

# Surface-Initiated Group Transfer Polymerization Mediated by Rare Earth Metal Catalysts

Ning Zhang,<sup>†</sup> Stephan Salzinger,<sup>†</sup> Frank Deubel,<sup>†</sup> Rainer Jordan,<sup>†,‡</sup> and Bernhard Rieger<sup>\*,†</sup>

<sup>†</sup>WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching bei München, Germany

<sup>‡</sup>Professur für Makromolekulare Chemie, Department Chemie, Technische Universität Dresden, Zellescher Weg 19, 01069 Dresden, Germany

**S** Supporting Information

**ABSTRACT:** We present the first example of a surface-initiated group transfer polymerization (SI-GTP) mediated by rare earth metal catalysts for polymer brush synthesis. The experimentally facile method allows rapid grafting of polymer brushes with a thickness of >150 nm in <5 min at room temperature. We show the preparation of common poly(methacrylate) brushes and demonstrate that SI-GTP is a versatile route for the preparation of novel polymer brushes. The method gives access to both thermoresponsive and proton-conducting brush layers.

Rare-earth-metal-mediated group transfer polymerization (GTP) was first reported by Yasuda et al. in 1992.<sup>1</sup> In view of the polymerization mechanism, it is also referred to as coordinative-anionic addition polymerization.<sup>2</sup> Over the past decades, intensive research has been carried out to optimize the reaction conditions and initiator efficiency and to broaden its use for a variety of monomers, e.g. different (meth)acrylates and (meth)acrylamides.<sup>2,3</sup> Due to its highly living character, rare earth (RE) metal-mediated GTP gives strictly linear polymers with very low dispersity (characterically <1.10), exhibits a linear increase in average molar mass upon monomer conversion, and allows the synthesis of block copolymers as well as the introduction of chain end functionalities.<sup>2,4</sup> Coordination of the growing chain end at the catalyst suppresses side reactions and allows stereospecific polymerization as well as activity optimization by variation of both the metal center and the catalyst ligand sphere.<sup>2,5</sup> RE metal-mediated GTP is applicable to common acrylic monomers as well as to several functional monomers of interest, i.e. dialkyl vinylphosphonates (DAVP) and 2-vinylpyridine.<sup>6,7,37,38</sup> Such monomers are of specific interest for the modification of solids for biomedical applications.

Until now, almost all polymerization types have been transferred to surface-initiated (SI) polymerizations to prepare dense polymer brushes. This spans tolerant free radical polymerization yielding less defined brushes to nontolerant but highly defined living cationic and anionic polymerizations.<sup>8–21</sup> Controlled radical polymerizations have been especially intensively studied in regard to their implementation for surface modification, as they are relatively tolerant toward impurities but allow the synthesis of quite defined polymer brushes.<sup>22</sup> For instance, surface-initiated atom transfer radical

polymerization (SI-ATRP) gained great interest, as it can be performed even at room temperature (rt) in aqueous solution.<sup>23</sup> However, to our knowledge, SI-GTP mediated by RE metals has not been employed yet, although it combines the advantages of both living ionic and coordinative polymerizations and would give access to several new polymer brush coatings that cannot be realized by current techniques. The most intriguing are poly(vinylphosphonate)s and other phosphorus-containing polymers. As coatings, they have attracted interest due to their halogen-free flame retardation and proton-conducting properties.<sup>24–27</sup> Because of the low toxicity,<sup>28</sup> much attention has recently been drawn to their use in biomedical applications such as nonfouling coatings,<sup>29,30</sup> tissue engineering,<sup>31</sup> drug delivery systems,<sup>32</sup> and cell proliferation.<sup>33</sup> However, only RE metal-mediated GTP allows the well-controlled polymerization of vinylphosphonates, as radical and classical anionic approaches result in low yields of polymer with unsatisfying degrees of polymerization.<sup>34–36</sup>

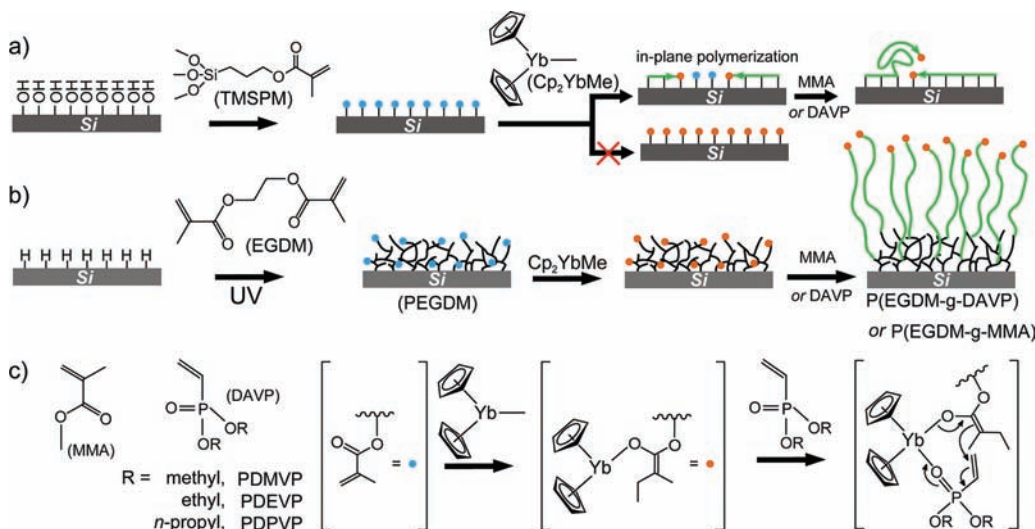
Here, we present the first example of SI-GTP mediated by RE metal catalysts. SI-GTP is applicable to the polymerization of common acrylic monomers such as methyl methacrylate (MMA) as well as special functional monomers such as DAVP. It is experimentally facile and can be performed at rt, and polymer layer thicknesses up to 300 nm can be achieved within a few minutes at rt.

We recently reported on the synthesis of PMMA–poly(diethyl vinylphosphonate) (PDEV) block copolymers using simple ytterbium complexes through a living GTP mechanism.<sup>37</sup> For the translation of GTP to a defined SI-GTP, we first followed the established strategy and employed self-assembled monolayers (SAMs) of 3-(trimethoxysilyl)propyl methacrylate (TMSPM) on oxidized silicon (Scheme 1a). Upon addition of bis(cyclopentadienyl)methyl ytterbium (Cp<sub>2</sub>YbMe), a highly active enolate initiating species is formed (Scheme 1) for SI-GTP with added vinyl monomers. The reaction mechanism for GTP of (meth)acrylates and DAVP has been previously outlined in detail.<sup>1,2,38</sup> In brief, the surface-bound enolate is transferred to a monomer coordinated at the Yb catalyst, and successive chain growth occurs via repeated conjugate addition over an eight-membered-ring intermediate (Scheme 1c).

Received: March 21, 2012

Published: April 12, 2012

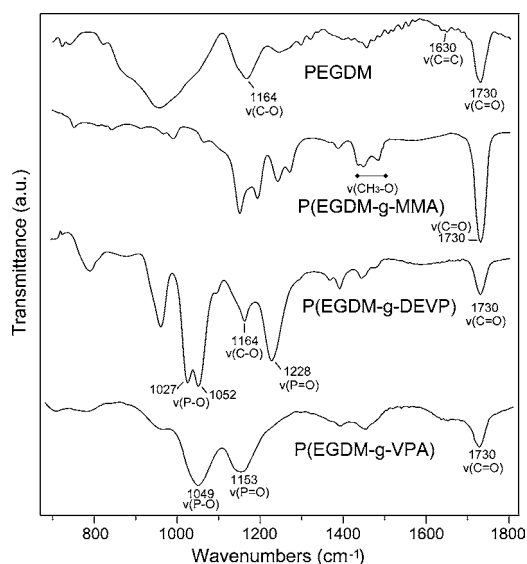
**Scheme 1.** Preparation of Precoating Layer, Ytterbocene Catalyst Immobilization, and Subsequent SI-GTP of MMA or DAVP from (a) a TMSPM Monolayer and (b) a PEGDM Film on Silicon Wafer; (c) Molecular Structure of MMA and DAVP, and SI-GTP Reaction Mechanism for Initiation and Chain Growth



However, after attempted SI-GTP with MMA or DAVP and thorough removal of physisorbed polymer and remaining catalyst residues using different solvents under ultrasonication, AFM measurements reveal a relatively rough and inhomogeneous surface topography, indicating insufficient coverage of the substrate by the polymeric layer (Supporting Information). The only partial SI-GTP may be due to the fact that the dense and rigid SAM initiator limits the accessibility of the terminal methacrylate moieties for the bulky  $\text{Cp}_2\text{YbMe}$ . Moreover, the close packing facilitates an in-plane topopolymerization via GTP of the surface-bound methacrylate functionalities in the organized monolayer (Scheme 1a). Hence, the consumption of surface methacrylate moieties does not allow the formation of a reactive monolayer of the enolate initiating species.

To cope with this problem, the precoating layer should offer high surface coverage of the catalyst binding sites, which are prone to in-plane topopolymerization. This can be realized by a thin cross-linked polymer precoating with embedded but isolated (meth)acrylate units. A facile and direct approach for the synthesis of such binding layers is the self-initiated photografting and photopolymerization (SI-PGP) of, e.g., ethylene glycol dimethacrylate (EGDM) on hydrogen-terminated silicon.

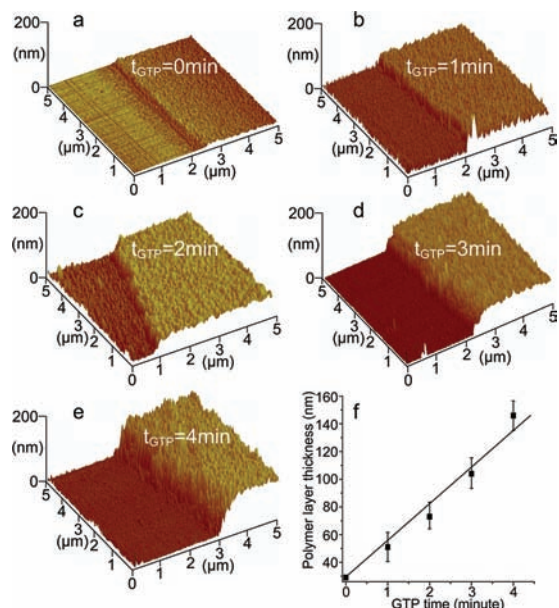
First, H-terminated silicon substrates were prepared by means of oxide layer stripping using hydrofluoric acid and subsequently irradiated by UV light [spectral distribution between 300 and 400 nm ( $\lambda_{\text{max}} = 350$  nm) in bulk EGDM]. UV irradiation of  $\sim 350$  nm without oxygen and solvents results in direct grafting of unsaturated compounds by formation of stable Si–C bonds via photoactivated hydrosilylation.<sup>39–42</sup> Moreover, the (meth)acrylate units can also undergo polymerization via the SI-PGP mechanism via H-abstraction from the Si–H surface as well as from C–H moieties of already grafted EGDM.<sup>43–48</sup> Because of the low bond dissociation energy of Si–H,<sup>49</sup> direct grafting is likely by both mechanisms, and recent findings by some of us indicate the occurrence of both grafting reaction mechanisms.<sup>44</sup> In any case, surface dangling bonds are created and responsible for efficient surface grafting of EGDM, resulting in a cross-linked PEGDM network film grafted to silicon via Si–C bonds of superior thermal and chemical



**Figure 1.** IR spectra of poly(ethylene glycol dimethacrylate) [PEGDM], poly(ethylene glycol dimethacrylate-graft-diethyl vinylphosphonate) [P(EGDM-g-DEVVP)], poly(ethylene glycol dimethacrylate-graft-vinylphosphonic acid) [P(EGDM-g-VPA)], and poly(ethylene glycol dimethacrylate-graft-methyl methacrylate) [P(EGDM-g-MMA)] brushes on a silicon wafer.

stability.<sup>50</sup> To our knowledge, this is also the first example of direct photografting of polymers onto H-terminated silicon.

After UV irradiation, the substrate was rigorously cleaned (ultrasonication in several solvents with different polarities) to ensure that only chemically grafted polymer remains on the substrate. The successful grafting of PEGDM was confirmed by IR spectroscopy (Figure 1). The strong bands around 1730 and 1164  $\text{cm}^{-1}$  are assigned to the C=O and C–O stretching modes. A weak band at 1630  $\text{cm}^{-1}$  assigned to the C=C stretching mode indicates that some of the methacrylate groups were preserved after photografting, which is crucial for catalyst immobilization.  $\text{Cp}_2\text{YbMe}$  was added to the PEGDM-modified silicon substrate to react with the remaining methacrylate functionalities to give the active initiating species for SI-GTP.

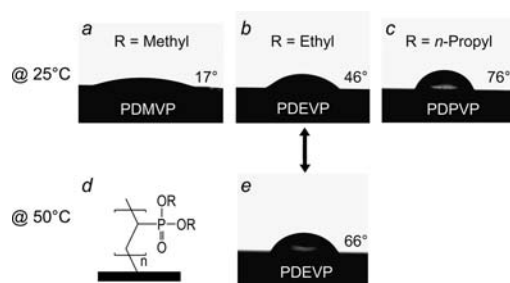


**Figure 2.** Three-dimensional representation of AFM scans of a PEGDM film on a silicon wafer and polymer brushes after SI-GTP of DEVP. (a) SI-PGP of EGDM for 30 min gives a PEGDM film with a thickness of  $29 \pm 6$  nm. (b–e) SI-GTP of DEVP on the same substrate after 1, 2, 3, and 4 min results in  $51 \pm 11$ ,  $73 \pm 9$ ,  $104 \pm 11$ , and  $146 \pm 12$  nm polymer brush layers, respectively. (f) P(EGDM-g-DEVP) layer thickness as a function of SI-GTP time.

Using  $Cp_2YbMe$  as the catalyst and silicon coated with a  $29 \pm 6$  nm (after 30 min UV irradiation) PEGDM primer layer, SI-GTP of diethyl vinylphosphonate (DEVP) results in an almost linear layer thickness increase with a constant growth rate of 26.5 nm/min (Figure 2). This rapid, constant growth rate is expected for a living SI-GTP.<sup>37</sup> AFM measurements also revealed homogeneous coverage of the entire substrate. The successful surface polymerization of DEVP was confirmed by IR spectroscopy (Figure 1). The  $1630\text{ cm}^{-1}$  band assigned to the C=C stretching mode disappears completely, and a new intensive band at  $1228\text{ cm}^{-1}$  is observed, characteristic for the P=O stretching mode of poly(vinylphosphonate)s. Formation of the PEGDM layer, immobilization of Yb, and formation of PDEVP brushes were further corroborated by systematic XPS measurements (Supporting Information).

Besides poly(vinylphosphonate)s, the current method is applicable to other monomers polymerizable by GTP. To demonstrate the general applicability of the method, SI-GTP of MMA was performed following the above-described procedure, resulting in very uniform PMMA brushes with a layer thickness of 316 nm within only 5 min at rt (Supporting Information). The remarkably high and constant layer growth rate of 57 nm/min and final layer thickness make SI-GTP an interesting alternative to SI-ATRP. The successful formation of PMMA brushes was confirmed by IR spectroscopy. As shown in Figure 1, upon SI-GTP of MMA on the PEGDM pre-coating layer, a new band arises at  $1485\text{--}1449\text{ cm}^{-1}$ , assignable to the typical  $CH_3\text{--O}$  stretching mode of PMMA.

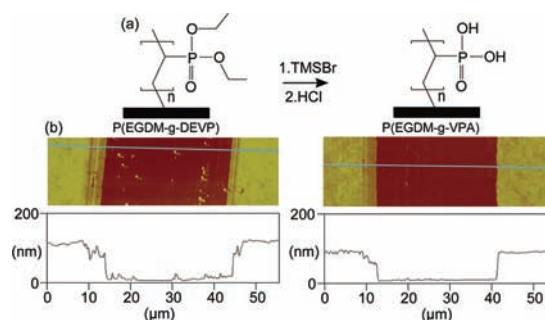
So far, we have successfully prepared poly(dimethyl, diethyl, and di-*n*-propyl vinylphosphonate) (PDMVP, PDEVP, and PDPVP, respectively) brushes on H-terminated silicon. The influence of the polymer pendant alkyl chain length on the hydrophilic/hydrophobic character of the polymer layer was investigated by contact angle (CA) measurements (Figure 3).



**Figure 3.** Molecular structure of poly(dialkyl vinylphosphonate)s (PDAVP) (d) and static water contact angle (CA) on different PDAVP coatings on silicon substrates at different temperatures. (a–c) CA of PDMVP, PDEVP, and PDPVP brushes at 25 °C. (e) CA of PDEVP brush at 50 °C.

The hydrophilic PDMVP gave a static water CA of  $17 \pm 3^\circ$ , while the more hydrophobic PDPVP displayed a CA of  $76 \pm 2^\circ$ . PDEVP displays a lower critical solution temperature of 40–46 °C, depending on molar mass and concentration.<sup>38</sup> The PDEVP-modified substrate was found to have a static water CA of  $44 \pm 2^\circ$  at rt that increased to  $66 \pm 2^\circ$  upon heating to 50 °C. The prepared PDMVP, PDPVP, and temperature-responsive PDEVP brushes have potential applications as bacterial, protein, peptide, and cell adhesion mediators and are first candidates for the study of (bio)mineralization in confined geometries.<sup>51</sup>

It was previously reported that poly(vinylphosphonate)s could be converted to poly(vinylphosphonic acid) (PVPA) by hydrolysis under mild conditions.<sup>38</sup> In this work, PVPA brushes were obtained analogously by treatment with trimethylsilyl bromide and successive HCl treatment to cleave the pendant alkyl groups from PDEVP brushes. The formation of PVPA brushes is apparent from the shift of the P=O stretching mode from  $1228$  to  $1153\text{ cm}^{-1}$  (Figure 1) and is in agreement with previous reports.<sup>52,53</sup> The hydrolysis of a 120 nm P(EGDM-g-DEVP) layer resulted in an 88 nm P(EGDM-g-VPA) film (Figure 4). The thickness decrease is ascribed to material loss after cleavage of the alkyl groups.



**Figure 4.** (a) Conversion from PDEVP to PVPA brushes by hydrolysis reaction. (b) AFM height images and section views along the indicated lines before and after reaction with TMSBr/HCl.

In summary, we have demonstrated a two-step method to efficiently prepare PMMA and PDAVP brushes using surface-initiated group transfer polymerization mediated by rare earth metal catalysts. First, a PEGDM network is prepared by photohydrosilylation/SI-PGP of EGDM directly on hydrogen-terminated silicon. The preserved methacrylate groups can be reacted with bis(cyclopentadienyl)methylterbium, serving as efficient initiators for the successive SI-GTP of (meth)acrylates



or dialkyl vinylphosphonates forming polymer brushes. Remarkably fast and almost constant polymer layer thickness growth rates of 57 and 26.5 nm/min were found for MMA and DEVP, respectively. The method is applicable to functional monomers that cannot be polymerized by other surface-initiated polymerizations and thus widens the range of accessible functional polymer brushes. Moreover, we show the preparation of functional thermoresponsive PDEVP brushes. Poly(vinylphosphonic acid) is now easily accessible under mild conditions. The nontoxic and thermoswitchable surfaces are of great interest for diverse biological and medical applications, including controlled cell growth and cell release from surfaces as well as proton conducting films.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed procedures for chemical reactions and XPS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

rieger@tum.de

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank Matthias Sachsenhauser for XPS measurement, Dr. Sergei Vagin and Dr. Marin Steenackers for valuable discussions, and Roche Diagnostics GmbH for financial support. S.S. is grateful for a generous scholarship from the Fonds der Chemischen Industrie. F.D. acknowledges Wacker Chemie AG for a stipend within the Institute of Silicon Chemistry. R.J. is thankful for DFG support via the Center for Regenerative Therapies Dresden.

## ■ REFERENCES

- (1) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.
- (2) Chen, E. Y.-X. *Chem. Rev.* **2009**, *109*, 5157.
- (3) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097.
- (4) Yasuda, H. *Prog. Polym. Sci.* **2000**, *25*, 573.
- (5) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53.
- (6) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 19626.
- (7) Rabe, G. W.; Komber, H.; Haeussler, L.; Kreger, K.; Lattermann, G. *Macromolecules* **2010**, *43*, 1178.
- (8) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühle, J., Eds. *Polymer Brushes*; Wiley-VCH: Weinheim, 2004.
- (9) Jordan, R., Ed. *Surface-initiated Polymerization I & II*; Advances in Polymer Science 197 & 198; Springer-Verlag: Berlin, 2006.
- (10) Jordan, R.; Ulman, A. *J. Am. Chem. Soc.* **1998**, *120*, 243.
- (11) Jordan, R.; Ulman, A.; Kang, J. F.; Rafailovich, M. H.; Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016.
- (12) Dronavajjala, K. D.; Rajagopalan, R.; Uppili, S.; Sen, A.; Allara, D. L.; Foley, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 13040.
- (13) Prucker, O.; Rühle, J. *Langmuir* **1998**, *14*, 6893.
- (14) Bao, Z.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2006**, *128*, 9056.
- (15) Dong, H.; Zhu, M.; Yoon, J. A.; Gao, H.; Jin, R.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2008**, *130*, 12852.
- (16) Husemann, M.; Mecerreyes, D.; Hawker, C. J.; Hedrick, J. L.; Shah, R.; Abbott, N. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 647.
- (17) Ulbricht, M.; Yang, H. *Chem. Mater.* **2005**, *17*, 2622.
- (18) Tria, M. C. R.; Grande, C. D. T.; Ponnampati, R. R.; Advincula, R. C. *Biomacromolecules* **2010**, *11*, 3422.
- (19) Kong, H.; Gao, C.; Yan, D. *J. Am. Chem. Soc.* **2004**, *126*, 412.
- (20) Fan, X.; Lin, L.; Dalsin, J. L.; Messersmith, P. B. *J. Am. Chem. Soc.* **2005**, *127*, 15843.
- (21) Zhou, F.; Huck, W. T. S. *Chem. Commun.* **2005**, 5999.
- (22) Barbey, R.; Lavanant, L.; Paripovic, D.; Schuwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H. A. *Chem. Rev.* **2009**, *109*, 5437.
- (23) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2003**, *24*, 1043.
- (24) Price, D.; Pyrah, K.; Hull, T. R.; Milnes, G. J.; Ebdon, J. R.; Hunt, B. J.; Joseph, P. *Polym. Degrad. Stab.* **2002**, *77*, 227.
- (25) Parvole, J.; Jannasch, P. *Macromolecules* **2008**, *41*, 3893.
- (26) Steininger, H.; Schuster, M.; Kreuer, K. D.; Kaltbeitzel, A.; Bingöl, B.; Meyer, W. H.; Schauff, S.; Brunklaus, G.; Maier, J.; Spiess, H. W. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1764.
- (27) Wagner, T.; Manhart, A.; Deniz, N.; Kaltbeitzel, A.; Wagner, M.; Brunklaus, G.; Meyer, W. H. *Macromol. Chem. Phys.* **2009**, *210*, 1903.
- (28) Gemeinhart, R. A.; Bare, C. M.; Haasch, R. T.; Gemeinhart, E. J. *J. Biomed. Mater. Res., Part A* **2006**, *78A*, 433.
- (29) Seo, J. H.; Matsuno, R.; Takai, M.; Ishihara, K. *Biomaterials* **2009**, *30*, 5330.
- (30) Goda, T.; Matsuno, R.; Konno, T.; Takai, M.; Ishihara, K. *J. Biomed. Mater. Res., Part B* **2009**, *89B*, 184.
- (31) Macarie, L.; Iliu, G. *Prog. Polym. Sci.* **2010**, *35*, 1078.
- (32) Georgieva, R.; Tsevi, R.; Kossev, K.; Kusheva, R.; Balgiska, M.; Petrova, R.; Tenchova, V.; Gitsov, I.; Troev, K. *J. Med. Chem.* **2002**, *45*, 5797.
- (33) Monge, S.; Canniccionni, B.; Graillet, A.; Robin, J. *Biomacromolecules* **2011**, *12*, 1973.
- (34) Bingöl, B.; Hart-Smith, G.; Barner-Kowollik, C.; Wegner, G. *Macromolecules* **2008**, *41*, 1634.
- (35) Bingöl, B.; Meyer, W. H.; Wagner, M.; Wegner, G. *Macromol. Rapid Commun.* **2006**, *27*, 1719.
- (36) Markova, D.; Kumar, A.; Klapper, M.; Muellen, K. *Polymer* **2009**, *50*, 3411.
- (37) Seemann, U. B.; Dengler, J. E.; Rieger, B. *Angew. Chem., Int. Ed.* **2010**, *49*, 3489.
- (38) Salzinger, S.; Seemann, U. B.; Plikhta, A.; Rieger, B. *Macromolecules* **2011**, *44*, 5920.
- (39) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. *Langmuir* **2000**, *16*, 5688.
- (40) Stewart, M. P.; J. Buriak, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3257.
- (41) Stewart, M. P.; Robins, E. G.; Geders, T. W.; Allen, M. J.; Choi, H. C.; Buriak, J. M. *Phys. Status Solidi A* **2000**, *182*, 109.
- (42) Huck, L. A.; Buriak, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 489.
- (43) Deng, J.; Yang, W.; Rånby, B. *Macromol. Rapid Commun.* **2001**, *22*, 535.
- (44) Deubel, F.; Stutzmann, M.; Garrido, J. A.; Jordan, R. Poster presented at Frontiers in Silicon Chemistry, Munich, April 14–15, 2011; PA38.
- (45) Steenackers, M.; Lud, S. Q.; Niedermeier, M.; Bruno, P.; Gruen, D. M.; Feulner, P.; Stutzmann, M.; Garrido, J. A.; Jordan, R. *J. Am. Chem. Soc.* **2007**, *129*, 15655.
- (46) Zhang, N.; Steenackers, M.; Luxenhofer, R.; Jordan, R. *Macromolecules* **2009**, *42*, 5345.
- (47) Steenackers, M.; Küller, A.; Stoycheva, S.; Grunze, M.; Jordan, R. *Langmuir* **2009**, *25*, 2225.
- (48) Chen, T.; Amin, I.; Jordan, R. *Chem. Soc. Rev.* **2012**, *41*, 3280.
- (49) Van de Walle, C. G.; Street, R. A. *Phys. Rev. B* **1994**, *49*, 14766.
- (50) Sieval, A. B.; Demirel, A. L.; Nissink, J. W. M.; Linford, M. R.; Van der Maas, J. H.; De Jeu, W. H.; Zuilhof, H.; Sudhölter, E. J. R. *Langmuir* **1998**, *14*, 1759.
- (51) Tugulu, S.; Harms, M.; Fricke, M.; Volkmer, D.; Klok, H. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7458.
- (52) Ellis, J.; Wilson, A. D. *Polym. Int.* **1991**, *24*, 221.
- (53) Ingrassia, M.; Elomaa, M.; Jannasch, P. *Polym. Chem.* **2010**, *1*, 739.