

Photoinduced Polysiloxane Architectures from Spirosiloxane Precursors via Intramolecular Hydrosilylation

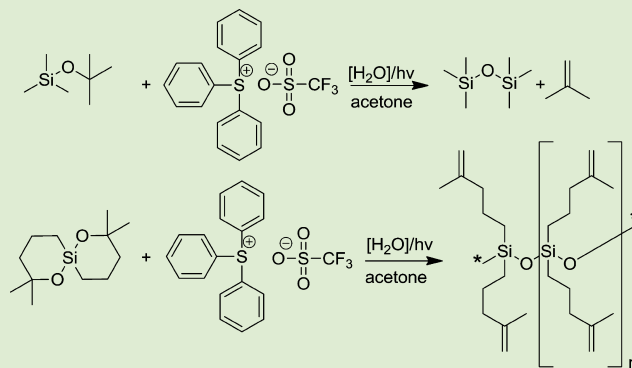
Christian A. Anger,[†] Konrad Hindelang,[†] Tobias Helbich,[†] Tobias Halbach,[‡] Jürgen Stohrer,[‡] and Bernhard Rieger^{*,†}

[†]Institut für Siliciumchemie, Technische Universität München, Lichtenbergstraße 4, Garching bei München 85747, Germany

[‡]Consortium für Elektrochemische Industrie der Wacker Chemie AG, Zielstattstraße 20, München 81379, Germany

S Supporting Information

ABSTRACT: In this letter a method is described to synthesize new polysiloxane architectures by photoacid catalysis. An oxasilaspirocycle is designed that is able to undergo a photoacid generator catalyzed ring-opening reaction leading to either a homopolymer or to copolymers with hydroxyl-terminated polydimethylsiloxane. These polymers feature a defined amount of double bonds in the backbone, which is controlled by the ratio of oxasilaspirocycle to the comonomer. The former was prepared by tris(pentafluorophenyl)borane-catalyzed intramolecular hydrosilylation of a dialkenyloxysilane with an appropriate structural motif. The UV-initiated polymerization was characterized via in situ IR spectroscopic studies to determine the rate of reaction.



Polysiloxanes are of great interest because of their advantageous properties, such as thermal stability, electrical resistance, or hydrophobicity.^{1,2} These are often produced by ring-opening polymerization of cyclic monomers, the most well-known example being the polymerization of hexamethylcyclotrisiloxane (D3), which is mainly catalyzed by trifluoromethanesulfonic acid.³ In addition, studies have dealt with the polymerization and equilibration of octamethylcyclotetrasiloxane (D4).^{4–7} Most cationic polymerizations of this type are catalyzed by strong protic acids, such as concentrated sulfuric- and trifluoromethanesulfonic acid, as well as by electron-deficient organosilicon reagents.⁸ The functionalization of polysiloxanes in most cases is based on modification of the cyclic monomers. Functional side groups along the polymer chain can have a significant influence on the physical properties of the resulting polymers and act as handles for further synthetic manipulation.² Among these functionalities, vinylic side groups offer the possibility for further cross-linking reactions to create defined polymer networks.⁹ Here we describe an efficient method to introduce the olefinic side groups into polysiloxane structures by use of a photoacid generator (PAG) catalyzed ring-opening reaction of a novel oxasilaspirocycle.

The latter were accessed by tris(pentafluorophenyl)borane-catalyzed double intramolecular hydrosilylation of bis(2-methylpent-4-en-2-yl)oxy)silane. Although oxasilacycles and oxasilaspirocycles are commonly prepared by intramolecular hydrosilylation via Karstedt's or similar catalyst, such an approach could not be applied in our system because of the poor product selectivity.^{10–12}

By contrast, tris(pentafluorophenyl)borane is widely used as a catalyst in organic reactions such as allyl stannation of aldehydes¹³ and allylation¹⁴/silylation¹⁵ of alcohols. Hydro-silylation of olefinic compounds and benzophenone^{16,17} is also promoted by this catalyst, however, its use for intramolecular hydrosilylation reactions is extremely scarce. To the best of our knowledge there is only one report that describes the regioselective intramolecular hydrosilylation of oxasilanes with tris(pentafluorophenyl)borane as a catalyst.¹⁸ Mechanistic studies by Ganachaud et al. show this reaction proceeds through activation of the Si–H bond with Lewis acids,¹⁹ whereas the nature of subsequent hydrosilylation was described by Gevorgyan and co-workers.²⁰

Our spirocyclic structure offers the advantage of stability toward moisture and air and circumvents the problem of volatile organic side products.

RESULTS AND DISCUSSION

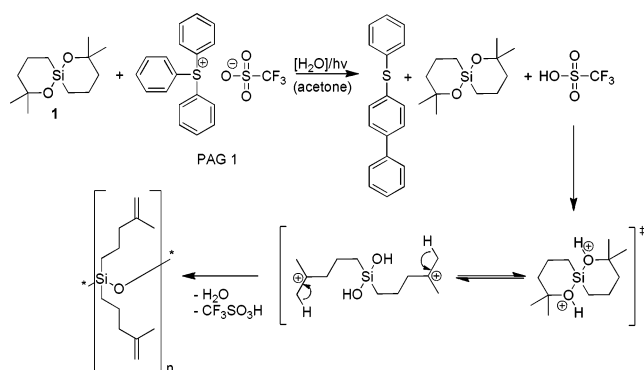
Synthetic route to 2,2,8,8-tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane: From a retrosynthetic perspective, the introduction of olefinic groups into a polymeric backbone can be achieved by the acid-catalyzed ring-opening reaction of spirocycles, as shown in Scheme 1, assuming selective and quantitative cleavage of the C–O bond. To optimize the reaction conditions, a series of elimination test experiments with isopropoxytrimethyl-, *tert*-butoxytrimethyl-, and ethoxy-

Received: August 8, 2012

Accepted: September 12, 2012

Published: September 28, 2012

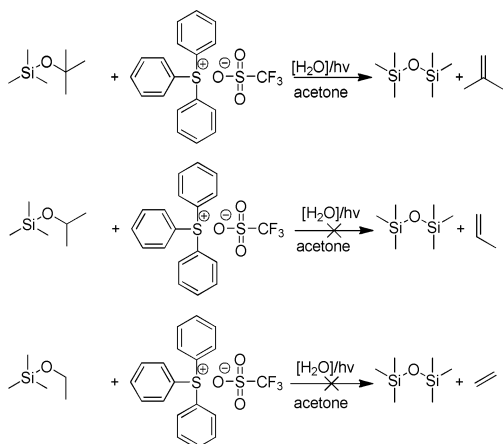
Scheme 1. Photoacid Generator Catalyzed Polymerization of **1**^a



^a*End groups are presumably hydroxyl groups.

trimethylsilane as model substrates were performed (Scheme 2). Reactions with the *tert*-butoxy substrate were shown to

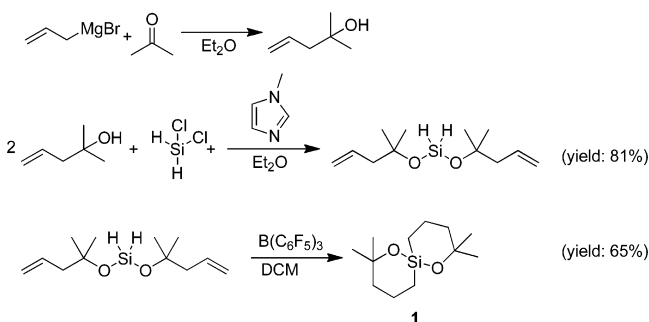
Scheme 2. Elimination Test Reactions



provide the best results as the elimination proceeds in quantitative yield, with complete conversion to hexamethyldisiloxane observed in 2 h. In the case of trimethylisopropoxy- and trimethylethoxysilane, quantitative conversion could not be achieved. In relation to these results, the synthesis route for 2,2,8,8-tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane **1** was designed.

Scheme 3 outlines the formation of **1**. The three-step synthesis route achieves moderate to good yields and high purity after distillation in each step. The intermediate bis((2-

Scheme 3. Three Step Synthesis of **1**

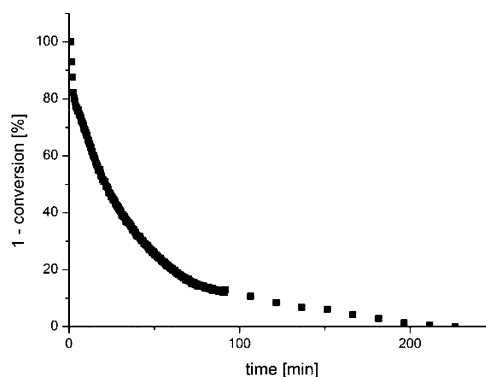


methylpent-4-en-2-yl)oxy)silane is formed via a condensation reaction of dichlorosilane with 2 equiv of 2-methylpent-4-en-2-ol. This reaction proceeds smoothly with the addition of equimolar quantities of *N*-methylimidazole to absorb the HCl byproduct. It is essential, as free HCl in the reaction mixture would otherwise lead to bond cleavage of the internal isobutoxy fragment. The formation of **1** takes place under carefully controlled conditions to avoid the formation of linear polymer side products. A precise concentration of 0.04 mol/L of bis((2-methylpent-4-en-2-yl)oxy)silane in dichloromethane (DCM) and a long reaction time (ca. 12 h) at room temperature are essential to selectively afford the spirocycle. The concentration of the trispentafluorophenylborane catalyst also plays a key role: if the catalyst concentration is allowed to rise above 2 mol %, the formation of oligomers is observed. Interestingly, the use of other alternative catalysts, such as Speier^{21,22} or Pd complexes,²³ does not afford the target spirocycle, whereas the use of Karstedt's catalyst results in the formation of thermodynamically stable five-membered ring structures, which are inert under the conditions of photoacid catalyzed polymerization experiments.

Photopolymerization of 2,2,8,8-tetramethyl-1,7-dioxa-6-silaspiro[5.5]undecane: A variety of PAG-catalyzed polymerizations have been described in the literature.^{24,25} For example, those photoacid generators are used in photoinduced sol-gel polymerizations, photoinduced cross-linking of polymers, and photoinduced transformation of functional groups in polymer chains.^{26–30} In our process, we use a light-induced formation of acids to selectively cleave the carbon–oxygen bond of the oxasilaspirocycle, as shown in Scheme 1. Triphenylsulfonium triflate (PAG 1) and diphenyliodonium triflate (PAG 2) were used as catalysts.

In the time-resolved study, the cleavage of the O–C bond of **1** is followed by in situ IR spectroscopy. The reaction mixture is constantly irradiated with UV light between 200 and 300 nm in the presence of a small quantity of acetone, which is a suitable solvent for the PAG 2. The photoinduced polymerization of **1** with PAG 2 as a catalyst shows a conversion of 90% in 2 h (Chart 1) and quantitative conversion after 3 h. The fast initial

Chart 1. Time-Resolved Study of the Polymerization of **1** Using the Absorption at 1014 cm⁻¹

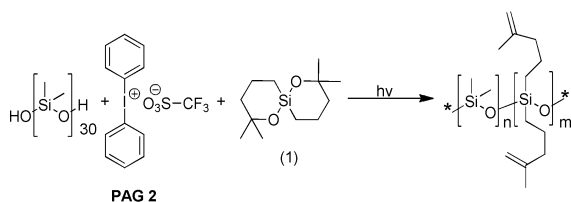


reaction rate slows after approximately one hour reaction time. This behavior is consistent with a rapid generation of the acid which is followed by a subsequent cleavage of the oxygen–carbon bond, correlating to a first order kinetic process (Supporting Information, SI Figure 1). The polymer is initially obtained as a highly viscous colorless substance. After drying,

the material is insoluble in organic solvents, presumably due to an acid-catalyzed cationic cross-linking of the polymer double bonds. The presence of a catalytic quantity of water in the mixture was found to be necessary for the polymerization due to the stability of the intermediate tertiary cation and the favored back reaction to **1** (Scheme 1). This catalytic quantity of water also promotes the condensation reaction to the desired polysiloxane, which bears two vinylic groups on each silicon atom. No polymerization activity was observed, neither by addition of water in the absence of a PAG nor by addition of a PAG in the absence of light.

Copolymerization of 2,2,8,8-tetramethyl-1,7-dioxo-6-silaspiro[5.5]undecane and hydroxyl-terminated poly(dimethylsiloxane): In these copolymerization experiments the obtained polymeric structures, with respect to viscosity and material properties, can be tuned by variation of the ratio of **1** to hydroxyl-terminated poly(dimethylsiloxane) (**OH-PDMS**; Scheme 4). The photoacid generator **PAG 1** and **PAG 2** were

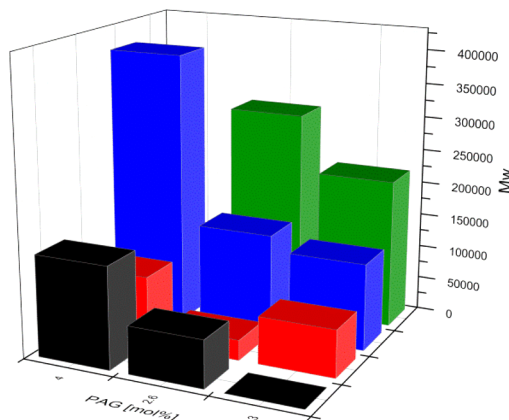
Scheme 4. Photoacid Catalyzed Copolymerization of OH-PDMS and **1^a**



^a*End groups are presumably hydroxyl groups.

tested as catalysts with a constant amount of **1** (5 mol %) and **OH-PDMS** (95 mol %) as a comonomer. It is noteworthy that the addition of water in these copolymerizations was not necessary. The polymerization and the condensation reactions start immediately by irradiation (Chart 2). The molecular masses of the resulting soluble polysiloxanes was determined by gel permeation chromatography (GPC) relative to a polystyrene standard in tetrahydrofuran. The M_w of produced polymers were near-identical and independent of the PAG used.

Chart 2. Polymerization of **1 with OH-PDMS^a**



^aPAG **1** = triphenylsulfonium triflate; PAG **2** = diphenyliodonium triflate; black bar = reference experiment PAG **2**; red bar = reference experiment PAG **1**; blue bar = copolymerization PAG **2**; green bar = copolymerization PAG **1**.

The first two rows of Chart 2 show reference experiments of the photoinduced homopolymerization of **OH-PDMS** with **PAG 1** and **PAG 2**. In both cases, a moderate increase in the obtained molecular mass is observed, with a maximum of 150,000 g/mol (PDI = 2.4). This increase can be explained by the acid-catalyzed autocondensation of the **OH-PDMS**. All GPC measurements were taken after 2 h irradiation time, as the polycondensation cannot be terminated at specific points, leading to potential inconsistencies in the data. At low concentrations of **PAG 2** (1.31 mol %), no reaction in the reference experiments was observed.

Copolymerization of **OH-PDMS** with **1** resulted in polymers of remarkably higher molecular mass up to 400,000 g/mol (PDI = 3.5) in comparison to the described reference experiments. The molecular weight of the polymer was found to be strongly dependent on the amount of added **PAG** catalyst. The properties of the obtained polymer can be related to the amount of catalyst in the copolymerization mixture. In the reaction with the highest concentration of **PAG 1** with 5 mol % **1**, an insoluble colorless polysiloxane was obtained which could not be analyzed by GPC. ¹H NMR spectroscopy performed on a 500 MHz NMR spectrometer of all soluble polymers did not assist in their structural determination as the vinylic groups were not resolved, due to the low overall concentration of double bonds in the polysiloxane. (¹H NMR spectra and GPC spectra exemplary shown in the Supporting Information; S6/S11) With higher concentrations of **1** solubility problems are occurring due to before described cationic cross-linking side reactions. (Supporting Information, S5: M_w , PDI and ratios)

EXPERIMENTAL SECTION

All chemicals were purchased from commercial sources and were used as received. Diethyl ether and dichloromethane were dried and purified directly before their usage by a solvent purification system (MBRAUN SPS-800). 1-Methylimidazole was dried by distillation over sodium and stored over molecular sieves (3 Å). Infrared spectra were recorded on a ReactIR 45 m from Mettler-Toledo and the irradiation was executed with a MAX-302 of ASAHI SPECTRA. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 UltraShield (500 MHz) and an Avance 300 (300 MHz) spectrometer. They were recorded in ppm and the solvent was used as an internal standard (CDCl₃ at 7.24 ppm for ¹H and at 77.0 ppm for ¹³C(¹H)). The coupling constants *J* are given in Hertz (Hz) and the multiplicities were abbreviated as follows: *s* = singlet, *d* = doublet, *m* = multiplet. Mass spectra were recorded on a Thermo Scientific DFS (electron impact, EI, 70 eV). 2-Methylpent-4-en-2-ol and tris-(pentafluorophenyl)borane were prepared according to literature methods.

Bis(2-methylpent-4-en-2-yl)oxy)silane. 2-methylpent-4-en-2-ol was synthesized according to literature preparation.³¹ In a baked out Schlenk three-necked flask fitted a dropping funnel, reflux condenser and an Ar inlet about one-quarter of the previously prepared mixture of 31.9 g (389 mmol, 2 equiv) 1-methylimidazole and 38.9 g (389 mmol, 2 equiv) 2-methylpent-4-en-2-ol in 50 mL diethyl ether were added from the dropping funnel to 250 mL diethyl ether. The 19.6 g (194 mmol, 1 equiv) dichlorosilane which precondensed into a Schlenk tube at -78 °C was allowed to slowly diffuse into the stirred reaction mixture at -78 °C. Meanwhile the residual mixture from the dropping funnel was slowly added to the reaction mixture which is then stirred for a further 10 h at room temperature. The resulting methylimidazole hydrochloride was then filtrated through a Schlenk frit and the solvent removed under reduced pressure (200 mbar). After fractionated condensation in vacuum (0.3 mbar, 60 °C), 35.7 g (156 mmol, 81%) bis((2-methylpent-4-en-2-yl)oxy)silane were obtained as a colorless liquid. ¹H NMR (300 MHz, CDCl₃, 300 K): δ [ppm] =

5.97–5.76 (m, 2H), 5.14–5.00 (m, 4H), 4.67 (s, 2H), 2.29 (d, $^3J = 7.3$ Hz, 2H), 1.3 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3 , 300 K): δ [ppm] = 134.8 (s), 117.7 (s), 75.5 (s), 49.0 (s), 29.1 (s). MS (EI), m/z (%): 213.16 (13) [(M – CH_3) $^+$], 187.13 (100), 129.08 (87). [(M – $\text{C}_6\text{H}_{11}\text{O}$) $^+$]. HRMS ($\text{C}_{11}\text{H}_{21}\text{O}_2$ ^{28}Si = [(M – CH_3) $^+$): calcd, 213.1311; found, 213.1305.

2,2,8,8-Tetramethyl-1,7-dioxo-6-silaspiro[5.5]undecane 1. Trispentafluorophenylborane was synthesized according to a literature procedure.³² To 23.8 g (104 mmol, 1 equiv) of the bis((2-methylpent-4-en-2-yl)oxy)silane in 400 mL of dry dichloromethane, 1.06 g (2.07 mmol, 2 mol %) $\text{B}(\text{C}_6\text{F}_5)_3$ was added with constant stirring at room temperature. The reaction mixture was then stirred for a further 12 h. The solvent was then removed under reduced pressure (200 mbar). Purification of the liquid residue by fractionized condensation (0.3 mbar, 60 °C) yielded 15.45 g (67.6 mmol, 65%) of the spiro compound as a colorless liquid. ^1H NMR (300 MHz, CDCl_3 , 300 K): 1.91–1.64 (m, 4H), 1.60–1.38 (m, 4H), 1.29 (s, 6H), 1.20 (s, 6H), 0.68–0.42 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3 , 300 K): 74.4 (s), 40.9 (s), 31.7 (s), 30.2 (s), 17.8 (s), 12.1 (s). ^{29}Si NMR (99 MHz, CDCl_3 , 300 K): 14.41 (s). MS (EI), m/z (%): 228 (7) [M^+], 213 (100), [(M – CH_3) $^+$], 185 (21), 129 (26), 131 (27), 129 (39), 127 (34), 103 (33), 99 (50). HRMS ($\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$): calcd, 228.1546; found, 228.1542.

Photoacid Activated Polymerization. In a two-necked quartz Schlenk tube, a solution of 75.3 mg (0.18 mmol, 2 mol %) of the photoacid generator **PAG 2** and 0.79 mL (0.044 mmol, 0.5 mol %) of water in 5 mL of dry acetone was prepared and used for the background measurement of the IR spectrometer. The recording was then started, and after 1 min, 2.00 g (8.75 mmol, 1 equiv) of 2,2,8,8-tetramethyl-1,7-dioxo-6-silaspiro[5.5]undecane was added to the solution. The light source was activated and the reaction mixture was irradiated for 2 h.

Copolymerization Experiments. All copolymerizations were performed in the same way: To a stirred sample of OH-terminated polydimethylsiloxane **1** in a two-necked quartz Schlenk tube was added a solution of **PAG 1** or **PAG 2** in acetone via a syringe. The mixture was then irradiated (200–300 nm) for 2 h, after which the reaction was immediately assayed by GPC using THF as a solvent. The parameters varied within individual reactions are described in the Supporting Information (SI; Tables 1 and 2).

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed description of experimental procedures as well as NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rieger@tum.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding from Consortium für Elektrochemische Industrie der Wacker Chemie AG is acknowledged. Dr. S. Vagin and Dr. C. Anderson are thanked for their help with the preparation of this manuscript.

■ REFERENCES

- (1) *Silicon in Organic, Organometallic and Polymer Chemistry*; Brook, M. A., Ed.; John Wiley & Sons, Inc.: New York, 2000.
- (2) Kern, W. *Angew. Chem., Int. Ed. Eng.* **1971**, *10*, 360.
- (3) Qayouh, H.; Lahcini, M.; Six, J.-L.; Kricheldorf, H. R. *J. Appl. Polym. Sci.* **2012**, *124*, 4114.
- (4) Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 2294.
- (5) Patnode, W.; Wilcock, D. F. *J. Am. Chem. Soc.* **1946**, *68*, 358.

(6) Lebrun, J.-J.; Sauvet, G.; Sigwalt, P. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 757.

(7) Toskas, G.; Besztercey, G.; Moreau, M.; Masure, M.; Sigwalt, P. *Macromol. Chem. Phys.* **1995**, *196*, 2715.

(8) Wang, Q.; Zhang, H.; Prakash, G. K. S.; Hogen-Esch, T. E.; Olah, G. A. *Macromolecules* **1996**, *29*, 6691.

(9) Abdellah, L.; Boutevin, B.; Caporiccio, G.; Guida-Pietrasanta, F. *Eur. Polym. J.* **2002**, *38*, 1515.

(10) Young, D. G. J.; Hale, M. R.; Hoveyda, A. H. *Tetrahedron Lett.* **1996**, *37*, 827.

(11) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693.

(12) Lewis, L. N.; Sy, K. G.; Bryant, G. L.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

(13) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295.

(14) Rubin, M.; Gevorgyan, V. *Org. Lett.* **2001**, *3*, 2705.

(15) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.

(16) Harrison, D. J.; McDonald, R.; Rosenberg, L. *Organometallics* **2005**, *24*, 1398.

(17) Rendler, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997.

(18) Shchepin, R.; Xu, C.; Dussault, P. *Org. Lett.* **2010**, *12*, 4772.

(19) Pouget, E.; Holgado-Garcia, E.; Vasilenko, I. V.; Kostjuk, S. V.; Campagne, J. M.; Ganachaud, F. *Macromol. Rapid Commun.* **2009**, *30*, 1128.

(20) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.

(21) Denmark, S. E.; Pan, W. *Org. Lett.* **2000**, *3*, 61.

(22) Li, F.; Roush, W. R. *Org. Lett.* **2009**, *11*, 2932.

(23) Widenhoefer, R. A.; Krzyzanowska, B.; Webb-Wood, G. *Organometallics* **1998**, *17*, 5124.

(24) Shirai, M.; Tsunooka, M. *Prog. Polym. Sci.* **1996**, *21*, 1.

(25) Shirai, M.; Sumino, T.; Tsunooka, M. *Eur. Polym. J.* **1993**, *29*, 831.

(26) Chemtob, A.; Ni, L.; Croutxé-Barghorn, C.; Demarest, A.; Brendlé, J.; Vidal, L.; Rigolet, S. *Langmuir* **2011**, *27*, 12621.

(27) Chemtob, A.; Peter, M.; Belon, C.; Dietlin, C.; Croutxé-Barghorn, C.; Vidal, L.; Rigolet, S. *J. Mater. Chem.* **2010**, *20*, 9104.

(28) Croutxé-Barghorn, C.; De Brito, M.; Allonas, X.; Belon, C.; Chemtob, A.; Ni, L.; Mureau, N.; De Paz, H.; El Fouhaili, B.; Dietlin, C. *J. Photopolym. Sci. Technol.* **2012**, *25*, 131.

(29) De Paz, H.; Chemtob, A.; Croutxé-Barghorn, C.; Le Nouen, D.; Rigolet, S. *J. Phys. Chem. B* **2012**, *116*, 5260.

(30) Shirai, M.; Tsunooka, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2483.

(31) Taillier, C.; Hameury, T.; Bellosta, V.; Cossy, J. *Tetrahedron* **2007**, *63*, 4472.

(32) Lehmann, M.; Schulz, A.; Villinger, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 7444.