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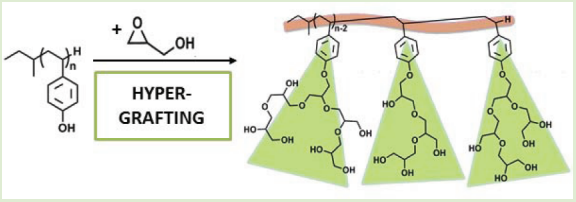
Controlled Synthesis of Linear Polymers with Highly Branched Side Chains by "Hypergrafting": Poly(4-hydroxy styrene)-*graft*-hyperbranched Polyglycerol

Christoph Schüll and Holger Frey*

Institute of Organic Chemistry, Johannes Gutenberg−University, Duesbergweg 10−14, D-55128 Mainz, Germany

Supporting Information

ABSTRACT: Linear polymers with hyperbranched side chains are unusual macromolecular structures due to their high number of functional groups in the side chains as well as their potential cylindrical conformation in bulk or solution. In a three-step synthesis combining anionic and oxy-anionic polymerization, hyperbranched polyglycerol was "hypergrafted" from linear poly(4-hydroxy styrene) macroinitiators to yield poly(4-hydroxy styrene)-*graft*-hyperbranched polyglycerol. Successful grafting with control over molecular weight (10−31 kg·mol^{-1}) and low PDIs (<1.4) was shown by various characterization techniques. All polymers have a high side chain density, due to rapid transfer of the initiating functional groups to the linear backbone. DSC studies give insight into the thermal properties of the resulting polymers.



The formation of supramolecular structures and "nano-objects" based on single molecules draw much attention to the macromolecular synthesis community during the last decades. There are several concepts leading to the formation of unimolecular cylinders in bulk or solution. Besides brush type polymers,[1] dendronized polymers (DenPols) consisting of a linear backbone and perfectly branched dendritic side chains represent a well-established class of macromolecules. The sterically demanding, perfectly branched dendritic side chains force the linear backbone of these polymers into an extended conformation.[2,3] In a recently published elegant work, Schlüter and co-workers described the synthesis of a cylindrical-shaped dendronized polymer in the size range of the tobacco mosaic virus.[4] The large number of functional groups at the "surface" and cylindrical shape render these polymers attractive for various applications.[5]

Hyperbranched polymers represent an interesting alternative to dendrimers because they are usually accessible in a single reaction step, despite the expense of a certain polydispersity. Still, they possess many properties attributed to dendrimers, such as their globular shape and their multifunctionality.[6,7] Surprisingly, only few reports on linear polymers grafted with hyperbranched side chains have been published, albeit with polydispersities commonly exceeding 2.[8−12] This class of macromolecules represents an interesting approach toward cylindrical-shaped macromolecules, because the synthesis of perfectly branched side chains in Denpols remains challenging and time-consuming. Hyperbranched polyglycerol (*hb*PG)[13,14] is available in a broad range of molecular weights by ring-opening multibranching polymerization (ROMBP) of the latent AB_2 monomer glycidol.[15] *Hb*PG has been "hypergrafted" successfully from multifunctional macroinitiators, for example, to obtain *hb*PG with high molecular weights[16] or linear-hyperbranched block copolymers.[17]

Poly(4-hydroxy styrene) (PHOS) can be polymerized by carbanionic polymerization of 4-*tert*-butoxy styrene (tBOS) and subsequential removal of the ether protective groups.[18] The monomer is commercially available and stable during the basic reaction conditions in the carbanionic polymerization process. PHOS is a known linear macroinitiator for the synthesis of graft-copolymers, where linear side chains are grafted by anionic polymerization. For instance, the hydroxyl groups were used as initiating functionalities for the ring-opening polymerization of ethylene oxide and propylene oxide.[19,20]

Within this work we present a synthetic approach to linear polymers with hyperbranched side chains using a convenient three-step protocol. We combined carbanionic polymerization for the generation of the PHOS backbone and oxy-anionic ring-opening multibranching polymerization (ROMBP) of glycidol for the synthesis of the highly branched side chains. By using only anionic polymerization techniques it is possible to tailor the size of the linear backbone and of the side chains individually with narrow molecular weight distributions and controlled molecular weights.[21]

First, poly(4-*tert*-butoxy styrene) (P*t*BOS) was synthesized using living carbanionic polymerization initiated by *sec*-butyl lithium with control over molecular weight and narrow molecular weight distributions (see Supporting Information). Removal of the *tert*-butoxy protective groups to obtain poly(4-hydroxy styrene) (PHOS, **2**) was achieved under acidic conditions. SEC (Figure 1) shows the preservation of low

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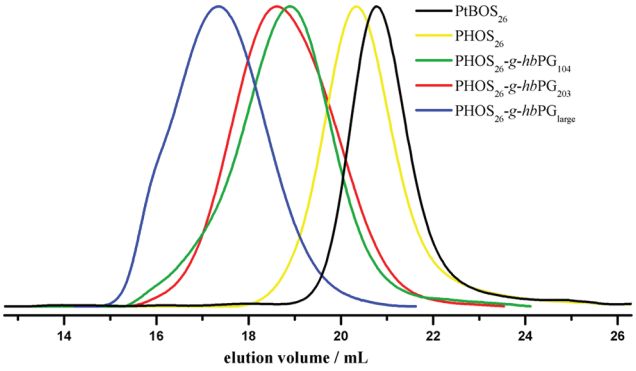
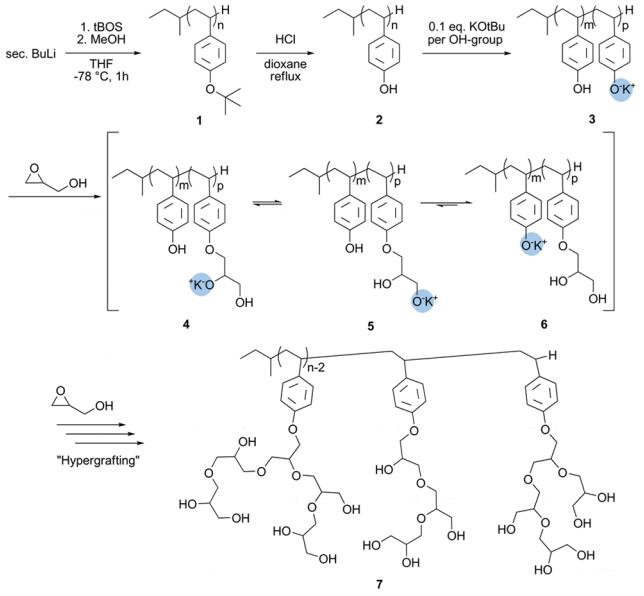


Figure 1. SEC traces (measured in DMF) of $PtBOS_{26}$, the $PHOS_{26}$ macroinitiator, and the corresponding series of PHOS-*g*-*hb*PG samples.

PDIs and monomodal molecular weight distributions after the removal of the protective groups. It is noteworthy that the removal of the protective groups leads to an apparent increase in the molecular weight in the SEC elugrams. This can be explained by a larger hydrodynamic radius of PHOS compared to P*t*BOS, caused by the polar free hydroxyl groups. MALDI–TOF mass spectrometry and IR spectroscopy confirm quantitative removal of the ether protective groups (see Supporting Information). Therefore, every repeat unit of PHOS should be capable of initiating the hypergrafting of glycidol. Two macroinitiators $PHOS_{26}$ and $PHOS_{64}$ were used. The index represents the respective degree of polymerization, calculated from the corresponding ^{1}H NMR spectra.

Several samples of poly(4-hydroxy styrene- *graft*-hyperbranched polyglycerol (PHOS-*g*-*hb*PG) with molecular weights ranging from 10.9 to 30.5 kg·mol^{-1} were synthesized using PHOS as a linear macroinitiator (Table 1). A high degree of deprotonation of the initiator is crucial to attain control over the polymerization process. Unfortunately, this leads to poor solubility of the initiating salt in the reaction solvent. Incomplete dissolution of the deprotonated macroinitiator leads to polymers with broader, still moderate PDIs (<1.4), because there is no simultaneous initiation from every PHOS macroinitiator possible during the polymerization of glycidol. In a typical procedure, PHOS was deprotonated by 10% (Scheme 1, structure **3**), using potassium *tert*-butanolate. Higher degrees of deprotonation lead to the formation of low molecular weight side products, due to deprotonation and self-initiation of glycidol in the reaction mixture. The established slow monomer-addition (SMA) of glycidol enables control of the

Scheme 1. Synthesis Strategy for PHOS-*g*-*hb*PG (7) and Detailed Mechanism (4–6) of the Hypergrafting Reaction



hypergrafting reaction, profiting from the rapid proton exchange in the reaction system.

Molecular weight determination by SEC (Figure 1) shows an increase in molecular weight for increasing targeted molecular weight of the side chains. In all cases, monomodal molecular weight distributions were found, which is not in disagreement with the assumption of complete conversion of the PHOS macroinitiator. Molecular weights of PHOS-*g*-*hb*PG determined by SEC are underestimated compared to calculated values because branched elements were referenced to linear poly(ethylene glycol) standards.

In the ^{1}H NMR spectrum (Figure 2), separated signals for the aromatic backbone of PHOS (δ = 6.80–6.10 ppm, (b), the aliphatic backbone of PHOS (δ = 2.20–0.92 ppm, (a), as well as the broad signal of the aliphatic polyether backbone of *hb*PG (δ = 4.20–3.41 ppm, (c), are observed. Thus, ^{1}H NMR spectroscopy allows the determination of the number average molecular weight of PHOS-*g*-*hb*PG by comparison of the intensity of the *hb*PG signals with the aromatic signals of PHOS and referencing the result to the known molecular weight of the PHOS macroinitiator. Moreover, the molar glycerol/4-hydroxy styrene ratio (G/S) in PHOS-*g*-*hb*PG can be calculated by comparing the integrals of the aromatic styrene unit signals and the aliphatic glycerol backbone signals. The calculated G/S ratios are in good agreement with the targeted values (Table 1).

Table 1. Charaterization Data of All Polymer Samples

	polymer	G/S[a]	G/S[b]	M_n[c]	M_n[b]	M_n[d]	PDI[d]	T_g[e]
1	$PHOS_{26}$			3.9	3.2	3.5	1.17	122.1
2	$PHOS_{64}$			8.8	7.8	7.4	1.11	166.8
3	$PHOS_{64}$-*g*-*hb*PG_{70}	1.0	1.1	12.5	13.0	10.5	1.19	85.1/ −13.3
4	$PHOS_{26}$-*g*-*hb*PG_{104}	3.0	4.0	10.1	10.9	7.5	1.41	−18.6
5	$PHOS_{64}$-*g*-*hb*PG_{237}	3.0	3.7	17.3	25.3	14.0	1.34	−12.1
6	$PHOS_{64}$-*g*-*hb*PG_{307}	5.0	4.8	31.6	30.5	18.0	1.39	−14.2
7	$PHOS_{26}$-*g*-*hb*PG_{203}	7.0	7.8	18.0	18.2	7.7	1.40	−31.7
8	$PHOS_{26}$-*g*-*hb*PG_{large}	15.0		36.0		16.0	1.38	−35.8

[a]Targeted value. [b]Determined by ^{1}H NMR. [c]Targeted molecular weight in kg·mol^{-1}. [d]Molecular weight determined by SEC (DMF, PEG-standard) in kg·mol^{-1}. [e]Glass transition temperature in °C.

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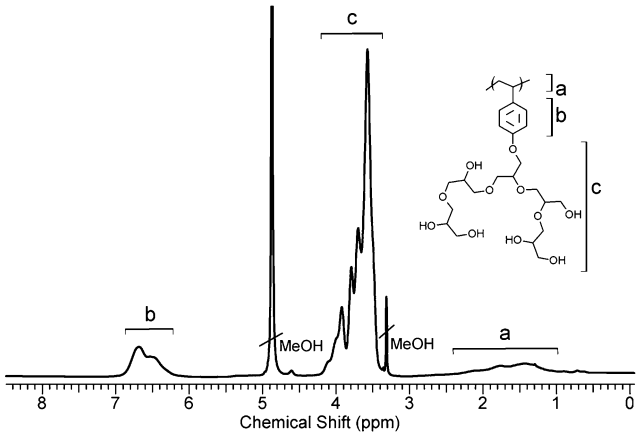

Figure 2. ^{1}H NMR spectrum (400 MHz, MeOH-d_4) of PHOS$_{64}$-*g*-*hb*PG$_{307}$.

Consequently, it is possible to control the amount of *hb*PG attached to PHOS and the molecular weights of PHOS-*g*-*hb*PG simply by varying the G/S ratio in the hypergrafting reaction. Assuming complete functionalization of the PHOS backbone, the G/S ratio can be used to calculate the number of glycerol units attached to each PHOS repeat unit as well as the "pseudo-generation" of the branched side chains.[22] It has to be emphasized that in hyperbranched polymers there are no generations like in dendrimers due to the randomly branched structure. Still, the concept of "pseudo-generations" renders a comparison between hyperbranched side chains and perfectly branched dendrons like in DenPols, when assuming that all *hb*PG side chains are of similar size. A G/S ratio of 1 would correspond to a first generation dendronized polymer, a G/S ratio of 3 to a second etc. Taking this into account, by using the hypergrafting approach, it is possible to synthesize dendronized-like polymers with third or fourth pseudo generation side chains (table 1, entries 7 and 8) in merely three synthesis steps.

The high number of hydroxyl groups in PHOS-*g*-*hb*PG compared to PHOS and the hydrophilic character of *hb*PG in general leads to improved solubility of PHOS in polar solvents such as methanol. For high molecular weight *hb*PG side chains, for example, polymer sample **8**, the structures become water-soluble.

The grafting efficiency, that is, the amount of PHOS repeat units functionalized with *hb*PG, is an important structural aspect in this type of graft-copolymers, especially because of the sterical demand of the side chains. Inverse-gated (IG) ^{13}C NMR measurements allow for the integration of signal intensities in ^{13}C NMR spectroscopy. Figure 3 shows the aromatic region of the IG ^{13}C NMR spectra of the PHOS$_{64}$ macroinitiator and the corresponding hypergrafted copolymers. The signal of the quaternary *para*-carbon in PHOS is shifted if an ether bond (δ = 158.3 ppm) instead of a free hydroxyl group (δ = 155.9 ppm) is attached. In PHOS$_{64}$ we find only one signal resulting from unfunctionalized hydroxyl groups. In PHOS$_{64}$-*g*-*hb*PG$_{70}$ with a G/S ratio of 1.1, approximately 81% of the PHOS repeat units are functionalized, despite the fact that only 10% of the hydroxyl groups of PHOS were deprotonated at the initial stage of the glycidol polymerization. Due to the rapid proton transfer in the system (Scheme 1, structures **4**–**6**), we can deduce a high grafting density for all samples, owing to the higher acidity of the phenolic alcohols compared to the aliphatic ones formed by the PG structure. The active chain end will always be transferred to the PHOS backbone (Figure 2,

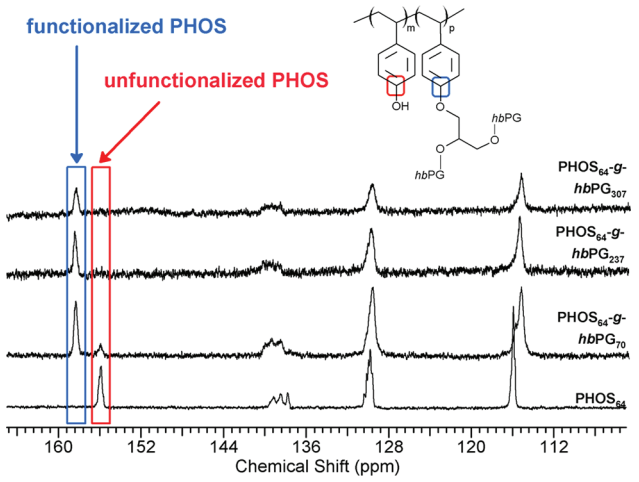

Figure 3. Aromatic region of the inverse-gated ^{13}C NMR spectra (125 MHz, MeOH-d_4) of PHOS$_{64}$ and the corresponding series of PHOS$_{64}$-*g*-*hb*PG$_n$ polymers.

structure **6**) via proton transfer benefiting from the slow addition of glycidol. For a higher G/S ratio of 3.7 in PHOS$_{64}$-*g*-*hb*PG$_{237}$ and 4.8 in PHOS$_{64}$-*g*-*hb*PG$_{307}$ we find quantitative conversion of all PHOS units in the range of the accuracy of the method (>95%). From these results it can be concluded that from the use of an approximately 4-fold molar excess of glycerol over hydroxyl styrene repeat units guarantees quantitative functionalization of the backbone hydroxyls. Once the conversion of each hydroxyl group of PHOS with glycidol is complete, the size of each *hb*PG side chain increases. A high density of side chains along the linear backbone accompanied with maximum sterical hindrance might force the backbone to stretch to a cylindrical conformation at a certain molecular weight of the backbone and the side chains.

The different linear, dendritic and terminal repeat units of the *hb*PG side chains can be assigned according to literature by IG ^{13}C NMR spectroscopy (see Supporting Information).[15] For all samples we observe excellent control over the ring-opening multibranching polymerization (ROMBP) of glycidol, leading to a typical distribution of structural units. The degree of branching (DB) is an important parameter to evaluate hyperbranched structures compared to perfectly branched dendrons. The DB was calculated using an established equation,[23] leading to values between 0.55 and 0.57 for the *hb*PG side chains in PHOS-*g*-*hb*PG. These results are in good agreement with data for *hb*PG homopolymers, confirming the anticipated highly branched structure of the *hb*PG side chains.[16]

The optical appearance of the samples differs significantly depending on the G/S ratio. PHOS$_{64}$-*g*-*hb*PG$_{70}$ (G/S = 1.1) is a white solid and PHOS$_{64}$-*g*-*hb*PG$_{237}$ (G/S = 3.7) is a sticky white solid, while PHOS$_{26}$-*g*-*hb*PG$_{203}$ (G/S = 7.8) and PHOS$_{26}$-*g*-*hb*PG$_n$ (G/S > 15) are highly viscous liquids (see Supporting Information). As expected, the glass transition temperatures (T_g) of the samples depend on the *hb*PG content. Differential scanning calorimetry (DSC) measurements give precise insight into the thermal properties (Table 1 and Supporting Information). T_gs of the PHOS-*g*-*hb*PG samples (from −35.8 to +85.1 °C) are significantly lower than for the PHOS macroinitiators (122.8 and 166.8 °C). For G/S ratios exceeding 3.7, one finds T_gs between −12.1 and −35.8 °C, while an increase in the G/S ratio lowers the glass transition. Flexibility and branching of the *hb*PG side chains lead to T_gs below room

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temperature, while the stiff PHOS backbone leads to a solid amorphous material, due to the atactic character of PHOS. The thermal properties of PHOS are superposed by *hb*PG for high G/S ratios leading to just one low T_g, which confirms the high grafting density and can be described as a "shielding" of PHOS by *hb*PG. When comparing samples with similar G/S ratios and different degrees of polymerization of the linear PHOS backbone (Table 1, entries 4 and 5), we find a lower T_g for $PHOS_{26}$-*g*-*hb*PG_{104} of −18.6 °C compared to $PHOS_{64}$-*g*-*hb*PG_{237} with a T_g of −12.1 °C. It is obvious that the length of the PHOS backbone also has an influence on T_g, independent of the size of the *hb*PG side chains, because the same trend can be found for the pure PHOS macroinitiators, where lowerer molecular weight gives lower T_gs (Table 1, entries 1 and 2). For both series of hypergrafted polymers based on different PHOS macroinitiators we find a maximum reduction in T_g of approximately 180 °C. $PHOS_{64}$-*g*-*hb*PG_{70} with a G/S ratio of 1.1 shows two glass transitions at 85.1 and −13.1 °C. In this case, an inhomogeneous substitution pattern by the grafted side chains is probable, causing phase separation in the sample.

In summary, a new type of linear polymer with highly branched side chains, poly(4-hydroxy styrene)-*graft*-hyperbranched polyglycerol (PHOS-*g*-*hb*PG), has been synthesized in a three-step synthesis using anionic polymerization techniques. Successful grafting was shown by SEC and ^{1}H NMR spectroscopy. The length of the linear backbone and the branched side chains can easily be tailored by the monomer ratio, yielding polymers with low PDIs (<1.4) and various molecular weights ranging from 10000 to 31000 g·mol^{-1}. Inverse-gate ^{13}C NMR spectroscopy shows that all polymers have densely packed side chains, where in most cases quantitative functionalization of the PHOS repeat units with *hb*PG side chains is possible. The high grafting efficiency confirms the proposed mechanism of favored initiating site formation at the PHOS backbone during the slow monomer-addition because of the higher acidity of phenolic alkoxides compared to the aliphatic alkoxides. A molar excess of *hb*PG side chain repeat units over the PHOS backbone repeat units (G/S ratio) reduces the glass transition temperature of the materials significantly. For the first time, linear polymers with hyperbranched side chains were synthesized in a three-step protocol using the hypergrafting strategy. These well-defined polymers with controlled molecular weights and low PDIs are facile accessible candidates for the potential formation of cylindrical objects, comparable to dendronized polymers due to the highly branched side chains.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional NMR, IR, and MALDI-ToF spectra and SEC traces, as well as DSC traces and pictures of the samples. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hfrey@uni-mainz.de.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 759−785.
(2) Percec, V.; Ahn, C. H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161−164.
(3) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864−883.
(4) Zhang, B. Z.; Wepf, R.; Fischer, K.; Schmidt, M.; Besse, S.; Lindner, P.; King, B. T.; Sigel, R.; Schurtenberger, P.; Talmon, Y.; Ding, Y.; Kroger, M.; Halperin, A.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 737−740.
(5) Frauenrath, H. *Prog. Polym. Sci.* **2005**, *30*, 325−384.
(6) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183−275.
(7) Voit, B. I.; Lederer, A. *Chem. Rev.* **2009**, *109*, 5924−5973.
(8) Lam, D.; Little, S.; Rutherford, J.; Twyman, L. J.; Zheng, X. W. *Macromolecules* **2008**, *41*, 1584−1586.
(9) Ishizu, K.; Ohta, Y. *J. Mater. Sci. Lett.* **2003**, *22*, 647−650.
(10) Pusel, T.; Frey, H.; Lee, Y. U.; Jo, W. H. *Polym. Prepr. Am. Chem. Soc.* **2001**, *84*, 730.
(11) Kuo, P. L.; Ghosh, S. K.; Liang, W. J.; Hsieh, Y. T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3018−3023.
(12) Lach, C.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromol. Rapid Commun.* **1998**, *19*, 461−465.
(13) Wilms, D.; Stiriba, S. E.; Frey, H. *Acc. Chem. Res.* **2010**, *43*, 129−141.
(14) Calderón, M.; Quadir, M. A.; Sharma, S. K.; Haag, R. *Adv. Mater.* **2009**, *21*, 1−29.
(15) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240−4246.
(16) Wilms, D.; Wurm, F.; Nieberle, J.; Böhm, P.; Kemmer-Jonas, U.; Frey, H. *Macromolecules* **2009**, *42*, 3230−3236.
(17) Wurm, F.; Klos, J.; Räder, H. J.; Frey, H. *J. Am. Chem. Soc.* **2009**, *131*, 7954−7958.
(18) Conlon, D. A.; Crivello, J. V.; Lee, J. L.; O'Brien, M. J. *Macromolecules* **1989**, *22*, 509−516.
(19) Zhao, J.; Mountrichas, G.; Zhang, G.; Pispas, S. *Macromolecules* **2009**, *42*, 8661−8668.
(20) Jannasch, P. *Macromolecules* **2000**, *33*, 8604−8610.
(21) Szwarc, M. *Nature* **1956**, *178*, 1168−1169.
(22) Hanselmann, R.; Hölter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790−3801.
(23) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30−35.