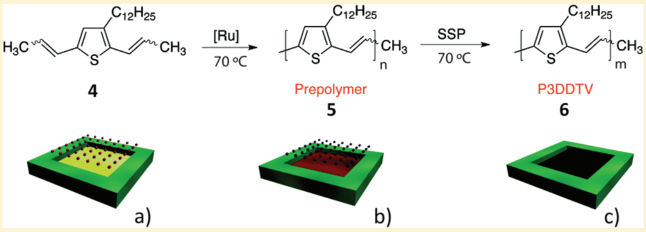
Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

Synthesis of Poly(3-dodecyl-2,5-thienylene vinylene) by Solid-State Metathesis Polycondensation

Paula A. Delgado, David Y. Liu, Zachary Kean, and Kenneth B. Wagener*

George & Butler Polymer Research Laboratory: Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

S *Supporting Information*



ABSTRACT: The synthesis of poly(thienylene vinylenes) (PTV) has been attracting attention due to the low band gaps and high electrical conductivities of these materials, making them applicable for charge storage devices, transparent conductive coatings, and electrochromic devices. Unsubstituted PTV is an intractable polymer that is usually synthesized via a processable precursor. This article reports the synthesis of conjugated polymers using solid-state metathesis conditions, demonstrating the efficiency of this methodology for preparation of a processable polymer, such a 3-dodecyl PTV (P3DDTV). The 3-dodecyl-2,5-dipropenylthiophene was synthesized and subsequently polymerized using ADMET conditions with Grubbs' second-generation catalyst. The prepolymer film (M_n = 4000 g/mol) was further polymerized in the solid state to give a final product with M_n = 14 000 g/mol (a 3.5-fold increase while in the solid state). The polymer obtained by this methodology exhibited thermal (T_g = 43 °C and T_m = 115 °C) and electrochemical (optical band gap of 1.65 eV and HOMO energy level of 5.35 eV) properties similar to those of PTV polymers synthesized by ADMET polymerization using a high boiling solvent or by cross-coupling reactions.

INTRODUCTION

The synthesis of poly(thienylene vinylene)s (PTVs) is an active research area in the manufacture of electroactive materials due to the relatively low band gaps and high conductivities achieved upon doping of PTV materials.[1−3]

Unfunctionalized PTV is an intractable polymer, and its polymerization is usually carried out by indirect synthesis of a processable prepolymer, but this route produces defects in the final polymer.[4−7] In contrast, substituted PTVs are processable and usually synthesized by the Wittig[8] or Wittig−Horner[12] methods, by cross-coupling reactions (e.g., the Stille,[9,10] Heck,[9] and Kumada[11] reactions), by oxidative polymerization,[11] or by ROMP.[13,14] However, functionalization may limit the applications of the resulting polymers.[15]

Acyclic diene metathesis (ADMET) polymerization has been used in the synthesis of conjugated polymers, including polyacetylene[16] functionalized PPVs,[17,18] polyfluorenes,[18] silylene/siloxane functionalized conjugated polymers,[19] and PTVs,[20] in bulk or in the presence of high-boiling solvents. The well-established mechanism, high selectivity for new *trans*-olefins, mild reaction conditions, tolerance for different functionalities, well-defined end-groups, absence of branching within the polymer structure, and the possibility of bulk polymerization make this methodology a useful tool for the synthesis of conjugated polymers.[21]

Solid-state polymerization (SSP) has been widely practiced in the polyester, polyamide, and polycarbonate industries. This polymerization starts in bulk at high temperature with the release of a small molecule to achieve a low molecular weight polymer (prepolymer), which is then cooled to obtain a powder or flakes. Polymerization then continues in the solid-state, at a temperature lower than the onset melting temperature, doubling its molecular weight while in the solid state.[22,23] Our group has been investigating the influence of solid-state polymerization on the molecular weights of polymers obtained by ADMET polymerization for a variety of functionalized polyolefins. Results for the polymerization of 1,9-decadiene showed an ∼20-fold increase in molecular weight using solid-state conditions.[24]

We have extended these investigations to the synthesis of a processable PTV by solid-state ADMET polymerization to characterize the polymer structure and compare its electronic properties with those made by other methodologies. This would be quite difficult for truly intractable material. Therefore, this report presents results for poly(3-dodecyl-2,5-thienylene vinylenes) (P3DDTV) to demonstrate the reliability of this process in the eventual synthesis of intractable PTV.

DISCUSSION

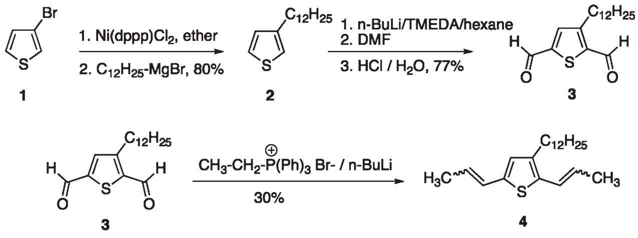
The monomer **4** was synthesized according to a literature method,[20] as shown in Scheme 1. The 3-bromothiophene was alkylated with 1-bromododecane by a Kumada coupling reaction with 80% yield.[25] Under Wittig reaction conditions,

Received: September 9, 2011
Revised: November 7, 2011
Published: November 30, 2011

3-dodecylthiophene (**2**) was then lithiated with *n*-butyllithium and formylated using DMF in the presence of tetramethylethylenediamine (TMEDA).[26] A Wittig reaction using the synthesized aldehyde and ethyltriphenylphosphonium bromide was performed to form monomer **4**, which was purified by distillation after passing through a filtration column to remove the triphenylphosphine oxide. The monomer proved to be unstable in air and light and was therefore kept cold in the dark under inert conditions.

Hillmyer et al.[20] have previously reported synthesis of an analogous monomer yielding a mixture of stereoisomers. In the present study, monomer **4** resulted in four diastereomers from the Wittig reaction having the following percentages: 32% 2*E*-5*E*, 26% 2*E*-5*Z*, 15% 2*Z*-5*Z*, and 27% 2*Z*-5*E*.[20] Referring to Figure 2, spectrum 1, the percentage of each diastereomer was evaluated from the aromatic protons (c, d, e, f). Because peak f overlaps with the olefinic protons, its integration was obtained indirectly. The total integration c + d + e + f should equal one-sixth of the total integration for the methyl end groups (multiplets b). The peak f integral was obtained by subtracting the sum of c + d + e from one-sixth of the integration for b.

Scheme 1. Synthesis of 3-Dodecyl-2,5-dipropenylthiophene Monomer 4



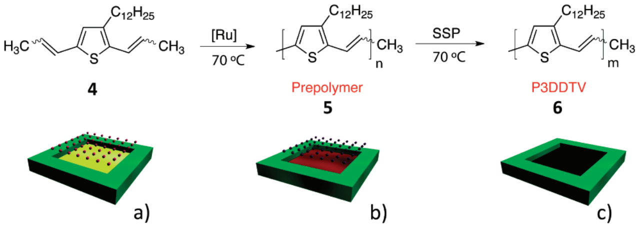


Figure 1. Solid-state polymerization of the 3-dodecyl-2,5-dipropenylthiophene monomer **4**. Figures represent the Teflon mold and the different stages of the polymerization, with the catalyst represented as brown dots. (a) Liquid monomer **4** before the polymerization. (b) Prepolymer **5** represented as a red shiny film. (c) Final polymer **6**.

Monomer **4** was then placed in a Teflon mold (Figure 1a) and subjected to ADMET polymerization conditions using Grubbs' second-generation catalyst at 70 °C for 3 h to yield a solid prepolymer **5** with a number-average molecular weight of 4000 g/mol (Figure 1b). Since step growth polymerization can continue in the solid state under the proper conditions (e.g., polyesters, nylon, etc.), the increment in the molecular weight of solid prepolymer **5** was investigated. The key to success was sprinkling of Grubbs' second-generation catalyst over prepolymer **5**, which resulted in an increase of molecular weight under vacuum at 70 °C. Catalyst was then sprinkled every 3 days (0.2 mol % dose) under an inert atmosphere to ensure the catalyst activity and a productive metathesis polymerization. Since the polymer was designed to be soluble (the dodecyl chain left in place), the molecular weight increase under solid-state conditions was determined by gel permeation chromatography (GPC, Table 1) and ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of monomer **4** is shown at the top of Figure 2, where the four possible diastereomers are observed. Terminal methyl units give peaks between 1.90 and 1.82 ppm, with methyl groups resulting from the combination of *Z*-stereoisomers at 1.90 ppm and from *E*-stereoisomers at 1.85 ppm. Because the monomer is unstable in air and light, its decomposition is evidenced by the presence of aldehyde protons between 9.0 and 9.5 ppm. After monomer polymerization via ADMET (middle spectrum in Figure 2), the progress of the polymerization was analyzed by the peak area ratios of the terminal methyl unit (b) and the methylene unit attached to the thiophene ring (a). Monomer **4** presents a ratio of 3:1, while prepolymer **5** exhibits a 1:5 ratio, confirming the diminution of terminal methyl units in the system and thereby corroborating the GPC results of a number-average molecular weight of 4000 g/mol. Aromatic protons were observed as three broad peaks, which became less shielded as the degree of polymerization increased. After the third week of polymerization under solid-state conditions (Figure 2, bottom), the methyl group units in the polymer backbone were almost undetectable (in a 1:16 ratio), confirming the increase of the molecular weight to 14 000 g/mol indicated by GPC.

Different conditions were attempted in order to obtain the highest molecular weight by this methodology. Formation of prepolymer **5** was studied at 40 and 70 °C with Grubbs' second-generation catalyst. At 40 °C, low molecular weight films were obtained (M_n = 2300 g/mol, entry 2, Table 1) after a longer period of time (10 h), while a M_n of 4000 g/mol was obtained after 3 h of polymerization at 70 °C (entry 3, Table 1). After a sprinkle of catalyst (0.2 mol %) was added to prepolymer **5**, the molecular weight was analyzed every week. During the first 2

Table 1. Molecular Weight Analysis for the Synthesis of P3DDTV

entry	conditions	catalyst addition (mol %)	M_n (kg/mol)[a]	M_w (kg/mol)[a]	M_w/M_n[a]	DP	yield[b]
1	40 °C, G1, 24 h	0.6	1.3	1.8	1.5	5	35
2	40 °C, G2, 10 h	0.6	2.3	4.4	1.9	8	80
3	70 °C, G2, 3 h	0.6	4.0	7.7	1.9	14	87
4	70 °C, G2, 2 weeks	1.2	5.3	10.8	2.1	18	86
5	70 °C, G2, 3 weeks	1.8	14.0	33.3	2.3	48	88
6	70 °C, G2, 4 weeks	2.4	14.5	31.8	2.2	50	85
7	60 °C, G2, 3 weeks-bulk	1.8	2.4	4.4	1.9	8	55

[a] Molecular weight determined using GPC analysis (PS standards) and corroborated by ^{1}H NMR spectroscopy. G1 and G2 refer to Grubbs' first- and second-generation catalyst, respectively. [b] Isolated yield after quenching with ethyl vinyl ether and precipitation from methanol.

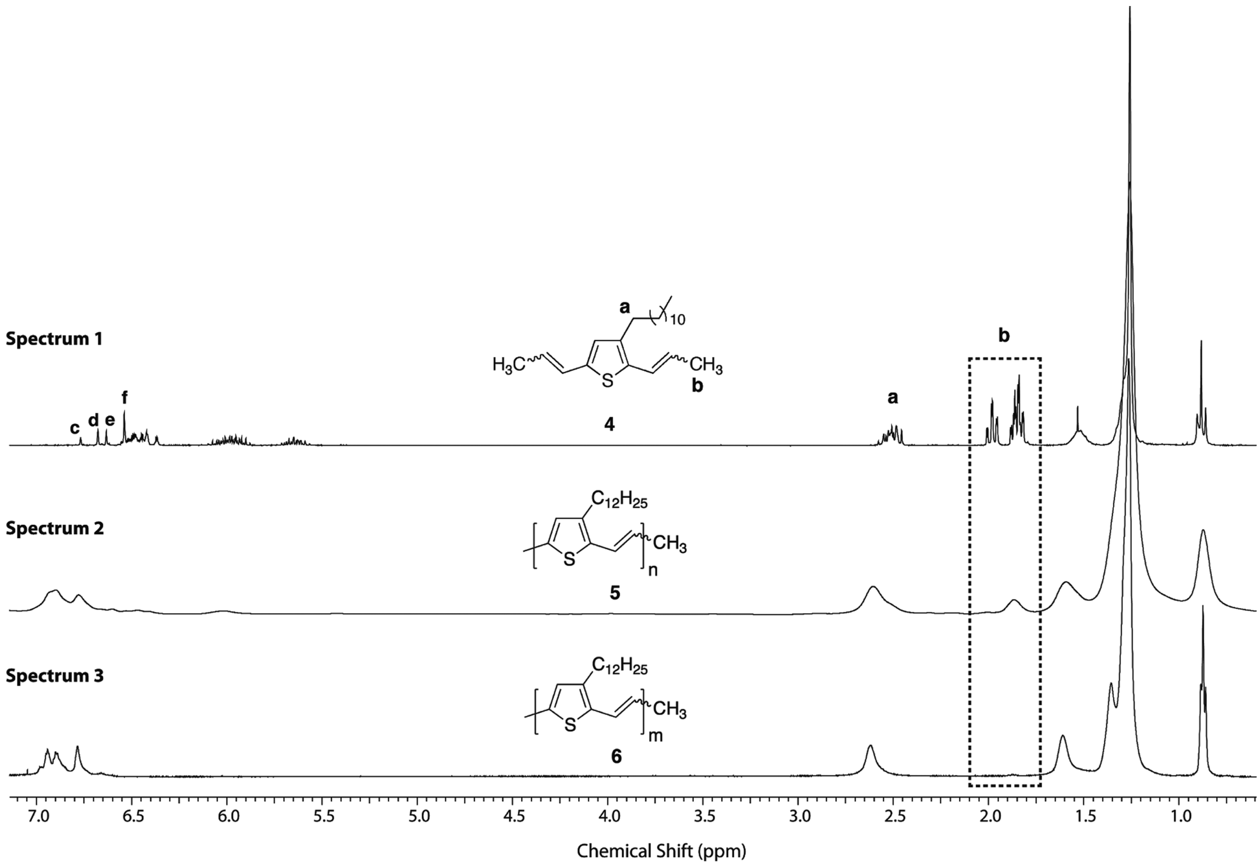


Figure 2. ^{1}H NMR of 3-dodecyl-2,5-dipropenylthiophene monomer **4** (spectrum 1), P3DDTV prepolymer **5** (spectrum 2), and P3DDTV **6** (spectrum 3).

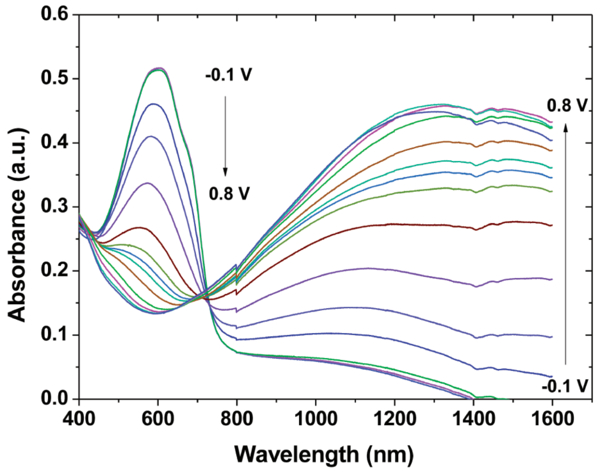


Figure 3. Spectroelectrochemistry of P3DDTV. Film was spray-cast onto ITO-coated glass from dichloromethane solutions (~1 mg mL^{-1}). Electrochemical oxidation of the film was carried out in 0.1 M TBAPF$_6$/ACN supporting electrolyte using an Ag/AgNO$_3$ reference electrode and a platinum counter electrode. The applied potential was increased in 100 mV increments from −0.1 to 0.2 V, in 25 mV steps from +0.225 to +0.35 V, and in 100 mV steps from +0.4 to +0.8 V.

weeks only a slight increase was noticed (M_n = 5300 g/mol, entry 4, Table 1). The largest increase was observed after the third week, when the molecular weight increased to 14 000 g/mol (entry 5, Table 1), in agreement with a polycondensation mechanism, where high monomer conversion is needed to obtain a high molecular weight polymer. After the third week, polymerization growth decreased substantially.

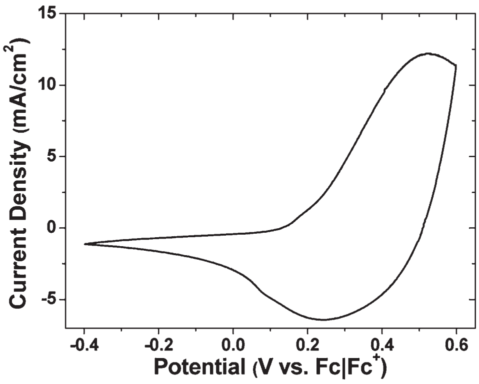


Figure 4. Cyclic voltammogram of P3DDTV drop-cast from CHCl$_3$ solution (2 mg mL^{-1}) onto a platinum button electrode (0.02 cm^2) in 0.1 M TBAPF$_6$/ACN supporting electrolyte using a scan rate of 50 mV/s.

Bulk polymerization (rather than solid-state polymerization) was also attempted in order to compare the two techniques. With this methodology, only low molecular weight polymers (M_n = 2400 g/mol) were obtained (entry 7, Table 1). This can be explained by the decreased accessibility of the propenyl units to the active catalyst species as polymers solidify into clumps. Hillmyer et al. also obtained molecular weights of 2500 g/mol using the same bulk conditions. We also tried the polymerization using Grubbs' first-generation catalyst, but only pentamers were obtained, possibly because of the catalyst's lower reactivity (entry 1, Table 1).

Hillmyer et al. studied the synthesis of 3-hexyl PTV (P3HTV) by ADMET polymerization using a variety of high-boiling solvents, catalysts, and temperatures. They concluded that P3HTV can be obtained by ADMET polymerization with a molecular weight of 10 200 g/mol using second-generation Grubbs' catalyst at 90 °C for 48 h with trichlorobenzene as a solvent.[20] On the other hand, our results show that solid-state polymerization in a Teflon mold can definitely increase the accessibility of active propenyl units without the need for solvents to obtain higher molecular weight polymers with the desired final shape.

To determine if the electronic and morphological characteristics of 3-dodecyl PTV obtained under solid-state conditions are consistent with those of the previously reported preparations, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), optical spectroscopy, and cyclic voltammetry (CV) were performed.

The TGA and DSC results showed that P3DDTV is thermally stable to 353 °C, with a glass transition temperature of 43 °C and a broad endotherm at 115 °C, which could correspond to the melting transition of the polymer. The UV−vis absorption spectra shown in Figure 3 exhibit an onset of the low-energy absorption edge (onset of the $\pi-\pi^*$ transition) for the neutral spectrum at 750 nm, which corresponds to an optical band gap of 1.65 eV. The electrochromic behavior was observed by recording the spectral changes upon oxidation of the polymer thin film. The cyclic voltammogram (Figure 4) exhibits an onset of polymer oxidation at +0.25 V vs Fc/Fc$^+$, which corresponds to a HOMO energy level of 5.35 eV. (The conversion of the HOMO energy was accomplished by adding 5.1 eV to the onset of the oxidation of the polymer, assuming that Fc/Fc$^+$ is at 5.1 eV below the vacuum level.[1,20]) These results all agree with the corresponding data for previous synthesized 3-alkyl PTVs using ADMET polymerization in high-boiling solvents[20] or by cross-coupling reactions,[1] thereby demonstrating the applicability of this methodology for the synthesis of P3DDTV.

CONCLUSIONS

There is no question that solid-state polymerization creates the analogous polymer, poly(3-dodecyl-2,5-thienylene vinylene), as was reported by Hillmyer using conventional polymerization procedures. The approach is simple: sprinkle catalyst occasionally on the solid-state polymerizing mass. The catalyst "reacts" its way into the polymer and performs ADMET chemistry, allowing the release of 2-butene (in this case). Molecular weights are similar to (actually slightly larger than) those reported by conventional techniques.

This polymerization was chosen to demonstrate the viability of solid-state methodology. The real opportunity lies in using solid-state polymerization techniques to create truly "intractable" polymers, those that cannot be made by any other direct polymerization method (for example, if the $C_{12}H_{25}$ alkyl branch were omitted in the case of thienylene vinylenes). Removing the branch would yield a "cleaner" polymer, one not diluted by solubilizing branches. Pure conjugated polymers might be made in this fashion. We are pursuing this objective now.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures with complete spectral and thermal analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wagener@chem.ufl.edu.

ACKNOWLEDGMENT

The authors thank NSF for support and the Army Research Office for their contribution in understanding catalyst activity. We also thank Materia Inc. for their help.

REFERENCES

(1) Zhang, C.; Sun, J.; Li, R.; Sun, S.; Lafalce, E.; Jiang, X. *Macromolecules* **2011**, *44*, 6389.

(2) Onoda, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Yoshino, K. *J. Chem. Phys.* **1991**, *95*, 8584.

(3) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303–1315.

(4) Tsuie, B.; Wagener, K. B.; Reynolds, J. R. *Polym. Prepr.* **1999**, *40*, 790.

(5) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys., Part 2* **1983**, *22*, 412.

(6) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys., Part 2* **1983**, *22*, 567.

(7) Kreja, L.; Kurzawa, M.; Kurzawa, J. *Macromol. Chem. Phys.* **1997**, *198*, 643.

(8) Kossmehl, G.; Haertel, M.; Manecke, G. *Makromol. Chem.* **1970**, *131*, 15.

(9) Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214.

(10) Galarini, R.; Musco, A.; Pontellini, R.; Bolognesi, A.; Destri, S.; Catellani, M.; Mascherpa, M.; Zhuo, G. *J. Chem. Soc., Chem. Commun.* **1991**, *6*, 364.

(11) Blohm, M. L.; Pickett, J. E.; Van Dort, P. C. *Macromolecules* **1993**, *26*, 2704.

(12) Jestin, I.; Frere, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150.

(13) Wagaman, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *30*, 3978.

(14) Bazan, G. C.; Miao, Y.; Renak, M. L.; Sun, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 2618.

(15) Frechet, J. M. J. *Prog. Polym. Sci.* **2005**, *30*, 844.

(16) Tao, D.; Wagener, K. B. *Macromolecules* **1994**, *27*, 1281.

(17) Nomura, K.; Miyamoto, Y.; Morimoto, H.; Geerts, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6166.

(18) Weychardt, H.; Plenio, H. *Organometallics* **2008**, *27*, 1479.

(19) Mukherjee, N.; Peetz, R. M. *Macromolecules* **2008**, *41*, 6677.

(20) Quin, Y.; Hillmyer, M. A. *Macromolecules* **2009**, *42*, 6429.

(21) Hatice, M.; Lucas, M. d. E.; Meier, M. A. R. *Chem. Soc. Rev* **2011**, *40*, 1404.

(22) Vouyiouka, S. N.; Karakatsani, E. K.; Papaspyrides, C. D. *Prog. Polym. Sci.* **2005**, *30*, 10.

(23) Oakley, G. W.; Wagener, K. B. *Macromol. Chem. Phys.* **2004**, 206.

(24) Oakley, G. W.; Lehman, S. E.; Smith, J. A.; Gerven, P. V.; Wagener, K. B. *Macromolecules* **2003**, *36*, 539.

(25) Jian, P.; Jing, N.; Xing-Hua, Z.; Xiao-Yu, C.; Yee-Hing, L. *J. Org. Chem.* **2002**, *67*, 4924.

(26) Feringa, B. L.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, *4*, 316.