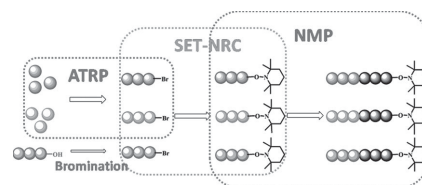


A Tandem Controlled Radical Polymerization Technique for the Synthesis of Poly(4-vinylpyridine) Block Copolymers: Successive ATRP, SET-NRC, and NMP

Yin-Ning Zhou, Zhi-Chao Chen, Chuan Wei,* Zheng-Hong Luo*

Poly(methyl methacrylate)-*block*-poly(4-vinylpyridine), polystyrene-*block*-poly(4-vinyl pyridine), and poly(ethylene glycol)-*block*-poly(4-vinylpyridine) block copolymers are synthesized by successive atom transfer radical polymerization (ATRP), single-electron-transfer nitroxide-radical-coupling (SET-NRC) and nitroxide-mediated polymerization (NMP). This paper demonstrates that this new approach offers an efficient method for the preparation of 4-vinylpyridine-containing copolymers.



1. Introduction

Poly(4-vinylpyridine) (P4VP)-based block copolymers have received great attention due to their unique properties and applications in various fields.^[1] These well-defined pyridine-based polymers have usually been prepared by living anionic polymerization.^[1b,c] However, such experimental work should be conducted under extremely strict conditions, such as ultra-low temperatures, rigorous anhydrous, and anaerobic environment. In contrast, controlled radical polymerization (CRP) conducting under moderate conditions experiences a period of remarkable development, and has had a profound influence on polymer chemistry in recent years.^[2] Three well-known CRP techniques, namely atom transfer radical polymerization (ATRP),^[3a-d]

reversible addition–fragmentation chain transfer (RAFT) polymerization,^[3e-g] and nitroxide-mediated polymerization (NMP),^[3h,i] have proven to be efficient tools for the synthesis of copolymers with desired molecular weights and narrow molecular weight distributions.^[3]

As for pyridine-based monomer (i.e., 4-vinylpyridine (4VP)), ATRP technique has been successfully employed in some cases,^[1d,4a] but it requires rational selection of initiating/catalytic systems to control the polymerization because of the strong metal catalyst coordinating ability of both 4VP and P4VP.^[4b] Moreover, although RAFT polymerization has also been carried out for 4VP,^[1e,f] the challenge remains to conserve the end functionality of chain during the polymerization of basic monomers in aqueous media.^[5a] In addition, the RAFT end group can be another impact factor on polymer properties.^[5b,c] Therefore, NMP technique is considered as an efficient tool for controlled polymerization of 4VP.^[1g] However, the polymerization of MMA with controlled manner cannot be satisfied by NMP because of side reactions happen at high polymerization temperature.^[6] For example, Shoji et al. prepared poly(vinylpyridine) block copolymer through stepwise ATRP and NMP using a novel bifunctional initiator.^[7]

Y.-N. Zhou, Z.-C. Chen, Prof. Z.-H. Luo
Department of Chemical Engineering, School of Chemistry
and Chemical Engineering, Shanghai Jiao Tong University,
Shanghai 200240, PR China
E-mail: luozh@sjtu.edu.cn
Dr. C. Wei
Skshu Paint Co., Ltd., 518 North Liyuan Avenue, Licheng
District, Putian, Fujian 351100, PR China
E-mail: milleroo828@gmail.com

In this work, we introduce an efficient tandem controlled radical polymerization (TCRP) technique for preparing P4VP block copolymers without the complex synthesis process of a bifunctional initiator. Single-electron-transfer nitroxide-radical-coupling (SET-NRC) as a rapid and highly efficient method for functionalizing bromide end-groups bridges the gap of ATRP and NMP, as well as a powerful tool for the synthesis of diblock copolymers.^[8] Additionally, both the ATRP and the NMP systems are governed by the persistent radical effect (PRE),^[9] where active radicals undergo a reversible activation–deactivation process. Consequently, the TCRP technique presented here not only permits the polymerization of 4VP proceeding in broader monomer range, but also follows similar kinetic behavior (power-law system).^[9]

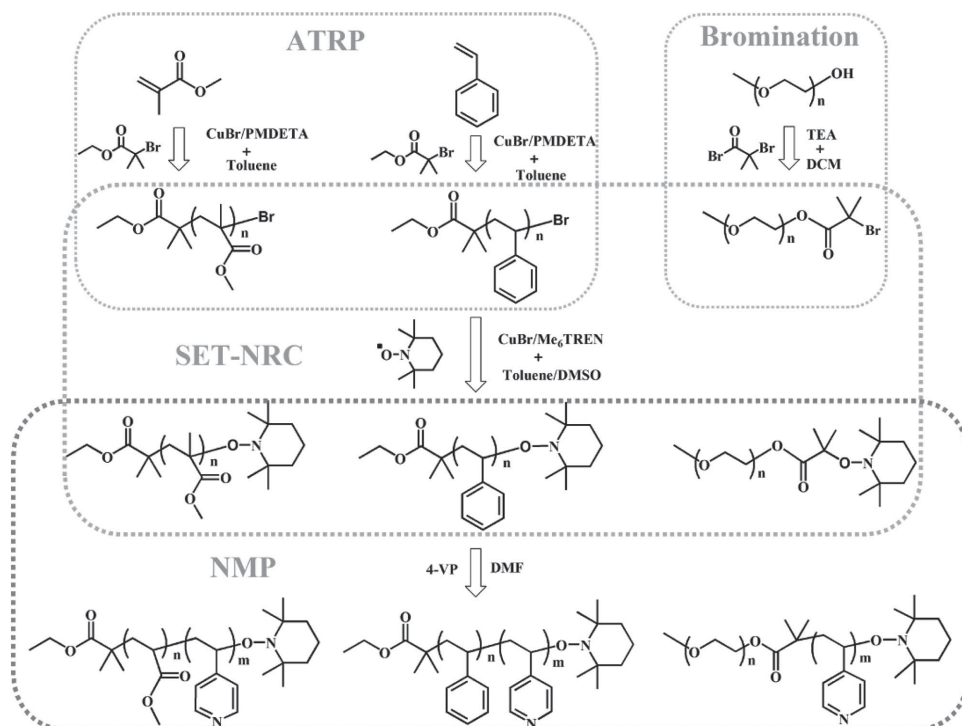
Here, the new strategy for the synthesis of P4VP-containing block copolymers is represented in Scheme 1. Starting with ATRP, poly(methyl methacrylate) (PMMA) with bromine end groups (–Br) was prepared. Subsequently, SET-NRC was utilized to functionalize the first block polymer chain end with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). Finally, polymerization of 4-vinylpyridine monomer was carried out by the NMP technique for the resulting block copolymer (PMMA-*b*-P4VP). To extend the scope of copolymers involving P4VP blocks, polystyrene-*block*-poly(4-vinyl pyridine) (PSt-*b*-P4VP) was also prepared via TCRP and poly(ethylene glycol)-*block*-poly(4-vinylpyridine) (PEG-*b*-P4VP) was

synthesized through successive bromination, SET-NRC, and NMP in this work.

2. Results and Discussion

ATRP of MMA (M) was conducted using ethyl 2-bromoisobutyrate (Eib-Br, I) as initiator and CuBr (C)/1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, L) as catalyst in toluene at [M]:[I]:[C]:[L] = 100:1:1:2 and 90 °C. The PMMA-Br macroinitiator was confirmed by ¹H NMR as shown in Figure 1A (bottom, red line). The degree of polymerization (DP_n) calculated through the ratio of the integral area of methoxyl protons at $\delta = 3.55\text{--}3.65$ ppm (peak a) to that of CH₃CH₂O– protons at $\delta = 4.00\text{--}4.20$ ppm (peak d) is approximately 55, namely $\bar{M}_{n,\text{NMR}} = 5710$ g mol⁻¹ (see Supporting Information for calculation process). The GPC result for PMMA-Br displayed in Figure 2 is 5930 g mol⁻¹, which agrees with $\bar{M}_{n,\text{NMR}}$ within allowable error. The narrow polydispersity ($\mathcal{D} = 1.17$) of the resulting polymer (PMMA-Br) implies the polymerization was conducted in a controlled manner.

Subsequently, the macroinitiator with the Br end group synthesized by ATRP was functionalized by SET-NRC. Under moderate experimental conditions (25 °C), PMMA-alkoxyamine (PMMA-TEMPO) was obtained after 15 min (see Supporting Information for details). The ¹H NMR spectra of PMMA-TEMPO is shown as the green line in Figure 1B. In addition, the molecular weight and



■ Scheme 1. Synthesis route of poly(4-vinylpyridine)-containing block copolymers.

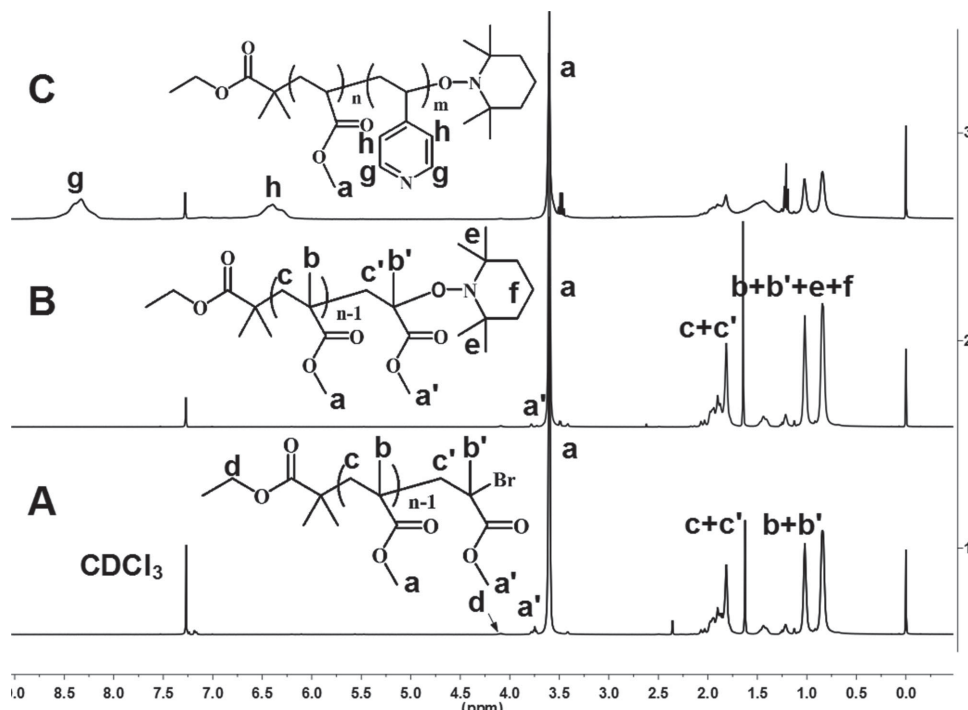


Figure 1. ¹H NMR spectra of PMMA-Br (A), PMMA-alkoxyamine (TEMPO) (B), and PMMA-*b*-P4VP (C).

its polydispersity obtained by GPC are 5840 g mol⁻¹ and 1.17, respectively. It should be pointed out that the experimental temperature has a great influence on the efficiency of NRC reaction for PMMA-Br, which significantly decreases with the increase of temperature.^[10] Previous studies showed that there is a side reaction happening during the high-temperature PMMA-Br NRC reaction or CRP of MMA in the presence of TEMPO.^[11] During such reactions, the active β-hydrogen of methyl in PMMA can be captured by nitroxide radicals, leading to form PMMA chain with a double bond in terminal unit, which is usually confirmed by ¹H NMR signals at 5.50 and 6.20 ppm (characteristic of olefinic methylene protons).^[10,11] From the spectrum of PMMA-TEMPO in Figure 1B, no signal due to the olefinic methylene protons was found, which indicates that the functionalization of PMMA-Br with TEMPO may be feasible under SET-NRC conditions.

The resulting PMMA polymer terminal with TEMPO was then used as macroinitiator (I) for the NMP of 4VP (M) in dimethyl formamide (DMF) at [M]:[I] = 400:1 and 130 °C. As depicted in Figure 1C (top, blue line), the characteristic signals at δ = 8.10–8.80 ppm (peak g) and δ = 6.00–6.80 ppm (peak h) are assigned to -CC₄H₄N protons. According to the ratio of the integral area of peak g to that of peak a, the DP_n of P4VP block is approximately 70. Therefore, the $\bar{M}_{n,NMR}$ of block copolymer (PMMA₅₅-*b*-P4VP₇₀) yielded by the chain extension of macroinitiator PMMA₅₅-TEMPO is 13140 g mol⁻¹ by ¹H NMR. In addition, compared with the GPC trace of PMMA₅₅-TEMPO, the

diblock copolymer shifted to higher molecule weight direction with $\bar{M}_{n,GPC} = 15700$ g mol⁻¹ and $\mathcal{D} = 1.25$ (Figure 2). The broad polydispersity implies that the irreversible radical termination happened during reaction.

On the other hand, the polymerization kinetics of 4VP are displayed in Figure 3. First, the pseudo-first-order kinetics in Figure 3A indicate the nearly constant concentration of radicals in the polymerization system and the evolution of \bar{M}_n has a linear increase with conversion. Both features show a typical and successful controlled radical polymerization. Although the \bar{M}_w/\bar{M}_n

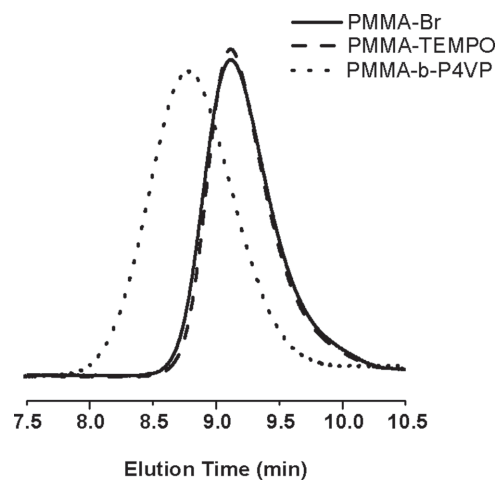


Figure 2. GPC traces of PMMA-Br, PMMA-alkoxyamine (TEMPO), and PMMA-*b*-P4VP.

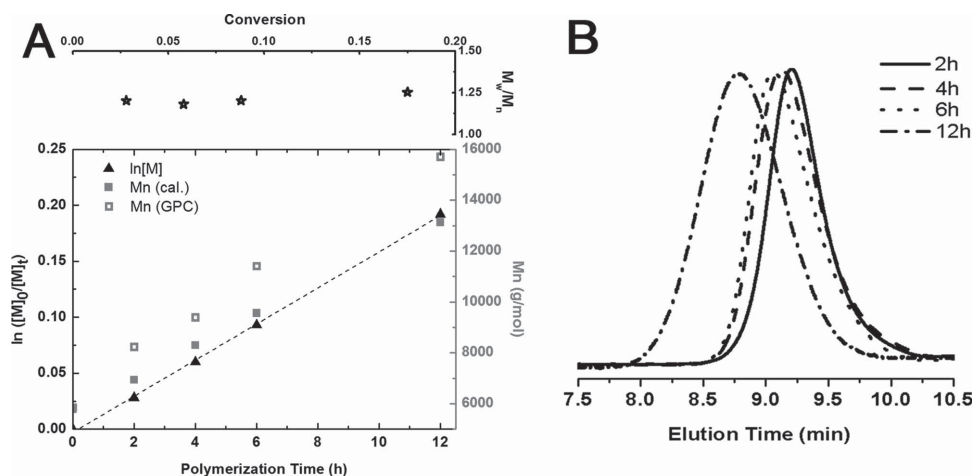


Figure 3. Kinetic plot (A) and GPC traces with monomer conversion (B) for the synthesis of PMMA-*b*-P4VP.

of copolymer is higher than that of PMMA-TEMPO, the values remained below 1.30. The deviation of $\bar{M}_{n,GPC}$ from the theoretical value might be attributed to the difference between the resulting copolymers and the narrow PMMA standards. Second, Figure 3B demonstrates the retention time in GPC for copolymer decreases monodirectionally with increasing reaction time, indicating the increment of molecular weight. However, there is a slight tailing toward low molecular weight, indicating the inefficient initiation or/and the formation of dead chains.

Another two diblock copolymers containing 4VP were also prepared by NMP using PS-TEMPO and PEG-TEMPO macroinitiators (see Supporting Information for details). The GPC traces and ^1H NMR spectra of the resulting copolymers are shown in Figure 4, and Figure S1 and S2 in the Supporting Information. As shown in Figure 4, GPC traces for both polymerization systems show a shift from low molecule weight to high molecule weight side,

indicating a successful chain extension of macroinitiator. The polydispersity of both resulting copolymers is 1.32 and 1.29 for PS-*b*-P4VP and PEG-*b*-P4VP, respectively, which remain about 1.30 and feature the nature of controlled polymerization. A slight tailing toward low molecular weight indicates the formation of dead chains.

3. Conclusion

Three different P4VP-containing block copolymers were prepared by the TCRP technique in a controlled manner for the first time. In particular, the synthesis of PMMA-*b*-P4VP copolymer was well controlled under the present conditions, which was confirmed by a kinetics study. It is firmly believed that this new approach offers an efficient method for the preparation of 4-vinylpyridine-containing copolymers.

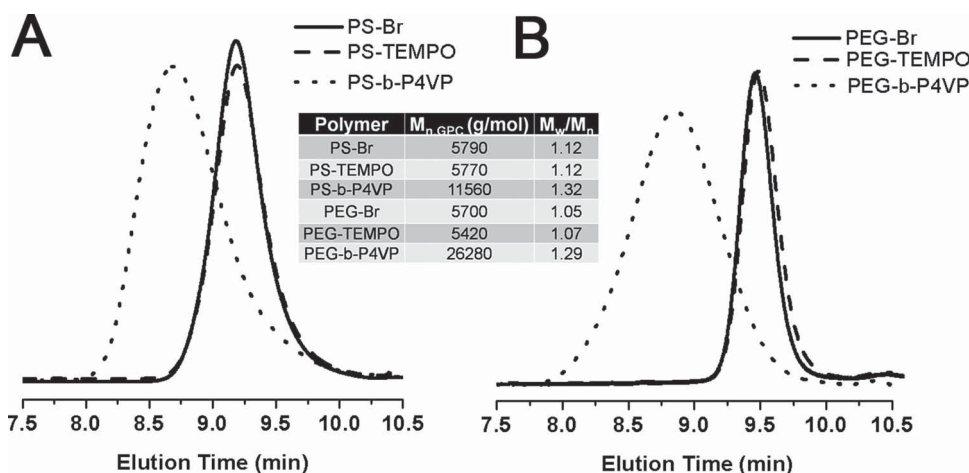


Figure 4. GPC traces of PS-Br, PS-TEMPO, and PS-*b*-P4VP (A); PEG-Br, PEG-TEMPO and PEG-*b*-P4VP (B).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: Financial support from the National Natural Science Foundation of China (No. 21276213), the National 863 plan project of China (No. 2013AA032302), and the Research Fund for the Doctoral Program of Higher Education (No. 20130073110077) is gratefully acknowledged.

Received: September 16, 2014; Published online: November 14, 2014; DOI: 10.1002/macp.201400483

Keywords: atom transfer radical polymerization; block copolymers; nitroxide-mediated polymerization; poly(4-vinylpyridine); single-electron-transfer nitroxide-radical-coupling

- [1] a) C. Cummins, D. Borah, S. Sasappa, A. Chaudhari, T. Ghoshal, B. M. D. O'Driscoll, P. Carolan, N. Petkov, J. D. Holmes, M. A. Morris, *J. Mater. Chem. C* **2013**, *1*, 7941; b) N.-G. Kang, B.-G. Kang, H.-D. Koh, M. Changez, J.-S. Lee, *React. Funct. Polym.* **2009**, *69*, 470; c) J. I. Clodt, V. Filiz, S. Rangou, K. Buhr, C. Abetz, D. Höche, J. Hahn, A. Jung, V. Abetz, *Adv. Funct. Mater.* **2013**, *23*, 731; d) N. Rocha, J. Mendes, L. Durães, H. Maleki, A. Portugal, C. F. G. C. Geraldes, A. Serraa, J. Coelho, *J. Mater. Chem. B* **2014**, *2*, 1565; e) A. J. Convertine, B. S. Sumerlin, D. B. Thomas, A. B. Lowe, C. L. McCormick, *Macromolecules* **2003**, *36*, 4679; f) J.-T. Sun, C.-Y. Hong, C.-Y. Pan, *Polym. Chem.* **2013**, *4*, 873; g) R. H. Lohwasser, M. Thelakkat, *Macromolecules* **2012**, *45*, 3070.
- [2] a) K. Matyjaszewski, J. Spanswick, *Mater. Today* **2005**, *8*, 26; b) W. A. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.* **2007**, *32*, 93; c) H. Gao, K. Matyjaszewski, *Prog. Polym. Sci.* **2009**, *34*, 317.
- [3] a) J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614; b) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721; c) K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015; d) K. Matyjaszewski, N. V. Tsarevsky, *J. Am. Chem. Soc.*, **2014**, *136*, 6513; e) J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559; f) G. Moad, E. Rizzardo, S. H. Thang, *Acc. Chem. Res.* **2008**, *41*, 1133; g) G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2012**, *65*, 985; h) M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules* **1993**, *26*, 2987; i) J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, B. Charleux, *Prog. Polym. Sci.* **2013**, *38*, 63.
- [4] a) J. Xia, X. Zhang, K. Matyjaszewski, *Macromolecules*, **1999**, *32*, 3531; b) N. V. Tsarevsky, W. A. Braunecker, S. J. Brooks, K. Matyjaszewski, *Macromolecules*, **2006**, *39*, 6817.
- [5] a) D. B. Thomas, A. J. Convertine, R. D. Hester, A. B. Lowe, C. L. McCormick, *Macromolecules* **2004**, *37*, 1735; b) C. Barner-Kowollik, J. P. Blinco, S. Perrier, in *Materials Science and Technology*, (Eds: D. Schlüter, C. Hawker, J. Sakamoto), Wiley-VCH, Weinheim, Germany **2013**, 601; c) X. Li, H. ShamsiJazeyi, S. L. Peseck, A. Agrawal, B. Hammouda, R. Verduzco, *Soft Matter* **2014**, *10*, 2008.
- [6] a) B. Charleux, J. Nicolas, O. Guerret, *Macromolecules* **2005**, *38*, 5485; b) J. Nicolas, S. Brusseau, B. Charleux, *J. Polym. Sci., Part A Polym. Chem.* **2010**, *48*, 34.
- [7] M. Shoji, M. Eguchi, J. M. Layman, M. P. Cashion, T. E. Long, H. Nishide, *Macromol. Chem. Phys.* **2009**, *210*, 579.
- [8] a) J. Kulis, C. A. Bell, A. S. Micallef, Z. Jia, M. J. Monteiro, *Macromolecules* **2009**, *42*, 8218; b) Z. Jia, C. A. Bell, M. J. Monteiro, *Macromolecules* **2011**, *44*, 1747; c) W. Lin, Q. Fu, Y. Zhang, J. Huang, *Macromolecules* **2008**, *41*, 4127; d) Q. Fu, Z. Zhang, W. Lin, J. Huang, *Macromolecules* **2009**, *42*, 4381; e) A. Debuigne, M. Hurtgen, C. Detrembleur, C. Jérôme, C. Barner-Kowollik, T. Junkers, *Prog. Polym. Sci.* **2012**, *37*, 1004; f) D. Yang, C. Feng, J. Hu, *Polym. Chem.* **2013**, *4*, 2384; g) G. Wang, J. Huang, *Polym. Chem.* **2014**, *5*, 277.
- [9] a) H. Fischer, *Chem. Rev.* **2001**, *101*, 3581; b) A. Goto, T. Fukuda, *Prog. Polym. Sci.* **2004**, *29*, 329.
- [10] W. Lin, B. Huang, Q. Fu, G. Wang, J. Huang, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2991.
- [11] a) T. Nishikawa, T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1997**, *30*, 2244; b) R. Nicolay, L. Marx, P. Hemery, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 9217; c) M. Edeleva, S. R. A. Marque, D. Bertin, D. Gigmes, Y. Guillaneuf, S. V. Morozov, E. G. Bagryanskaya, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6828; d) M. Y. Khan, X. Chen, S. W. Lee, S. K. Noh, *Macromol. Rapid Commun.* **2013**, *34*, 1225.