1990 *Macromolecules* **2004,** *37,* 1990−1993

Synthesis of Terpyridine-Containing Polymers with Blocky Architectures

Khaled A. Aamer and Gregory N. Tew*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, 120 Governors Drive, Amherst, Massachusetts 01003

Received August 20, 2003

Revised Manuscript Received December 22, 2003

Self-assembly is a powerful tool to generate multifunctional materials, and supramolecular polymeric structures with well-defined architecture are of growing interest for various applications.[1] Self-assembly uses a variety of strategies to direct molecules including hydrogen and metal bonds, $\pi-\pi$ and donor−acceptor associations, electrostatics, hydrophilic−hydrophobic, and van der Waals forces.[2] Metal−ligand interactions are a good choice since these are strong enough to allow robust assembly and cause the appearance of new properties characteristic of the metal complex (e.g., metal-to-ligand or ligand-to-metal charge-transfer bands), leading to luminescence, magnetism, and thermochromism while, at the same time, weak enough to allow the manifestation of intrinsic properties of the metal and ligands (e.g., ligand-centered and metal-centered absorption bands and redox waves).[3] In addition, the complexes have well-controlled geometry and stoichiometry which are defined by the choice of ligand and metal ion.

Previous work on supramolecular polymers has used metal−ligand interactions to guide the process. Pyridine-based metal−ligands including bipyridine (bipy) and terpyridine (terpy) have been used by a few groups to design and synthesize polymeric structures with different architectures.[4−7] Polyoxazolines were prepared containing bipy with thermal reversibility.[8−10] Employing both the convergent and divergent approach, Fraser reported several systems based on bipy cores including star-shaped polymers.[11−19] Schubert reported structures based on a single terpy ligand at the chain end by polymerization from a terpy functionalized alkoxyamine initiator.[21−24] Both Schubert and our lab reported methyl methacrylate (MMA) polymers containing terpy in the side chain.[24,25] We showed the solution viscosity of these polymers increased upon addition of copper(II) ions.[25] For macromolecules containing terpy in the side chain, the ability to localize the metal ligand to one segment would provide block copolymer architectures for use in supramolecular polymer science. To date, no control over polymer architecture has been achieved for polymers containing metal−ligand side chains. In this paper, we report the synthesis and characterization of block−random polymer architectures based on styrene and MMA with narrow polydispersity index containing terpy in the side chain using living controlled radical polymerization (CRP).

Table 1. Molecular Weight Characteristics of Copolymers Synthesized by NMP and RAFT

polymer	architecture	M_n (kDa)	M_w (kDa)	MWD	mol % terpy
1	P(Sty-*ran*-$\mathrm{Sty}_{\mathrm{Terpy}}$)	32.2	42.9	1.30	10
2	P(Sty-*b*-(Sty-*ran*-$\mathrm{Sty}_{\mathrm{Terpy}}$)	67.2	93.1	1.40	7.5
3	P(MMA-*b*-(MMA-*ran*-$\mathrm{Sty}_{\mathrm{Terpy}}$))	37.3	45.4	1.22	2.5

CRP including atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMP), and reversible addition−fragmentation chain transfer polymerization (RAFT) are valuable techniques to control polymer architecture and are tolerant to a broad range of functionalities.[28,32−36] As part of our program on supramolecular polymers, we aimed to synthesis structures containing terpy ligands in the side chain with well-defined architectures including control over molecular weight (MW), molecular weight distribution (MWD), and mol % incorporation of the terpy ligands along the polymer backbone. In addition, the ability to control terpy incorporation into one or more segments of a block copolymer will generate ordered structures and is an important component of well-defined architectures. To achieve this goal, we studied the three common CRP techniques and found both NMP and RAFT were successful in preparing copolymers; however, to date ATRP has been unsuccessful, most likely due to the large molar ratio of terpy in the reaction.

Table 1 summarizes the polymers reported here, and their synthesis is shown in Figure 1. The key styrene-based monomer ($\mathrm{Sty}_{\mathrm{Terpy}}$, **5**) is shown and was synthesized from 5-([2,2′;6′,2″]-terpyridin-4′-yloxy)pentylamine,[23] **4**, by HOBT/DCC coupling in high yield (80%) and purity. Random copolymer **1** was synthesized using the alkoxyamine initiator **7**, which is known to allow controlled polymerization of functionalized styrene monomers.[27,28] The GPC trace of polymer **1** shows a molecular weight (MW) of 32.2 kDa at 66% conversion, which may be increased by changing the monomer/initiator ratio. On the basis of elemental analysis of the copolymer nitrogen content, there is 10 mol % terpyridine, which is consistent with the ^{1}H NMR integration. From the initial comonomer feed ratio (9:1 styrene:$\mathrm{Sty}_{\mathrm{Terpy}}$) and the 10 mol % terpy content found in this copolymer at 66% conversion, we conclude that the $\mathrm{Sty}_{\mathrm{Terpy}}$ monomer prefers to add to the growing chain slightly faster than styrene. This would explain the tendency of $\mathrm{Sty}_{\mathrm{Terpy}}$, **5**, to be incorporated faster than styrene in the copolymer; however, until detailed kinetic experiments are finished to provide quantitative values for reactivity ratios, further conclusions cannot be drawn.

Following successful synthesis of the random copolymer **1**, we turned our attention to block architectures. Copolymer **2** was synthesized using the polystyrene macroinitiator **6**, styrene (90 mol %), and **5** (10 mol %) at 125 °C according to Figure 1. The efficiency of the

10.1021/ma0352375 CCC: $27.50

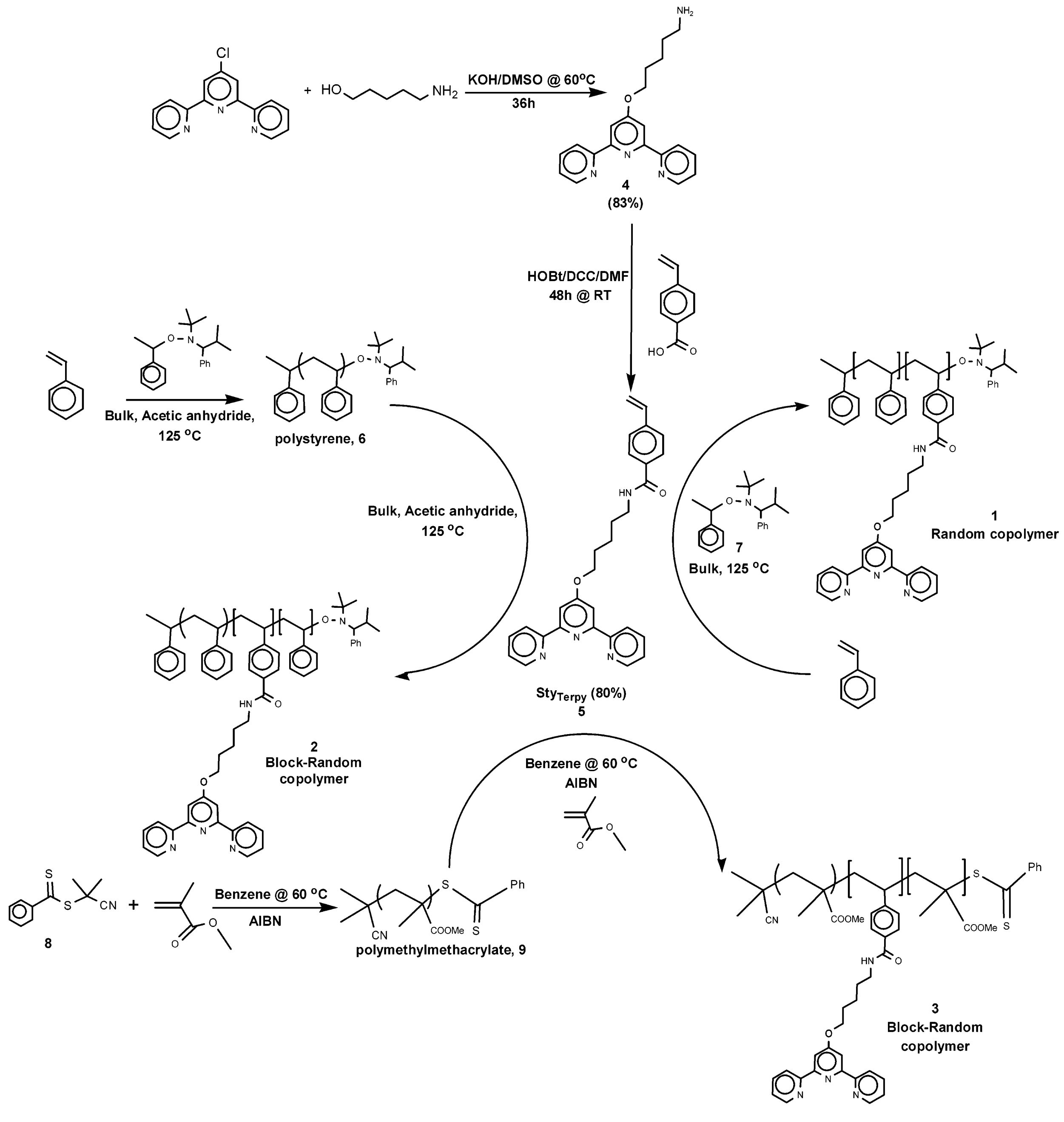

Figure 1. Scheme for the synthesis of monomer **5**, NMP, and RAFT copolymerization of **1**, **2**, and **3**.

polystyrene macroinitiator to reinitiate monomer is evidenced from the overlaid GPC chromatograms in Figure 2, which shows both the macroinitiator and copolymer.[27,28] The presence of the terpy causes broadening of the peak, which is consistent with previous reports on pyridine-containing polymers.[37] The high mol % incorporation of terpy obtained at 56% conversion is consistent with observations from the synthesis of **1** in which **5** appears to add to the growing chain in preference to styrene. These results show NMP allows blocky architectures, based on styrene, to be prepared in which the terpy unit is confined to one segment.

The synthesis of block–random MMA structures was undertaken to complement our initial report on random terpy-containing MMA polymers.[25] However, NMP is not the best choice for MMA synthesis, and so we explored RAFT polymerization.[30] Polymer **3** was successfully prepared using MMA macro-chain-transfer agent **9**, AIBN, MMA (90 mol %), and **5** (10 mol %) in benzene at 60 °C as shown in Figure 1. Figure 3 shows the overlaid GPC traces for **9** and copolymer **3**. The total mol % incorporation of terpy is only 2.5 mol % based on elemental analysis of the nitrogen content and ^{1}H NMR at 95% conversion. This indicates monomer **5** has a lower tendency to be incorporated than MMA in the copolymer under the RAFT conditions. The GPC trace shows little broadening in the peak, most likely due to the decreased mol % incorporation of terpy compared to **2**.

UV–vis spectroscopy in $CHCl_3$ confirms incorporation of terpy in all three polymer samples. Figure 4 shows the UV–vis spectrum of Sty$_{Terpy}$ monomer, **5**, which has

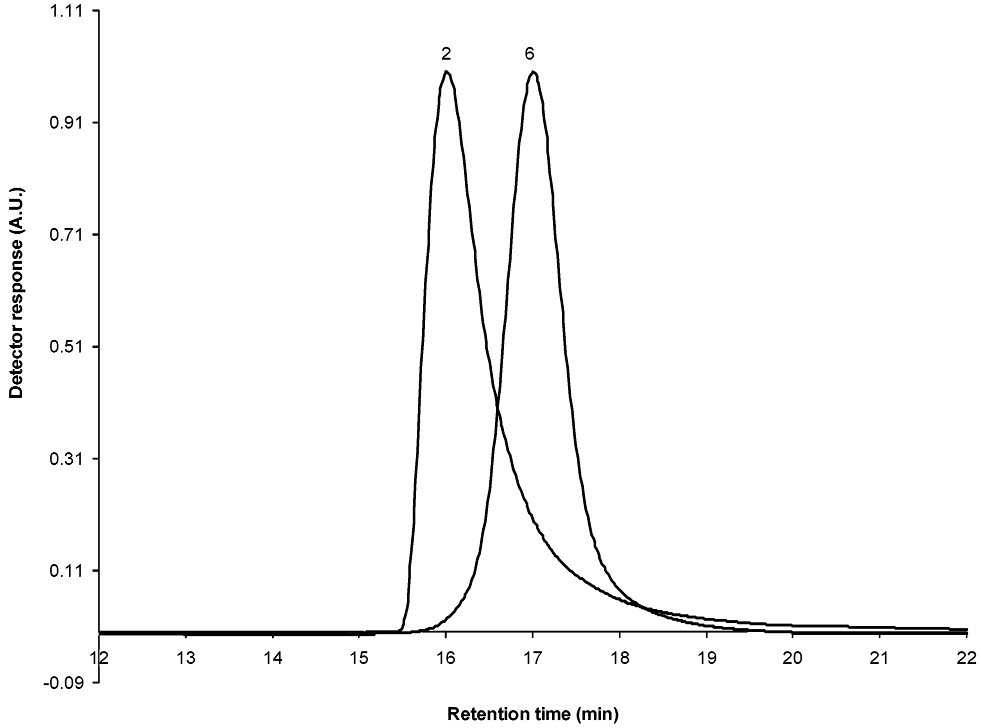

Figure 2. Overlaid GPC trace of polystyrene macroinitiator end-capped with the alkoxyamine, **6**, and poly(styrene-*b*-(styrene-*ran*-Sty_{Terpy})), **2**, synthesized via NMP in THF mobile phase.

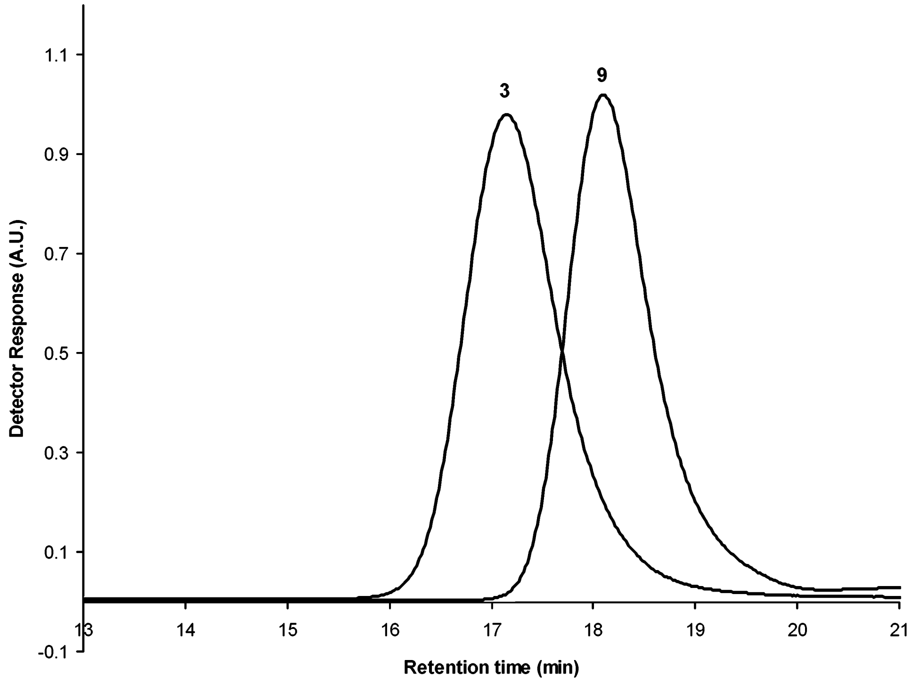

Figure 3. Overlaid GPC trace of α,ω-(thiobenzoylthio)poly(methyl methacrylate) macro-chain-transfer agent, **9**, and poly(MMA-*b*-(MMA-*ran*-Sty_{Terpy})), **3**, synthesized via RAFT in THF as mobile phase.

two distinct transitions at 277 and 244 nm. The spectra of **1** and **2** were normalized to **5**, showing similar peak intensity expected for these polymers since they contain both styrene and terpy functions. In contrast, the spectrum of **3** is not normalized since there is much less absorption at 244 nm due to the absence of styrene in the backbone and the low mol % terpy incorporation; however, the spectrum confirms terpy incorporation.

In conclusion, we report the first CRP of terpy monomers, based on vinylbenzamides, to synthesize styrene and MMA copolymers with terpy in the side chain and control over MW, MWD, composition, and architecture. CRP (NMP and RAFT) allows the synthesis of block copolymers with terpy functions confined to one block which represents a new architecture for supramolecular polymers containing pyridine ligands.

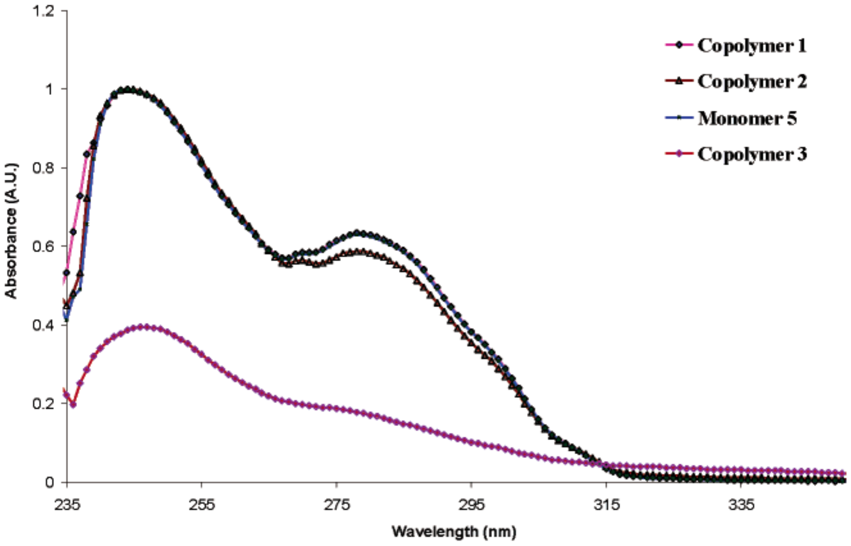

Figure 4. UV−vis spectra of copolymers **1**,**2**, and **3** and monomer **5** in chloroform containing 1% ethanol.

The successful syntheses of these block copolymers will facilitate the study of novel supramolecular polymers with interesting assembly properties.

Acknowledgment. This work was supported by the MRSEC program of the National Science Foundation under Award (DMR 9400488). G.N.T. thanks ONR for a Young Investigators Award and 3M Corporation for a Non-tenured Faculty Award. The authors thank Dr. Craig Hawker for fruitful discussion and providing the alkoxyamine initiator.

Supporting Information Available: Synthetic procedures and materials characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ikkala, O.; Brinke, G. T. *Science* **2002**, *295*, 2407−2409.
(2) Lehn, J.-M. *Supramolecular Chemistry—Concepts and Prospectives*; VCH: Weinheim, 1995.
(3) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759−833.
(4) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Polym Chem.* **2003**, *41*, 1413−1427.
(5) Potts, K. T.; Usifer, D. A. *Macromolecules* **1988**, *21*, 1985−1991.
(6) Hanabusa, K.; Nakano, K.; Koyama, T.; Shirai, H.; Hojo, N.; Kurose, A. *Makromol. Chem.* **1990**, *191*, 391−396.
(7) Hanabusa, K.; Nakamura, A.; Koyama, T.; Shirai, H. *Makromol. Chem.* **1992**, *193*, 1309−1319.
(8) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1993**, *26*, 6320−6323.
(9) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1993**, *26*, 6315−6319.
(10) Chujo, Y.; Sada, K.; Saegusa, T. *Polym. J.* **1993**, *23*, 599−608.
(11) Johnson, R. M.; Ng, C.; Samson, C. C. M.; Fraser, C. L. *Macromolecules* **2000**, *33*, 8618−8628.
(12) Lamba, J. J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801−1802.
(13) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 1341−1347.
(14) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 6925−6932.
(15) McAlvin, J. E.; Scott, S. B.; Fraser, C. L. *Macromolecules* **2000**, *33*, 6953−6964.
(16) Park, C. M.; McAlvin, J. E.; Fraser, C. L.; Thomas, E. L. *Chem. Mater.* **2002**, *14*, 1225−1230.
(17) Smith, A. P.; Fraser, C. L. *Macromolecules* **2003**, *36*, 2654−2660.
(18) Wu, X. F.; Collings, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812−2821.
(19) Wu, X. F.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053−4060.
(20) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926.
(21) Gohy, J. F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 555−560.
(22) Schubert, U. S.; Eschbaumer, C.; Andres, P.; Hofmeier, H.; Weidl, C. H.; Herdtweck, E.; Dulkeith, E.; Morteani, A.; Hecker, N. E.; Feldmann, J. *Synth. Met.* **2001**, *121*, 1249−1252.
(23) Schubert, U. S.; Eschbaumer, C.; Hien, O.; Andres, P. R. *Tetrahedron Lett.* **2001**, *42*, 4705−4707.
(24) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, *23*, 561−566.
(25) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090−6093.
(26) Newkome, G. R.; He, E. *J. Mater. Chem.* **1997**, *7*, 1237−1244.
(27) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.
(28) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(29) Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570−4772.
(30) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420−1425.
(31) Lee, J.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 2805−2811.
(32) Evans, R. A.; Rizzardo, E. *Macromolecules* **1996**, *29*, 6983−6989.
(33) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M. A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738−6745.
(34) Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol. Symp.* **2003**, *192*, 1−12.
(35) Donovan, M. S.; Sanford, T. A.; Lowe, A. B.; Sumerlin, B. S.; Mitsukami, Y.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4570−4772.
(36) Gotz, H.; Harth, E.; Schiller, S. M.; Frank, C. W.; Knoll, W.; Hawker, C. J. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 3379−3391.
(37) Peter, K.; Thelakkat, M. *Macromolecules* **2003**, *36*, 1779−1785.

MA0352375