_2$), 4.14 (t, 2H, NCH_2—CH_2), 4.40 (t, 2H, CH_2—OCO), 6.15 (m, 2H, *CH* 3,4), and 6.68 (m, 2H, *CH* 2,5). ^{13}C NMR ($CDCl_3$): 30.71, 47.97, 55.34, 65.50, 108.72, 120.93, and 171.35 ppm.

Polymerization Techniques. a. Ring-Opening Polymerization Using Sn(Oct)$_2$. (Co)polymerizations were initiated using 2-pyrrolylethan-1-ol (previously dried over molecular sieves) using a catalytic amount of Sn(Oct)$_2$. In a typical experiment, ϵ-caprolactone (10 g, 88 mmol), 2-pyrrolylethylethan-1-ol (0.33 g, 3 mmol), and tin octanoate (20 mg, 0.05 mmol) were heated at 110 °C under dry nitrogen for 16 h. The polymer was then dissolved in THF and purified by precipitation into cold methanol (9.5 g, 94%).

b. Atom-Transfer Radical Polymerization. In a typical experience, $NiBr_2(PPh_3)_2$ (1.20 g, 1.6 mmol) was introduced in a flask. The flask is then closed with a three-way stopcock, and a cycle of vacuum—nitrogen is repeated three times to remove the oxygen. Then, methyl methacrylate (10 g, 100 mmol) and the initiator, 2-pyrrolylethyl 2-bromo-2-methylpropanoate (0.81 g, 3.3 mmol), were added via a syringe. The polymerization was carried 80 °C for 14 h. The polymer was purified by dissolving in THF and precipitation into cold hexanes (9.1 g, 90%).

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer. Size exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrene as the calibration standards. Four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6 Å) were used with THF at 40 °C as elution solvent.

Results and Discussion

In the single literature report about the synthesis of pyrrole macromonomers, Toppare et al. prepared pyrrole end-capped polytetrahydrofuran by terminating the cationic polymerization of THF with the potassium salt of pyrrole.[3] This end-capping strategy is always questionable when high molecular weight macromonomers or quantitative functionalizations are required. A more convenient way to prepare these semitelechelic polymers is to introduce the desired functionality during the polymerization by using functional initiators for living/controlled polymerizations. For this purpose, we have designed two different pyrrole functional initiators (Scheme 2). First, pyrrolylethan-1-ol (**1**) was prepared as reported[7] by reacting ethanolamine and 2,5-dimethoxytetrahydrofuran. Pyrrolylethan-1-ol, **1**, is a N-substituted pyrrole molecule bearing an alcohol functionality known for co-initiating different ring-opening polymerizations.[8] Esterification of **1** with 2-bromoisobutyryl bromide yielded our second initiator, 2-pyrrolylethyl-2-bromo-2-methylpropanoate, **2**. This molecule has an activated alkyl halide known for being an efficient initiator for the atom-transfer radical polymerization of different vinyl monomers.[11]

Table 1. Ring-Opening Polymerization of ϵ-Caprolactone As Initiated by 2-Pyrrolylethan-1-ol[a]

entry	reaction time (h)	yield (%)	$M_n{}^b \times 10^{-3}$ (target)	$M_n{}^c \times 10^{-3}$ (NMR)	$M_n{}^d \times 10^{-3}$ (SEC)	M_w/M_n
1a	18	95	2.0	1.7	2.1	1.40
1b	20	90	4.5	4.7	4.4	1.38
1c	24	95	8.0	8.1	9.0	1.50
1d	24	95	20.0		19.0	1.55

[a] Homopolymerization was carried out in bulk at 110 °C using Sn(Oct)$_2$ as catalyst. [b] Target of theoretical number-average molecular weight: $M_n = [\epsilon\text{-CL}]/[\text{init}] \times 114 + MW_{\text{init}}$. [c] Experimental number-average molecular weight as measured by ^1H NMR. [d] M_n determined by SEC using universal calibration for poly(ϵ-caprolactone).

First, we surveyed the ring-opening polymerization (ROP) of ϵ-caprolactone using **1** as (co)initiator. The ROP of lactones has been deeply investigated during the past years with the discovery that a great variety of metal alkoxides and carboxylates are efficient catalyst and/or

Scheme 3

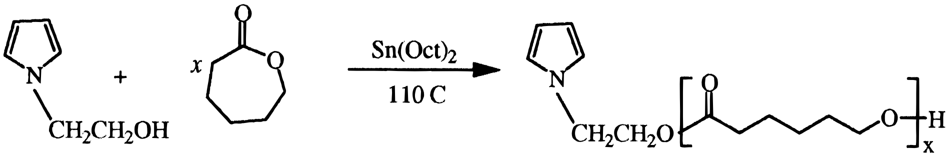


Table 2. Atom-Transfer Radical Polymerization of Different Monomers Initiated by 2-Pyrrolylethyl 2-Bromo-2-methylpropanoate

entry	monomer	temp (°C)	reaction time (h)	yield (%)	$M_n{}^a \times 10^{-3}$ (target)	$M_n{}^b \times 10^{-3}$ (NMR)	$M_n{}^c \times 10^{-3}$ (SEC)	M_w/M_n
2a[d]	MMA	80	14	90	10.0	11.0	9.3	1.30
2b[d]	MMA	80	14	90	5.0	5.5	4.2	1.25
2c[d]	MMA	80	14	95	3.0	3.5	3.2	1.19
2d[d]	*n*-butyl acrylate	95	18	65	3.0	4.0	4.2	1.35
2e[e]	*t*-butyl methacrylate	80	14	80	3.0	4.5	4.0	1.32
2f[e]	styrene	110	14	80	3.0	3.5	3.9	1.40
2g[e]	MMA:(dimethylamino)ethyl methacrylate 6:4	70	5	60	3.0	2.8	5.5	1.12
2h[d]	methoxyethoxyethyl methacrylate	80	5	85	3.0	3.5	4.5	1.35
2i[d]	poly(ethylene oxide) monomethacrylate ($M_n = 400$)	80	5	90	3.0	3.1	6.0	1.17

[a] Target of theoretical number-average molecular weight: M_n = [mon]/[init] × MW_{mon} + MW_{init}. [b] Experimental number-average molecular weight as measured by ^{1}H NMR. [c] M_n determined by SEC relative to polystyrene. [d] Polymerizations were carried out in bulk using 0.5 equiv with respect to initiator of $NiBr_2(PPh_3)_2$ as a catalyst. [e] Polymerizations were carried out in the presence of 20 wt % anisole using 0.5 equiv with respect to initiator of 1:3 CuBr: bipyridine as a catalyst.

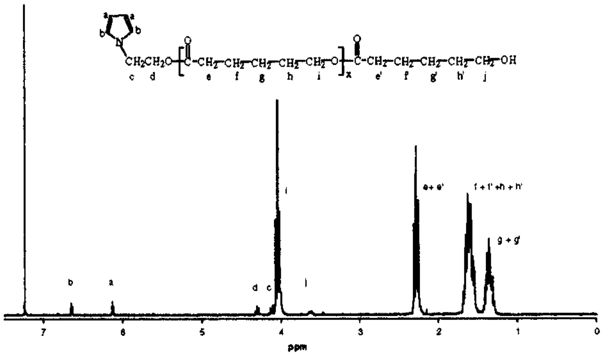
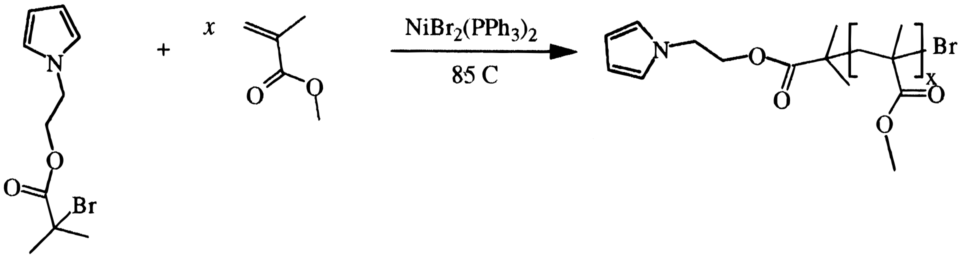


Figure 1. ^{1}H NMR spectrum of α-pyrrole−ω-hydroxyl poly(ϵ-caprolactone), 1a.

initiators.[8] Among them, stannous 2-ethyl-hexanoate ($Sn(Oct)_2$) is one of the most commonly used catalyst.[9] The ROP of ϵ-caprolactone was carried out in bulk at 110 °C using the functional alcohol **1** as co-initiator in the presence of catalytic amounts of $Sn(Oct)_2$ (Scheme 3). As shown in Table 1, the polymerizations were quantitative after 18−24 h. Although the polydispersities of the polymers are relatively large (1.4−1.6), the molecular weights are well controlled by the monomer-to-initiator molar ratio. These results are consistent with previous reports on $Sn(Oct)_2$ catalyzed ROP using monofunctional alcohol as co-initiators.[9] The most important observation comes from ^{1}H NMR spectroscopy (Figure 1), which clearly shows the resonances characteristics of the pyrrole end group at 6.7, 6.1, 4.4, and 4.2 ppm. Furthermore, the number-average molecular weight calculated by comparison of the integration of these end group resonances with the repeating unit resonances compares favorably with the molecular weight predicted by the monomer-to-initiator ratio and the one measured by SEC. This confirms that the chains are quantitatively functionalized to generate the desired α-pyrrole−poly(ϵ-caprolactone) macromonomers.

One of the most interesting advances in polymer chemistry during the past years has been the development of living/controlled polymerization methods based on radical chemistry.[10] These advances have provided new materials with exquisite properties such as amphiphilic block copolymers, new polymeric architectures, narrow polydispersed (co)polymers, and new macromonomers. Among these new methods, atom-transfer radical polymerization (ATRP) is probably the most versatile technique providing a variety of adjustable options such as a varied choice of monomers, catalyst, solvents, and reaction temperature.[11] In a study related to this work, Toppare et al. recently prepared thiophene functional poly(methyl methacrylate) macromonomers by ATRP.[5] Here, we describe the atom-transfer radical polymerization of different monomers initiated by the pyrrolic functional initiator, **2**. The experimental conditions and the results are listed in Table 2. As an example, the atom-transfer radical polymerization of methyl methacrylate (Scheme 4) was carried out at 85 °C as initiated by **2** using $NiBr_2(PPh_3)_2$ as a catalyst (entries 2a, 2b, and 2c in Table 2). The polymerizations were quantitative, and the molecular weight of the poly(methyl methacrylate) was very close to the molecular weight predicted by the monomer-to-initiator molar ratio.

Scheme 4



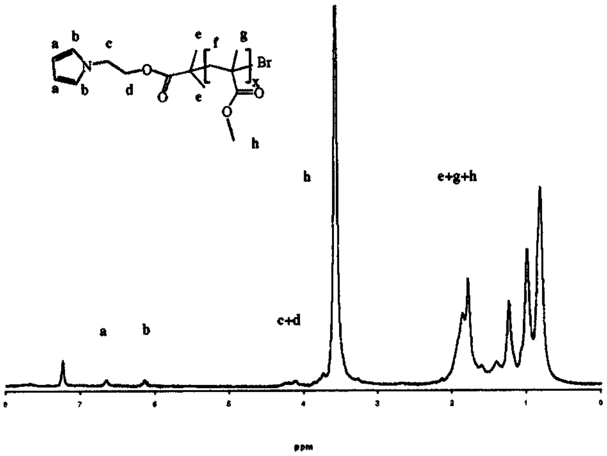


Figure 2. ^{1}H NMR spectrum of of α-pyrrole−ω-bromo poly(methyl methacrylate), 2a.

Furthermore, the polydispersities of the polymers were relatively narrow ($M_w/M_n = 1.2-1.3$), in good agreement with a living/controlled polymerization. The ^{1}H NMR spectrum of the PMMA 2a is shown in Figure 2. In good accordance with the proposed mechanism, the signals characteristics of the pyrrole end group are observed at 6.7, 6.1, and 4.3 ppm. Again, comparison of the integration of these signals with the signals of the repeating unit compares favorably with the theoretical molecular weight. The data shown in Table 2 suggest that **2** is an efficient initiator for the ATRP of methyl methacrylate, yielding new α-pyrrole−PMMA macromonomers.

Because of the versatility of ATRP, many different macromonomers can be prepared with variations in properties such as glass transition temperature and solubility. This is particularly important for fine-tuning the properties of the final graft copolymers with polypyrrole. Accordingly, Table 2 shows that controlled molecular weight and narrow polydispersities are obtained for low-T_g polymers such as poly(*n*-butyl acrylate), which are liquidlike at room temperature (entry 2d) and others of high T_g such as polystyrene (entry 2f). Since the polypyrrole of highest electrical conductivity is obtained using water as a solvent for the polymerization,[12] we have prepared macromonomers based on water-soluble polymers such as poly(*tert*-butyl methacrylate) (which is a precursor of poly(methacrylic acid)), poly((dimethylamino)ethyl methacrylate), and poly(ethylene oxide methacrylate) (entries 2e, 2g, and 2i).

In conclusion, new pyrrole functionalized initiators **1** and **2** have been synthesized and utilized for the preparation of α-pyrrole macromonomers by ring-opening polymerization of ϵ-caprolactone and atom-transfer radical polymerization of different vinyl monomers. Using these functional initiators and controlled polymerization methods, α-pyrrole homopolymers and copolymers of ϵ-caprolactone, styrene, methyl and *tert*-butyl methacrylate, *n*-butyl acrylate, ethylene oxide monomethacrylate, (dimethylamino)ethyl methacrylate, and methyloxyethylethyl methacrylate have been prepared with controlled molecular weights and fairly narrow polydispersities. The preparation of graft copolymers of polypyrrole with these new macromonomers will be reported in the near future.

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References and Notes

(1) Rempp, P.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1.
(2) Rodriguez, J.; Grande, H.; Otero, T. F. *Handbook of Organic Conductive Molecules and Polymers*; John Wiley: New York, 1997; Vol. 2, Chapter 10, p 415 and references therein.
(3) Alkan, S.; Toppare, L.; Hepuzer, Y.; Yagci, Y. *J. Polym. Sci., Polym. Chem* **1999**, *37*, 4218.
(4) Kizilyar, N.; Toppare, L.; Onen, A.; Yagci, Y. *J. Appl. Polym. Sci.* **1999**, *71*, 713.
(5) Stanke, D.; Hallensleben, M. L.; Toppare, L. *Synth. Met.* **1993**, *55*, 1108.
(6) Wusheng, Y.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 1129.
(7) Carpio, H.; Galeazzi, E.; Greenhouse, R.; Guzman, A.; Velarde, E.; Antonio, Y.; Franco, F.; Leon, A.; Perez, V.; Salas, R.; Valdes, D.; Ackrell, J. *J. Chem.* **1982**, *60*, 2295.
(8) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1 and references therein.
(9) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689. (b) Krickeldorf, H. R.; Kreiser-Sanders, I.; Stricker, A. *Macromolecules* **2000**, *33*, 702.
(10) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127. (b) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US-A 4581 429 [*Chem. Abstr.* **1985**, *102*, P221335g]. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314. (d) Veregin, R. P.; Georges, M. K.; Hamer, G. K.; Kazmaier, *Macromolecules* **1995**, *28*, 8722. (e) Benoit, D.; Chaplinski, R.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904. (f) Mayadunne, T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977.
(11) Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1995**, *28*, 1721. (b) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (c) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576. (d) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(12) Rapi, S.; Bocci, V.; Gardini, G. P. *Synth. Met.* **1988**, *24*, 217.

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