ACS Macro Letters
Letter
pubs.acs.org/macroletters

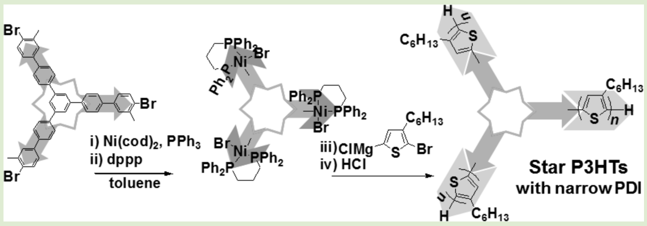
Constructing Regioregular Star Poly(3-hexylthiophene) via Externally Initiated Kumada Catalyst-Transfer Polycondensation

Mingjian Yuan, Ken Okamoto, Hugo A. Bronstein, and Christine K. Luscombe*

Materials Science and Engineering Department, University of Washington, Seattle, Washington 98195-2120, United States

Supporting Information

ABSTRACT: A synthetic route was developed for the preparation of di- and trifunctional Ni complex-based initiators. Each initiator affords well-defined 2-arm (V-shaped) and 3-arm (Y-shaped) regioregular poly(3-hexylthiophene) (rr-P3HT) with controlled molecular weight and narrow polydispersities by the externally initiated Kumada catalyst-transfer polycondensation. The core spacer length and end *o*-tolylhalide group of the functional initiators exhibited differences in reactivity and show that the biphenyl spacers are effective for the synthesis of V-shaped and Y-shaped rr-P3HTs.

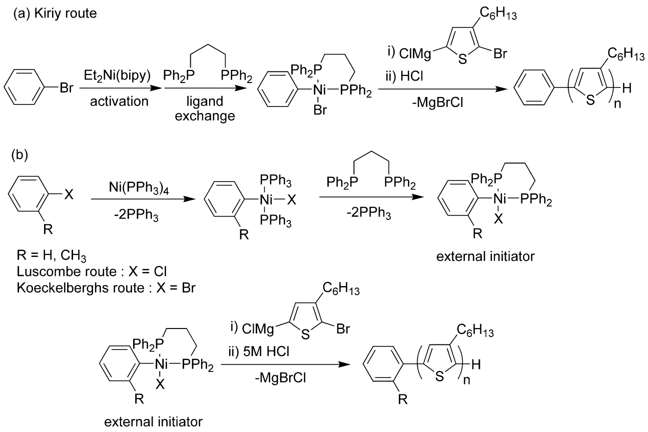


Extensive research for nonlinear polymers has been conducted to prepare multifunctional molecular architectures with higher dimensionalities such as star-shaped, disk-like, and hyperbranched polymers.[1] Their intrinsic compact structures and globular shape predetermine their unique properties in comparison with linear polymers, such as low viscosity and high solubility.[2] Furthermore, nonlinear polymers with well-defined shapes and dimensions may provide significant opportunities in areas such as drug delivery and nanotechnology.[3]

Star polymers are a class of nonlinear polymers and have attracted considerable attention due to their compact structures and high segment densities[4] which affects the crystalline, mechanical, optical, and electrical properties of the polymers.[5] Generally, star-shaped polymers can be prepared by two methods; the arm-first method and the core-first method.[6] The arm-first method is where the linear arms of the star polymer are synthesized first followed by attachment of the arms to the core. Conversely, the core-first method generates a reactive core prior to the addition of arm forming monomers. Using the first approach, the number of arms per star polymer is difficult to control but can be very high, whereas in the second approach, the number of arms is well-defined but remains limited by undeveloped synthetic method. To produce well-defined polymers, the core-first method would be preferable.

In this respect, living polymerization is an important strategy to use for the core-first method for the synthesis of star polymers because it enables us to realize the goal of controllable polymerizations. Recently, Kiriy et al.,[7a] Koeckelberghs et al.,[7b] and our group[7c] independently reported the controlled synthesis of externally initiated regioregular poly(3-hexylthiophene) (rr-P3HT) with controlled molecular weight and narrow polydispersity (Scheme 1). Although the external initiation method is based on the well-established method of Ni-catalyzed chain growth polycondensation, which was originally reported by McCullough and Yokozawa,[8] it offers several advantages over the conventional method. Namely, it can not only provide conjugated polymers with well-controlled molecular weight and molecular weight distribution but it also offers the possibility to allow for the synthesis of star-shaped semiconducting polymers using the core-first method.[9] It is well-known that rr-P3HT is of particular interest since the compounds show remarkable physical properties for applications in organic field effect transistors, organic photovoltaic devices, and organic photodetectors.[10] Star-shaped rr-P3HT have a different topology and should offer some characteristic physical properties in comparison to linear rr-P3HT.[11] As such, the synthesis of conjugated star polymers and the study of their physical properties have also attracted much current research

Scheme 1. Externally Initiated Kumada Catalyst-Transfer Polycondensation Pathways



Received: January 18, 2012
Accepted: February 20, 2012
Published: February 27, 2012

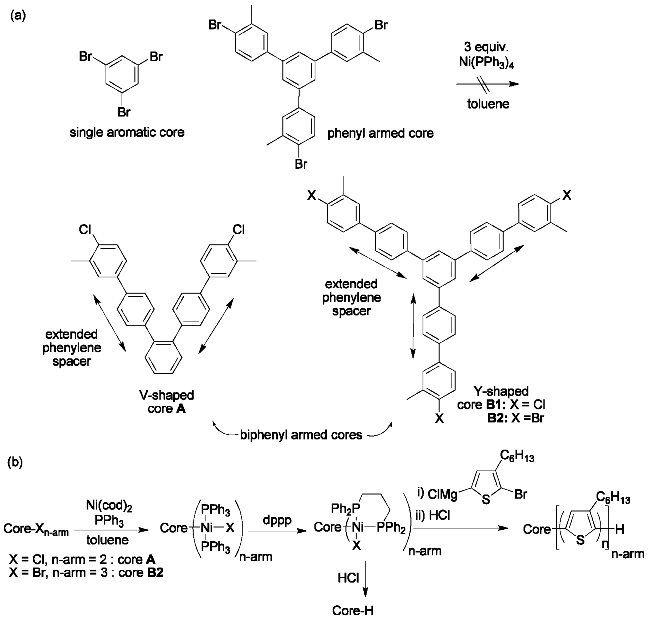
dx.doi.org/10.1021/mz3000368 | ACS Macro Lett. 2012, 1, 392−395

interest. However, examples for the synthesis of star rr-P3HT remain very scarce and are mainly limited by lack of efficient synthetic strategies.[12] Very recently, Kiriy et al. reported one approach to prepare the core-first star rr-P3HT by an externally initiated method; however, the polydispersity of the obtained core-first polymer is 1.98.[13] Thus, the synthetic methodology lacks control, and the end-product is ill-defined. We considered the key point for the synthesis of well-defined star rr-P3HT was in the first step where a multinuclear Ni complex initiator core is synthesized. However, to our knowledge, only few multinuclear Ni complexes with bridging allyl ligands[14] have been documented, although several unsuccessful attempts at their synthesis have been reported.[15] Koeckelberghs et al. have reported on the use of a binuclear Ni complex to synthesize a linear P3HT.[16] As such, significant efforts were made in our research to enable the design and synthesis of the core initiator.

Herein, we describe the design strategy for the initiator core molecule and report a method for the preparation of multifunctional initiators that mediate chain growth polycondensation of 2-bromo-5-chloromagnesio-3-hexylthiophene into star rr-P3HT.

At the beginning of the investigation, efforts were focused on the single aromatic core and the phenyl armed core as depicted in Scheme 2a. However, we soon realized that these cores were not suitable as the initiator for catalyst-transfer polycondensation. Black precipitates were obtained from the both reactions, and ^{31}P NMR spectra for the soluble part of the precipitates showed multiple peaks, which were very difficult to ascribe. These results suggested that the oxidative addition of Ni(0) to the core molecule does not afford a trisubstituted initiator at once, and undesired homocoupling reactions may be taking place between unreacted Br and partially formed Ni initiators leading to byproducts. The same phenomenon was observed by Kiriy et al.[13] Therefore, we designed and prepared a π-extended core which provides less steric hindrance for the oxidative addition step (Scheme 2a).

Scheme 2. A "Core-First" Synthesis of the V-Shaped and Y-Shaped P3HT



As expected, the V-shaped core **A** afforded the desired binuclear Ni complex. Initial work using $Ni(PPh_3)_4$ resulted in unwanted side reactions as a result of its slower reactivity,[17] while the use of core **A**, $Ni(COD)_2$ and PPh_3 at room temperature gave a light yellow precipitate. The formation of the Ni complex was observed by a change in color of the reaction mixture from brown to light yellow. Also the ^{31}P NMR spectrum shows a singlet peak at 20 ppm (Figure S1 of the Supporting Information), which is consistent with our previous reports about Ni-based initiator.[14] Subsequently, 2.4 equiv of 1,3-diphenylphosphinopropane (dppp) was added to the mixture. Ligand exchange was monitored by ^{31}P NMR. Two sets of doublets at 20 and −5 ppm are assigned as coordinated dppp to Ni (Figure S2). This ligand exchange has been documented in our previous experiments.[7c,18] The result shows that the extended phenylene core **A** is very effective for the preparation of binuclear Ni complex initiator (Scheme 2b).

This finding for the efficient preparation of the 2-arm initiator gave us the possibility to prepare multiarm initiators. With this in mind, the Y-shaped core **B1** was prepared (Scheme 2). Initial efforts using the chloride substituted π-conjugated 3-arm core (**B1**) was unsuccessful probably due to the low reactivity of the chloride. Based on this trial, we redesigned the structure of triarm core and replaced the chlorides with bromides instead (**B2**). Improvement of the core molecule reactivity was observed by ^{31}P NMR analysis. After formation of preinitiator Ni complex, dppp was added to the solution. A very similar result with core **A** was obtained from the ^{31}P NMR spectrum; two sets of doublets at 19 and −7 ppm were observed which were derived from the dppp ligand (Figure S5 of the Supporting Information).

To confirm complete reaction at all sites, a small amounts of the above multifunctional initiators were quenched with 1 M HCl, and the resulting crude products were analyzed by gas chromatography−mass spectrometry (GC-MS) and ^{1}H and ^{13}C NMR. Both mass spectra exhibited the existence of quenched core **A** molecule (m/z = 410) and core **B2** molecule (m/z = 577) as parent peaks, respectively (Figures S3 and S6 of the Supporting Information). These results indicate 100% conversion of *o*-tolylhalide moieties to the appropriate multinuclear Ni complexes.

The use of the Kumada catalyst-transfer polycondensation using these initiators was then studied. Polymerization was initiated by the addition of the crude complex mixture to a solution of 2-bromo-5-chloromagnesio-3-hexylthiophene in tetrahydrofuran (THF) at 0 °C, followed by stirring at room temperature for 2 h (Scheme 2b). The reaction mixture was quenched with 5 M HCl and precipitated in methanol, after which the polymer was isolated by filtration and washed with cold methanol and cold hexane.

Aiming for the preparation of the V-shaped P3HT with a degree of polymerization (DP) of 20 in each P3HT arm, the Grignard-type monomer was added to the solution of initiators at a monomer to initiator ratio of approximately 40:1. ^{1}H NMR analysis revealed the polymers regioregularity to be >95%[7c] (Figure S8 of the Supporting Information), with the presence of peaks corresponding to the initiating groups clearly visible in the aromatic region. Integration of the initiating peaks with respect to the polymer backbone signals indicates a DP of 23 for the V-shaped P3HT. The absolute molecular weight determined by size exclusion chromatography (SEC, triple detection) is 8.2 kDa which is very close to the calculated molecular weight of 8.0 kDa of the 23 unit 3-hexylthiophene in

Table 1. Overview of the Results from the Polymerization

	M_w[a] (kDa)	DP[b]	M_n[c] (kDa)	PDI
V-shaped	8.2	23	8.0	1.10
Y-shaped	7.6	15	7.9	1.15

[a] The obtained molecular weight (M_w) determined by size exclusion chromatography (SEC). [b] Degree of polymerization (DP) is calculated from ^{1}H NMR analysis. [c] The calculated molecular weight (M_n) is the ideal number using the value for DP from ^{1}H NMR.

each arm (see Table 1). The molecular weight calculated using NMR agrees well with the absolute molecular weight determined by SEC. The polydispersity index (PDI) value is 1.1 for the V-shaped P3HT, which shows the controllable polymerization mechanism with the dppp ligand. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis indicated only one set of peaks corresponding to the core/H-terminated P3HT, demonstrating that the polymerization was solely initiated by the multiarm initiators (Figure S7). The single triplet at 2.61 ppm in the ^{1}H NMR (Figure S9), corresponding to the α-methylene group on the terminal thiophene, also confirms that all polymers chains are H-terminated.[21] The integration of this peak versus the core methyl group reveals a 2:3 ratio confirming that polymerization occurred at both Ni sites.

For the Y-shaped P3HT synthesis, a polymerization was carried out targeting a DP of 15 in each P3HT arm to obtain a final polymer with a similar molecular weight as the V-shaped polymer. Addition of the initiator (6.7 mol %) to the Grignard-type monomer afforded a high regioregular Y-shaped P3HT with a PDI of 1.15. The molecular weight determined by SEC for Y-shaped P3HT is 7.6 kDa which is very close to the calculated molecular weight 7.9 kDa of the 15 unit 3-hexylthiophene in each arm. MALDI-TOF MS analysis indicated the majority of the peaks to be core/H-terminated (Figure S11 of the Supporting Information). Similarly to the V-shaped polymer, a single triplet at 2.61 ppm in the ^{1}H NMR confirms that the arms are H-terminated, and integration of this peak versus the core methyl group shows that all three Ni sites initiated the polymerization.

Proof of the star-like structure of the polymers in many cases is a highly challenging task.[19] However, in this work the assignment and integration of the ^{1}H NMR spectra are unequivocal. For example, in the aromatic region of the ^{1}H NMR spectra for Y-shaped P3HT (Figure 1; for overall view, see Figure S13 of the Supporting Information), besides the signals of internal thienyl rings (6.97 ppm), signals of the core groups (7.87, singlet; 7.80, doublet; 7.72, doublet; 7.57, singlet; 7.48, multiplet), a proton of the first thienyl ring adjacent to the core group (hidden in the solvent peaks), and a signal of terminal proton (6.91 singlet) were observed.[20] They integrate well with each other, and no other terminal groups can be observed within the accuracy of the NMR. Simple and clear peaks in the aromatic region imply that the molecule has a C_3-symmetric structure; otherwise, there would be multiple peaks showing in the aromatic region. Furthermore, it is possible for us to estimate the degree of polymerization (DP) from aromatic regions in ^{1}H NMR spectra. We calculated the DP as 15 for the Y-shaped P3HT by comparing the integrals of the end protons (6.91, H_i) and the internal thienyl protons (6.97, H_h). The polymer should contain around 45 repeat thienyl units in the whole backbone based on the absolute molecular weight data obtained from SEC. In this respect, the DP provides another key evidence for the star-like structure of the polymers. Proof for the V-shaped P3HT can also be obtained by analyzing the ^{1}H NMR (Figure S9). The above results confirm that we have successfully synthesized the V-shaped and Y-shaped P3HT via a controlled chain growth polymerization.

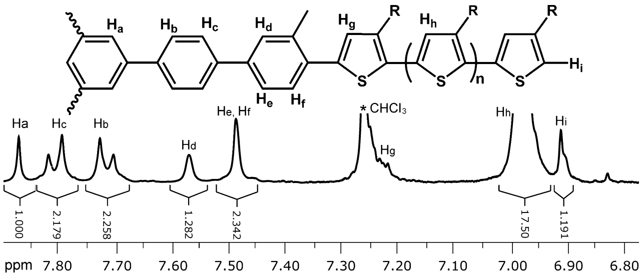


Figure 1. Regions of the ^{1}H NMR spectra showing signals of the core and the end H groups in each arm for the Y-shaped P3HT ($CDCl_3$ as solvent, 30 °C).

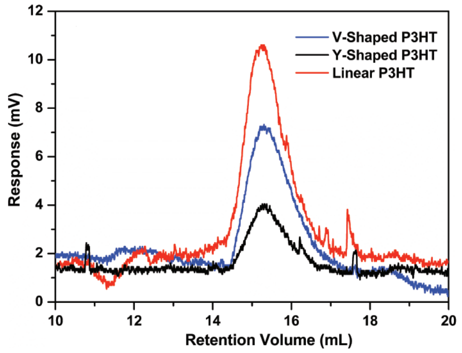


Figure 2. SEC viscometer response for the linear, V-shaped, and Y-shaped P3HT with the same absolute molecular weight.

Table 2. Comparison of the Shrinking Factor, g', as a Function of Number of Arms

	no. of arms	M_w[a] (kDa)	$[\eta]$ (dg/L)	g'
linear	1	7.9	0.149	1
V-shaped	2	8.0	0.132	0.88
Y-shaped	3	7.9	0.115	0.77

[a] The obtained molecular weight (M_w) determined by size exclusion chromatography (SEC).

To obtain further insight into the structure of the polymers, their intrinsic viscosities, $[\eta]$, were obtained from the SEC data as shown in Figure 2 and Table 2. The $[\eta]$ values of the V and Y-shaped P3HTs prepared in the present study were lower than those of the linear P3HT with the corresponding molecular weight, implying the existence of the branching architecture. The shrinking factor or contraction factor for the intrinsic viscosity of branched polymers, g', may be defined as[22]

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{1}$$

where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosity for the branched and linear polymers with the same M_w. Douglas et al. have developed an empirical relationship between g' and f, where f is the number of arms as shown in eq 2.[23]

$$g' = \left(\frac{3f-2}{f^2}\right)^{0.58} \frac{0.724 - 0.015(f-1)}{0.724} \tag{2}$$

The equation has been developed for coiled polymers in good solvents. As such, some deviation is expected for rigid polymers such as P3HT in THF. Nevertheless, using the equation, the f value was estimated to be 2.6 and 3.5 for the V- and Y-shaped polymers, respectively, confirming the shapes of the polymers synthesized, and that these polymers clearly differ from their linear counterparts.

In conclusion, we have successfully prepared V-shaped and Y-shaped rr-P3HT with controlled molecular weights and extremely narrow polydispersities by taking advantage of externally initiated Kumada catalyst-transfer polycondensation. Efforts show that the extended phenylene spacer is the key point in the preparation of multifunctional Ni-based initiator. This should pave the way for the future synthesis of well-defined complex semiconducting polymer architectures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{31}P NMR spectra of all of the Ni-complexes in the synthesis of 2-arm and 3-arm initiators and ^{1}H NMR and MALDI spectra for V-shaped and Y-shaped rr-P3HT. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: luscombe@u.washington.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the NSF (STC-MDITR DMR 0120967 (H.A.B.) and CAREER Award DMR 0747489 (M.Y.)), the AFOSR (FA9550-10-1-0430 (C.K.L.)), and as part of the Center for Interface Science: Solar Electric Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of the Basic Energy Sciences, under Award Number DE-SC0001084 (K.O.).

■ REFERENCES

(1) (a) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (c) Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109*, 5069.

(2) (a) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995. (b) Boydston, A. J.; Holcombe, T. W.; Unruh, D. A.; Fréchet, J. M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 5388. (c) Harth, E. M.; Hecht, S.; Helms, B.; Malmstrom, E. E.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926.

(3) Johnson, J. A.; Baskin, J. M.; Bertozzi, C. R.; Koberstein, J. T.; Turro, N. J. *Chem. Commun.* **2008**, 306.

(4) Meneghetti, S. P.; Lutz, P. J.; Rein, D.; Mishra, M. K.; Kobayashi, S., Eds. *Star and Hyperbranched Polymers*; Marcel Dekker: New York, 1999; p 27.

(5) (a) Li, Y, G.; Shi, P. J.; Pan, C. Y. *Macromolecules* **2004**, *37*, 5190. (b) Perny, S.; Allgaier, J.; Cho, D.; Lee, W.; Chang, T. *Macromolecules* **2001**, *34*, 5408.

(6) Altintas, O.; Vogt, A. P.; Barner-Kowollik, C.; Tunca, U. *Polym. Chem.* **2012**, *3*, 34.

(7) (a) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 153. (b) Smeets, A.; Van Den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2009**, *42*, 7638. (c) Bronstein, H.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894.

(8) (a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250. (b) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.

(9) (a) Sheina, E. E.; Liu, J. S.; Iovu, M. C.; Laird, D. W.; McCllough, R. D. *Macromolecules* **2004**, *37*, 3526. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542.

(10) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183. (c) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.

(11) Kim, H.; Lee, Y.; Hwang, S.; Choi, D.; Yang, H.; Baek, K. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 4221.

(12) (a) Wang, F.; Rauh, R. D.; Rose, T. L. *J. Am. Chem. Soc.* **1997**, *119*, 11106. (b) Bras, J.; Guillerez, S.; Pépin-Donat, B. *Chem. Mater.* **2000**, *12*, 2372.

(13) Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Tkachov, R.; Komber, H.; Lederer, A.; Stamm, M.; Sevrin, N.; Rabe, J. P.; Kiriy, A. *Macromol. Symp.* **2010**, *291–292*, 17.

(14) Hanko, R. *Angew. Chem., Int. Ed.* **1985**, *24*, 704.

(15) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155.

(16) Smeets, A.; Willot, P.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2011**, *44*, 6017.

(17) Sontag, S. K.; Marshall, N.; Locklin, J. *Chem. Commun.* **2009**, 3354.

(18) Doubina, N.; Paniagua, S. A.; Soldatova, A. V.; Jen, A. K. Y.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2011**, *44*, 512.

(19) Matmour, R.; Lebreton, A.; Tsitsilianis, C.; Kallitsis, I.; Heroguez, V.; Gnanou, Y. *Angew. Chem., Int. Ed.* **2004**, *44*, 284.

(20) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817.

(21) Verswyvel, M.; Monnaie, F.; Koeckelberghs, G. *Macromolecules* **2011**, *44*, 9489.

(22) Stockmayer, W. H.; Fixman, M. *Ann. N.Y. Acad. Sci.* **1953**, *57*, 334.

(23) Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168–4180.