Degenerative Transfer and Reversible Termination Mechanisms for Living Radical Polymerizations Mediated by Cobalt Porphyrins

Bradford B. Wayland,* Chi-How Peng, Xuefeng Fu, Zhi Lu, and Michael Fryd

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received July 20, 2006
Revised Manuscript Received October 9, 2006

Living radical polymerization (LRP) methods[1−14] can be divided into two broad categories currently referred to as reversible termination (RT) and degenerative transfer (DT).[15] Both RT and DT approaches for LRP use a dormant species (X−P) as a storage location for latent propagating radicals (P•) and relatively fast exchange of freely diffusing radicals (P′•) from solution with the latent radicals in X−P as the means for obtaining low polydispersity (eq 1). The clear distinction

$$P'^{\bullet} + X{-}P \rightleftharpoons X{-}P' + P^{\bullet} \quad (1)$$

between RT and DT pathways for LRP is the source and method for control of the propagating radicals and the features that give living character to the radical polymerization. The dormant complex (X−P) is the exclusive source of radicals (P•) for all reversible termination (RT) processes which can occur by either homolytic dissociation (DC,[16] SFRP,[10] NMP,[12] OMRP[17]) (eq 2) or atom transfer (ATRP) (eq 3).[1,4,5] Quasi-equilibria between freely diffusing radicals and a dormant complex described by eqs 2 and 3 provide a nearly constant low concentration of propagating radicals (P•) in solution which slowly declines as radical termination occurs. Control of the radical concentration by the dormant complex contributes to the living character for reversible termination (RT) processes through the suppression of bimolecular radical termination relative to polymer propagation by the persistent radical effect (PRE).[3,18]

$$X{-}P \rightleftharpoons X^{\bullet} + P^{\bullet} \quad (2)$$

$$X{-}P + Y \rightleftharpoons X{-}Y + P^{\bullet} \quad (3)$$

Processes that are currently called degenerative transfer (DT)[15] such as iodide-mediated polymerization[19] and RAFT[13] utilize a continual influx of radicals (R•) from an external radical source like AIBN to initiate polymerization of monomers and exchange with latent radicals in the dormant complex (X−P). The term degenerative transfer refers to the interchange of activity between active and dormant species.[15] Degenerative transfer in radical polymerization occurs when an active propagating radical in solution (P′•) interchanges roles with a latent radical (P•) in a dormant complex (P−X). The degenerative transfer reaction is usually depicted as an associative process,[14,15] but the same exchange of active and latent radicals can be accomplished by a two-step dissociative process (Scheme 1). If the radicals P• and P′• are polymeric radicals that differ only in the chain length, then the exchange process is nearly degenerate ($\Delta G^{\circ} \approx 0$) and the equilibrium constant approaches unity. The concentration of radicals for a DT process is primarily determined by the concentration of the external radical source (AIBN, V-70) and the rate constants for radicals to enter solution (k_i) and terminate (k_t) ($[R^{\bullet}] = (k_i[I]/2k_t)^{1/2}$). The concentration of radicals and rates of polymerization for DT processes approach the values for regular uncontrolled radical polymerization, and thus the persistent radical effect does not contribute living character to DT processes. This communication reports that organo-cobalt porphyrin complexes function as a dormant complex and latent source of radicals for living radical polymerization of acrylates by both degenerative transfer and reversible termination pathways which is a property previously demonstrated by mechanistic studies for organo-tellurium[14,20] and proposed for organo-titanium complexes.[21]

Scheme 1

Associative Degenerative Transfer:

$$P\text{-}X + P'\bullet \rightleftharpoons P'\text{-}X + P\bullet$$

Dissociative Degenerative Transfer:

$$P\text{-}X \rightleftharpoons P\bullet + X\bullet$$

$$X\bullet + P'\bullet \rightleftharpoons P'\text{-}X$$

LRP of Acrylates Mediated by (TMP)Co−R. Solutions of cobalt(II) tetramesitylporphyrin ((TMP)Co^{II}) (1.2×10^{-3} M), methyl acrylate (2.5 M), and V-70 ($(0.7-2.0) \times 10^{-3}$ M) in benzene were heated to 333 K, and the conversion to polymer was followed by ^{1}H NMR (Figure 1). The azo radical source V-70 has a half-life of 11 min and an initiator efficiency of 0.60 at 333 K in benzene. Effectively all of the V-70 has decayed during the first 90 min of heating at 333 K, and during that time 1.20 radicals are released into solution per V-70 molecule. The three representative experiments illustrated in Figure 1 have ratios of the total moles of radicals entering solution from V-70 to the initial moles of (TMP)Co^{II} ($R^{\bullet}_T/Co^{II\bullet}_i$) of 0.80, 1.20, and 2.0. The induction time periods correspond to the time required to generate sufficient radicals to convert effectively all of the (TMP)$Co^{II\bullet}$ into diamagnetic organometallic complexes, (TMP)Co−P. Conversion of the metallo-radical to organometallic species is directly observed by following the ^{1}H NMR during the induction period (Figure 2).

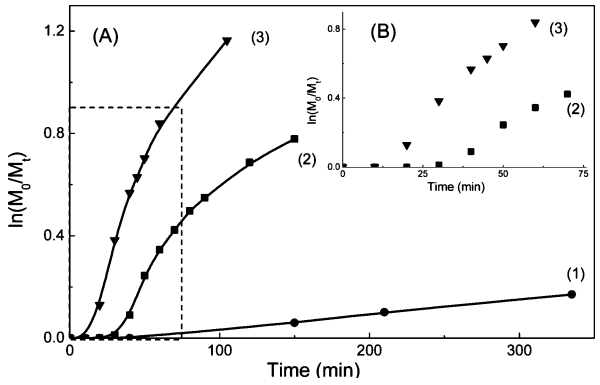

Figure 1. Kinetic plot for the radical polymerization of methyl acrylate in benzene at 333 K with $[MA]_i = 2.5$ M and $[(TMP)Co^{II\bullet}]_i = 1.2 \times 10^{-3}$ M. V-70 was added to produce different ratios for the total moles of external radicals that can enter solution to the total moles of cobalt porphyrin. (1) ($R^{\bullet}_T/Co^{II\bullet}_i$) = 0.80, conversion = 47%, t = 62 h, $M_n = 9.91 \times 10^4$, PDI = 1.11; (2) ($R^{\bullet}_T/Co^{II\bullet}_i$) = 1.2, conversion = 54%, t = 150 min, $M_n = 9.5 \times 10^4$, PDI = 1.06; (3) ($R^{\bullet}_T/Co^{II\bullet}_i$) = 2.0, conversion = 69%, t = 105 min, $M_n = 11.6 \times 10^4$, PDI = 1.06. (B) Enlargement to illustrate the induction times for samples 2 and 3.

* Corresponding author: Tel 215-898-8633; Fax 215-573-6743; e-mail wayland@sas.upenn.edu.

10.1021/ma061643n CCC: $33.50
Published on Web 10/27/2006

Scheme 2. Dominant Reactions during the Induction Period

4) V-70 $\longrightarrow$ $2 \bullet C(CH_3)(R)(CN)$ (= R•)

5) $(TMP)Co^{II} \bullet$ + $\bullet$ $CH(CH_3)(R)(CN)$ $\longrightarrow$ (TMP)Co-H + $(CN)(R)C=CH_2$

6) (TMP)Co-H + $CH_2=CH(CO_2CH_3)$ $\rightleftharpoons$ $(TMP)Co\text{-}CH(CH_3)CO_2CH_3$

7) $(TMP)Co\text{-}CH(CH_3)CO_2CH_3$ $\rightleftharpoons$ $(TMP)Co^{II} \bullet$ + $\bullet CH(CH_3)CO_2CH_3$

8) $CH_3CO_2(CH_3)HC\bullet$ + $(n+1)CH_2=CH(CO_2CH_3)$ $\xrightarrow{k_p}$

$CH_3(CO_2CH_3)HC\text{-}[CH_2CH(CO_2CH_3)]_n\text{-}CH_2(CO_2CH_3)(H)C\bullet$ (= P•)

9) $(TMP)Co\bullet$ + $\bullet$ P $\rightleftharpoons$ (TMP)Co-P

Scheme 3. Dominant Reactions during the Post Induction Period

10) R• + $CH_2=CH(CO_2CH_3)$ $\xrightarrow{k_p}$ $RCH_2(CO_2CH_3)HC\bullet$ (= R'•)

11) R'• + (TMP)Co-P $\rightleftharpoons$ (TMP)Co-R' + P•

12) P• + m $\xrightarrow{k_p}$ P'•

13) P'• + (TMP)Co-P $\rightleftharpoons$ (TMP)Co-P' + P•

The dominant reactions that occur during the portion of the induction period when significant amounts of $(TMP)Co^{II}\bullet$ are present are shown in Scheme 2, eqs 4−9. Hydrogen abstraction from the tertiary carbon radicals produced by V-70 forms a transient intermediate (TMP)Co−H which reacts with the methyl acrylate monomer to produce an organometallic complex, $(TMP)Co-CH(CH_3)CO_2CH_3$ (eqs 5 and 6). Thermal homolytic dissociation of $(TMP)Co-CH(CH_3)CO_2CH_3$ produces an organic radical ($\bullet CH(CH_3)CO_2CH_3$) that initiates methyl acrylate (MA) polymerization (eq 7) to form an oligomer radical that binds with $(TMP)Co^{II}\bullet$ (eqs 7−9). During the last stage of the induction period (eqs 7−9) the growth of the polymeric radical has living character from the persistent radical effect.

The reactions that predominate during the post-induction period where rapid polymerization occurs are given in Scheme 3 by eqs 10−13. Radicals (R•) entering solution from V-70 initiate polymerization of MA (eq 10), and the radicals in solution exchange with radicals in the dormant (TMP)Co−P complex by dissociative and associative pathways (eqs 11 and 13). In the specific case of (TMP)Co−P at 333 K the homolytic dissociation is sufficiently fast to account for the observed low polydispersity.

Methyl acrylate (MA) polymerizations are used to illustrate both the cobalt(II) metallo-radical-mediated RT process (Figure 1A(1)) and the organo-cobalt-mediated DT process (Figure 1A-(2, 3)) that simultaneously operate in the (TMP)Co system. When the ratio of total moles of radicals injected into solution from the radical source to the initial moles of $(TMP)Co^{II}\bullet$ is less than unity, the polymerization process is mediated by the excess of $(TMP)Co^{II}\bullet$. The polymerization is relatively slow because the radical is maintained at a low concentration by a quasi-equilibrium between $(TMP)Co^{II}\bullet$ and the (TMP)Co−P

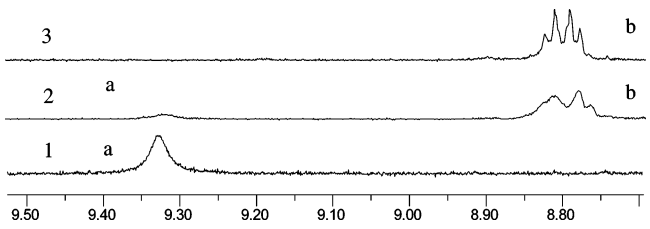

Figure 2. ^1H NMR (300 MHz) spectra in C_6D_6 during the induction period for the organo-Co(TMP)-mediated LRP of MA: (a) $(TMP)Co^{II}$ *m*-phenyl H; (b) $(TMP)Co-CH(CH_3)CO_2CH_3$ pyrrole AB pattern; (1) $(TMP)Co^{II}$; (2) $(TMP)Co^{II}$ and $(TMP)Co-CH(CH_3)CO_2CH_3$; (3) (TMP)Co−P, polymerization begins.

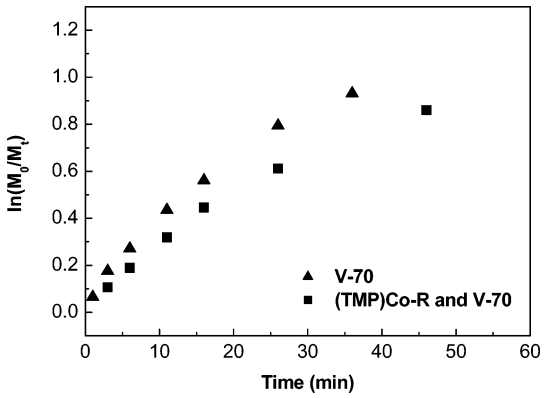

Figure 3. Radical polymerization of methyl acrylate ($[MA]_i = 2.50$ M, $T = 333$ K, C_6D_6) initiated by (A) $[V\text{-}70]_i = 5.2 \times 10^{-4}$ M, (B) $[V\text{-}70]_i = 5.2 \times 10^{-4}$ M, and $[(TMP)Co-CH(CH_3)CO_2CH_3]_i = 1.0 \times 10^{-3}$ M.

(Figure 1A(1); eq 7, $K(333\text{ K}) = [(TMP)Co^{II\bullet}][P^\bullet]/[(TMP)Co-P] = 7.8 \times 10^{-9}$) which fulfills Fukuda's criteria for a dissociation combination (DC)[16] type of RT process. The living character of this RT process has been ascribed to the persistent radical effect.[3,22]

Radical polymerization of MA for the condition where the total moles of radicals that enter solution from V-70 exceeds the initial moles of $(TMP)Co^{II}\bullet$ is illustrated in Figure 1A(2, 3). An induction period where a few percent conversion of the monomer occurs is followed by the onset of rapid polymerization at the time when effectively all of the $(TMP)Co^{II}\bullet$ has been converted to (TMP)Co−P. Starting with a preformed organometallic complex $(TMP)Co-CH(CH_3)CO_2CH_3$ there is no observed induction period which illustrates that the reaction of (TMP)Co−P with radicals does not form kinetically significant quantities of a bis(alkyl) complex, $(TMP)Co(P)_2$. The rate of polymerization at this condition approaches the rate for an uncontrolled polymerization at the same concentration of V-70 in the absence of $(TMP)Co^{II}$ (Figure 3) which fulfills the criteria for a degenerative transfer (DT) process.

The continued influx of radicals from V-70 changes the polymerization process from a cobalt(II)-mediated RT pathway to an organo-cobalt-mediated DT mechanism. The persistent radical effect ensures the living character for the polymer formed during the RT portion of the processes. The most important feature of the polymerization is that during the period of fast polymerization the process remains controlled and produces low-polydispersity polymers (Figure 1) where M_n increases linearly with monomer conversion (SI).[23] After a period of 90 min the influx of new radicals from V-70 has ended, and the polymerization reaction reverts to a slower RT pathway (Figure 1).

When the smaller steric requirement tetra(*p*-methoxyphenyl)-porphyrin derivative $(TAP)Co^{II}$ is substituted for $(TMP)Co^{II}$ as a mediator at the conditions for the RT polymerization of acrylates ($([R^\bullet_T]/[Co^{II\bullet}_T]) = 0.9$), the resulting polymers only grow to a maximum degree of polymerization of ~200 before

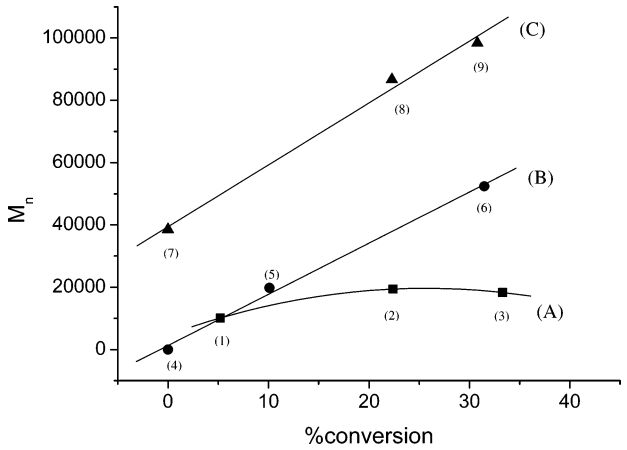

Figure 4. Changes in number-average molecular weight with conversion of MA to PMA ($[MA]_i = 2.5$ M; 333 K, C_6D_6). Polymerization mediated by (A) (TAP)Co^{II}; $[(TAP)Co^{II}]_i = 1.2 \times 10^{-3}$ M, $[V\text{-}70]_i = 0.9 \times 10^{-3}$ M, PDI (% conversion, M_n): (1) 1.20 (5.2, 1.01×10^4), (2) 1.38 (22.4, 1.94×10^4), (3) 1.51 (33.3, 1.83×10^4); (B) (TAP)-Co^{II}; $[(TAP)Co^{II}]_i = 1.0 \times 10^{-3}$ M, $[V\text{-}70]_i = 1.0 \times 10^{-3}$ M, PDI (% conversion, M_n): (4) origin, (5) 1.09 (10.1, 1.98×10^4), (6) 1.15 (31.5, 5.24×10^4), and block copolymerization mediated by (C) (TAP)Co−PtBA (PDI = 1.09, $M_n = 3.86 \times 10^4$); $[(TAP)Co\text{−}PtBA]_i = 1.2 \times 10^{-3}$ M, $[V\text{-}70]_i = 1.1 \times 10^{-3}$ M, PDI(% conversion, M_n): (7) 1.09 (0.0, 3.86×10^4), (8) 1.10 (22.3, 8.67×10^4), (9) 1.15 (30.8, 9.84×10^4).

cobalt(II) catalytic chain transfer occurs through β-H abstraction[24] and readdition to monomer (eqs 14 and 15) (Figure 4A).

$$(TAP)Co^{II\bullet} + {}^{\bullet}CH(CH_2\text{−}P)CO_2CH_3 \rightarrow (TAP)Co\text{−}H + (CO_2CH_3)(H)C{=}CH(P) \quad (14)$$

$$(TAP)Co\text{−}H + CH_2{=}CH(CO_2CH_3) \rightarrow (TAP)Co\text{−}CH(CH_3)CO_2CH_3 \quad (15)$$

Under the DT conditions of continual influx of radicals ($([R^{\bullet}_T]/[Co^{II\bullet}_T]) = 1.1$) the cobalt(II) is maintained at a sufficiently low concentration such that β-H abstraction is effectively quenched. The polymers grow much larger and have relatively small polydispersities (1.10−1.15) at the condition for a DT process (Figure 4B,C). The effective absence of cobalt(II) metalloradicals during the organo-cobalt-mediated DT process removes the requirement for having sterically demanding complexes as an approach to suppress β-H abstraction[3] from the growing oligomer/polymer radicals.

Living Character in Radical Polymerizations. Living character for RT processes including both major subdivisions of atom transfer radical polymerization (ATRP) and dissociation combination (DC) benefits from the persistent radical effect (PRE). The PRE results from a stable chemical species (X) that exclusively binds reversibly with the propagating radical ($P^{\bullet}$) to form a dormant complex (X−P) which controls a low concentration of radicals. Each latent radical ($P^{\bullet}$) in the dormant complex (P−X) has the capability of growing further and thus is said to be living. In RT processes where all the radicals come from the dormant complex each radical termination event reduces the number of living radicals. The fraction of living character at any time t is the ratio of concentration of the dormant complex at time t to the initial concentration (fraction living (RT) = $[P\text{−}X]_t/[P\text{−}X]_i$).

The primary origin of living character for degenerative transfer polymerizations also results from the presence of a dormant complex. In a DT process the total concentration of dormant complex species remains constant, and the number of chains equals the sum of the initial number of latent radicals ($P^{\bullet}$) in the dormant complex (P−X) and the number of radicals that enter solution from the external radical source ($P'^{\bullet}$). Fully living radicals correspond to radicals that are in the initial dormant complex that have repeatedly entered solution propagated with monomers and returned to the dormant complex through out the entire process. The number of fully living radicals decreases as new radicals from the external radical source exchange with the dormant complex and radicals terminate. The most obvious way to maintain the maximum number of fully living chains is to inject a minimum number of radicals from the external source. General procedures for DT processes like RAFT suggest setting the ratio of injected radicals to the dormant complex at ~0.1,[13] which ensures that at least 90% of the original latent radicals in the initial dormant complex will survive in the dormant complex after the radicals for the polymerization process terminate. The example given in Figure 1(3) has a relatively large ratio of 1.0 that results from one additional radical released into solution from V-70 per dormant (TMP)Co−P. There are thus two polymer chains per cobalt, and yet the polymer formed has a low polydispersity (1.06) and molecular weight ($M_n = 1.16 \times 10^5$) close to that expected for one living chain per cobalt ($M_n = 1.23 \times 10^5$). The vast majority of the converted monomers appear to occur in the latent living polymer chains in the dormant complex (TMP)Co−P. This observation suggests that the larger latent polymer chains stored in (TMP)Co−P propagate more than the small newly formed radicals from the radical source. The decrease in the radical termination constant (k_t) as the molecular weight of the polymeric radical increases[25] may result in preferential growth of the larger polymer chains and thus provide a contribution to the observed living character.

Acknowledgment. This research was supported by Grant NSF-CHE-0501198.

Supporting Information Available: Experimental details, measurements of radical initiator efficiency, polymerization rates, molecular weight, and polydispersity results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Matyjaszewski, K., Ed. *Advances in Controlled/Living Radical Polymerization; ACS Symp. Ser.* **2003**, *854*. (b) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization: From Synthesis to Materials; ACS Symp. Ser.* **2006**, *944*.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(3) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(5) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(6) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.
(7) 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.
(8) Fukuda, T.; Goto, A. *Macromol. Rapid Commun.* **1997**, *18*, 683.
(9) Debuigne, A.; Caille, J.-R.; Jèrôme, R. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1233.
(10) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921.
(11) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(12) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(13) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.
(14) Kwak, Y.; Goto, A.; Fukuda, T.; Kobayashi, Y.; Yamago, S. *Macromolecules* **2006**, *39*, 4671.
(15) Müller, A. H. E.; Yan, D.; Litvinenko, G.; Zhuang, R.; Dong, H. *Macromolecules* **1995**, *28*, 7335.
(16) Yoshikawa, C.; Goto, A.; Fukuda, T. *Macromolecules* **2003**, *36*, 908.
(17) Poli, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5058.
(18) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.

(19) (a) David, G.; Boyer, C.; Tonnar, J.; Ameduri, B.; Lacroix-Desmazes, P.; Boutevin, B. *Chem. Rev.* **2006**, *106*, 3936. (b) Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809. (c) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S. *Macromolecules* **1995**, *28*, 2093.
(20) Goto, A.; Kwak, Y.; Fukuda, T.; Yamago, S.; Iida, K.; Nakajima, M.; Yoshida, J. *J. Am. Chem. Soc.* **2003**, *125*, 8720.
(21) (a) Asandei, A. D.; Moran, I. W. *J. Am. Chem. Soc.* **2004**, *126*, 15932. (b) Asandei, A. D.; Moran, I. W.; Saha, G.; Chen, Y. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 2015.
(22) Wayland, B. B.; Basickes, L.; Mukerjee, S.; Wei, M. L.; Fryd, M. *Macromolecules* **1997**, *30*, 8109.
(23) Lu, Z.; Fryd, M.; Wayland, B. B. *Macromolecules* **2004**, *37*, 2686.
(24) Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611.
(25) Theis, A.; Feldermann, A.; Charton, N.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 2595.

MA061643N