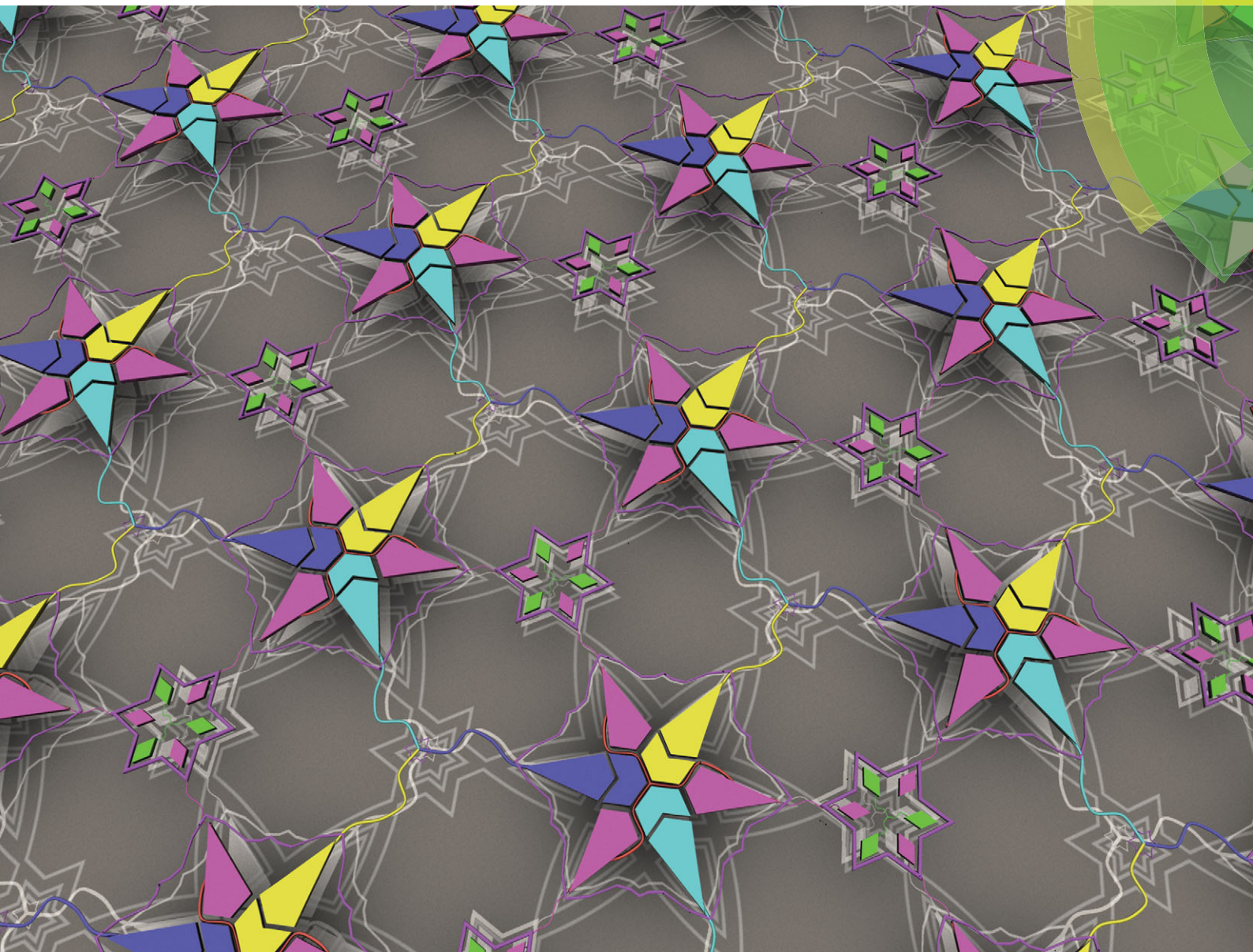


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Polyhomologation based on *in situ* generated boron-thexyl-silaboracyclic initiating sites: a novel strategy towards the synthesis of polyethylene-based complex architectures†

Zhen Zhang,^{ab} Hefeng Zhang,^{ab} Yves Gnanou^a and Nikos Hadjichristidis^{*ab}

A novel strategy, based on the *in situ* generated boron-thexyl-silaboracyclic initiating sites for the polyhomologation of dimethylsulfoxonium methylide, has been developed for the synthesis of complex polyethylene-based architectures. As examples, the synthesis of a 4-arm polyethylene star, three (polystyrene)(polyethylene)₂ 3-miktoarm stars and a PE-branched double graft copolymer is given.

Polyethylene (PE), the largest volume commodity polymer in the world, is indispensable in many applications ranging from packaging to precision-processed materials.¹ The low cost, excellent physical properties, easy processability and recyclability of PE have led to its commercial success.² However, the poor compatibility of PE with other polymers limits its further applications. To overcome this deficiency, the development of PE-based (co)polymeric materials with novel architectures is needed.³

Recently, Shea developed a living polymerization procedure leading to linear well-defined hydroxyl-terminated polymethylene (polyethylene).⁴ The general mechanism involves the formation of a complex between an ylide (monomer) and an organoborane (initiator) followed by migration/insertion of $-\text{CH}_2-$ into the initiator. As a consequence, the methylene groups are randomly inserted one by one (C1 polymerization) into the three arms of the initiator leading to a 3-arm polymethylene star. By oxidizing/hydrolysing the resulted star, an OH-terminated polymethylene (polyethylene) is obtained.

There are four methods for the synthesis of PE-based polymers with different architectures *via* polyhomologation: (1) direct use of the terminal $-\text{OH}$ of PE-OH for ring-opening polymerization (ROP),⁵ or post-polymerization modification of the $-\text{OH}$ appropriate for atom transfer radical (ATRP),⁶ or reversible addition-fragmentation chain-transfer polymerization (RAFT)⁷ initiating sites; (2) reaction of PE-OH with functionalized monomers to give macromonomers

followed by (co)polymerization to afford graft copolymers or molecular brushes;⁸ (3) stitching reactions to freeze the resultant polyhomologation star structure by transforming the sensitive to oxidation/hydrolysis boron-junction to stable carbon;⁹ and (4) design of novel borane initiators.¹⁰

For example, ROP of ϵ -caprolactone initiated directly from the PE-OH macroinitiator with stannous octanoate ($\text{Sn}(\text{Oct})_2$) as a catalyst affords polyethylene-*b*-poly(ϵ -caprolactone). By transforming the terminal $-\text{OH}$ of the diblock copolymer to the ATRP initiating site polyethylene-*b*-poly(ϵ -caprolactone)-*b*-poly(acrylic acid) triblock copolymers have been synthesized.^{5a} Well-defined PE brushes have been synthesized by ring opening metathesis polymerization (ROMP) of norbornyl PE-macromonomers prepared by reaction of PE-OH with 5-norbornene-2-carboxylic acid.⁸ Stitching reactions have been used to synthesize PE-based linear, macrocarbocyclic and 3-arm star structures.⁹ Utilizing novel borane initiators is another efficient way to obtain 3-arm star and multi-block copolymers. For example, polyhomologation of ylides with 1-boraadamantane led to a 3-arm PE¹⁰ and hydroboration of an allyl-terminated polystyrene oligomer with BH_3 gave an organoborane macroinitiator which by polyhomologation led to poly(ethylene-*b*-styrene) (PE-*b*-PS) block copolymers.¹¹ Our group synthesized 3-arm-polybutadiene, polystyrene and (polystyrene-*b*-polydiene)borane stars by reaction of the corresponding living macroanions with $\text{BF}_3 \cdot \text{EtO}_2$, which served as macroinitiators for the synthesis of OH-terminated di- and triblock co- and terpolymers.¹²

In this communication, we propose a novel general strategy based on the *in situ* formation of B-thexyl-silaboracyclic structure, having two silicon-connected initiating sites and one blocked, for the synthesis of PE-based complex macromolecular architectures.

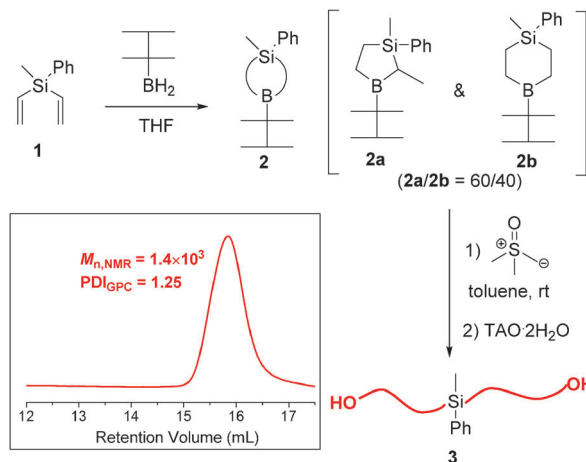
To check the principle of this strategy, B-thexyl-methylphenyl-silaboracycle **2** (mixture of **2a** and **2b** isomers), a small equivalent molecule, was prepared by hydroboration of methylphenyldivinylsilane **1** with thexylborane¹³ and used *in situ* to promote the polyhomologation of dimethylsulfoxonium methylide (Scheme 1). Details of the synthesis and characterization are given in the ESI.† After hydrolysis of the polyhomologation product, only α , ω -dihydroxy polymethylene was produced as evidenced by the

^a King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal 23955, Saudi Arabia. E-mail: nikolaos.hadjichristidis@kaust.edu.sa

^b King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, Thuwal 23955, Saudi Arabia

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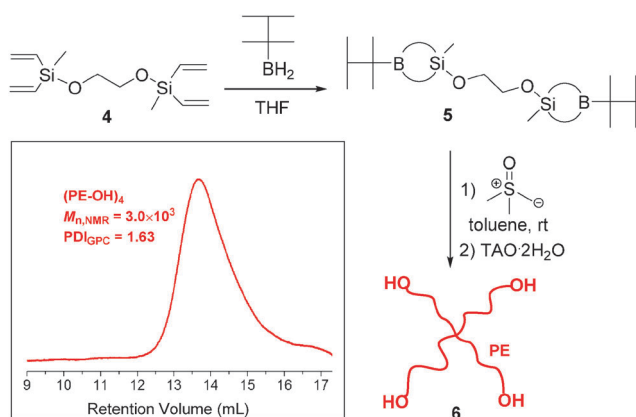
Scheme 1 Synthesis of α, ω -dihydroxyl PE and its GPC chromatogram.

appearance of only one peak in the GPC chromatogram and the absence of the hexyl group in the NMR spectrum, meaning that the B-thexyl site is inactive to polyhomologation and all other B-initiating sites (in **2a** and **2b** isomers) are equivalent, in agreement with Shea's work using B-*p*-methoxy-phenylethyl-9-BBN as an initiator.⁹ This is easy to explain since after the first insertion of a $-\text{CH}_2-$ on the boron-tertiary carbon (B-CH) all sites (B- CH_2) become equivalent.

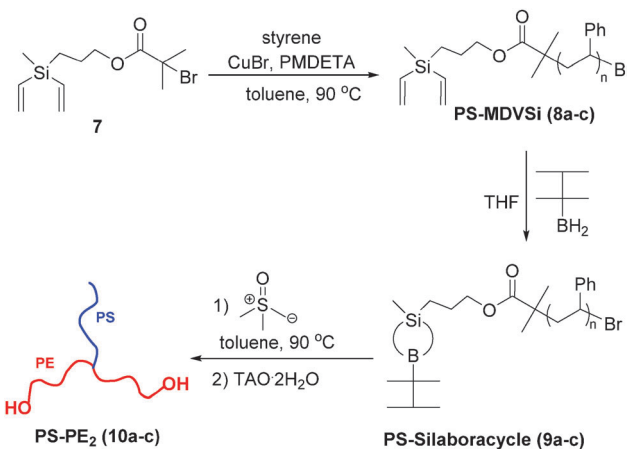
Subsequently, this strategy was employed for the macromolecular design and synthesis of a 4-arm polyethylene star, three (polystyrene)(polyethylene)₂ 3-miktoarm stars and a PE-branched double graft copolymer.

The general reaction scheme for the synthesis of a 4-arm star is given in Scheme 2. The hydroboration of 3,8-dimethyl-3,8-divinyl-4,7-dioxo-3,8-disiladeca-1,9-diene **4** with thexylborane gives bis-B-thexyl-silaboracycles **5**. After treating **5** with excess ylide and subsequent oxidation-hydrolysis reaction using TAO·2H₂O, 4-arm PE star **6** ($M_{n,\text{NMR}} = 3.0 \times 10^3$, $\text{PDI}_{\text{GPC}} = 1.63$) was obtained (Fig. S2, ESI[†]). Details are given in the ESI.[†]

The synthesis of PE-based 3-miktoarm stars was achieved according to Scheme 3 by combining polyhomologation with ATRP through an heterofunctional initiator, 3-(methyldivinylsilyl)-propyl-2-bromo-2-methylpropanoate **7** (the synthesis procedure is



Scheme 2 Synthesis of 4-arm PE star and its GPC chromatogram.



Scheme 3 Synthesis of PE-based 3-miktoarm star polymers by combination of ATRP and polyhomologation.

given in the ESI,[†] Scheme S4). The 2-bromo-2-methylpropanoate group was used to initiate the ATRP of styrene (CuBr/PMDETA (*N,N,N',N',N',N'*-pentamethyldiethylene-triamine)) and methyldivinylsilyl after transformation to B-thexyl-silaboracycles to initiate polyhomologation. Three samples of divinyl-terminated polystyrene with different molecular weights and low polydispersities have been designed and synthesized (**8a**: $M_{n,\text{GPC}} = 16.0 \times 10^3$, $\text{PDI}_{\text{GPC}} = 1.22$; **8b**: $M_{n,\text{GPC}} = 11.0 \times 10^3$, $\text{PDI}_{\text{GPC}} = 1.18$, $T_g = 85^\circ\text{C}$; **8c**: $M_{n,\text{GPC}} = 5.2 \times 10^3$, $\text{PDI}_{\text{GPC}} = 1.18$) (Fig. 1 and Fig. S3 and S4, ESI[†]). The terminal methyldivinylsilyl group was readily transformed to B-thexyl-silaboracycles by hydroboration with thexylborane resulting in the corresponding macroinitiators for polyhomologation (**9a-c**). High hydroboration efficiencies were indicated by quantitative consumption of the terminal vinyl groups ($\delta = 5.6$ to 6.2 ppm) revealed by ¹H NMR results. As an example, the NMR spectra of **8a** (before hydroboration) and **9a** (after hydroboration) are shown in Fig. 2 (spectra a and b). The resultant boron-macroinitiators were used *in situ* for the polyhomologation of dimethylsulfoxonium methylide leading to the corresponding PE-based 3-miktoarm stars.

The success of this strategy was confirmed by both GPC and NMR results (Fig. 1 and 2). After polyhomologation, the peak shifted to a higher molecular weight range keeping the narrow distribution profiles (**10a**: $M_{w,\text{GPC-LS}} = 506 \times 10^3$, $\text{PDI}_{\text{GPC-LS}} = 1.32$; **10b**: $M_{w,\text{GPC-LS}} = 367 \times 10^3$, $\text{PDI}_{\text{GPC-LS}} = 1.56$, $T_m = 116^\circ\text{C}$;

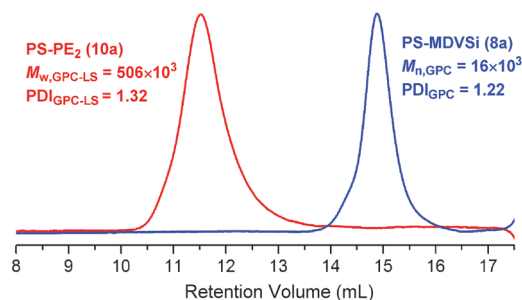


Fig. 1 GPC chromatograms of PS-MDVSil (**8a**) and the corresponding 3-miktoarm star (**10a**).



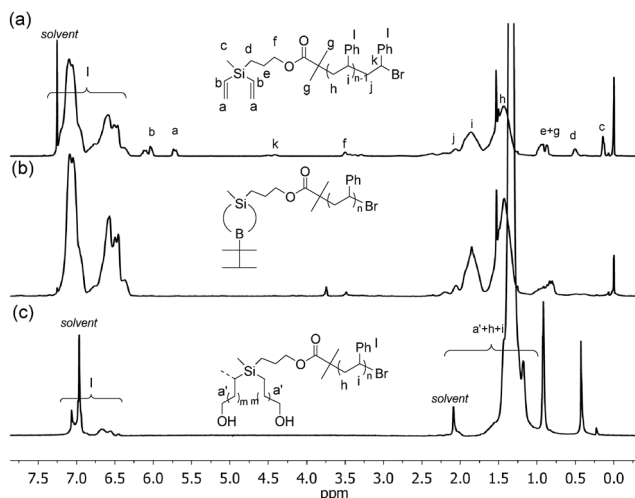
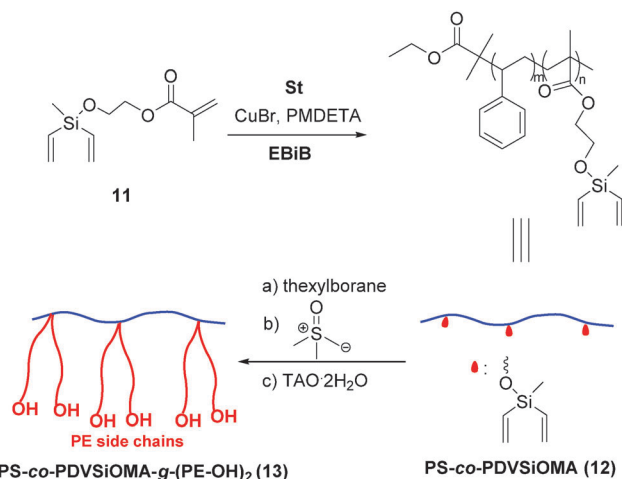


Fig. 2 ¹H NMR spectra of (a) PS-MDVSil (**8a**) (chloroform-*d*, 25 °C); (b) PS-Silaboracycle (**9a**) (chloroform-*d*, 25 °C); (c) PS-PE₂ (**10a**) (toluene-*d*₈, 80 °C).



Scheme 4 Synthesis of PE-branched double graft copolymer by combination of ATRP and polyhomologation.

10c: $M_{w,GPC-LS} = 423 \times 10^3$, $PDI_{GPC-LS} = 1.35$ (Fig. 1 and Fig. S3 and S4, ESI[†]). Also, the fingerprints of the PS and PE blocks were found in the ¹H NMR spectrum (Fig. 2c).

A “grafting from” strategy shown in Scheme 4 was developed to synthesize a double graft copolymer. First, copolymerization of styrene with 2-((methyldivinylsilyl)oxy)ethyl methacrylate (DVSilOMA, **11**) (for preparation see ESI[†] Scheme S6) by ATRP initiated by ethyl 2-bromoisobutyrate (EBiB) with the CuBr/PMDTA catalytic system led to PS-co-PDVSilOMA **12**. Then, the pendant divinylsilyl groups were transformed to B-thexylsilaboracycles by hydroboration with thexylborane, followed by polyhomologation. As an example, PS₃₈-co-PDVSilOMA₃ ($PDI_{GPC} = 1.31$) was synthesized (feed ratio 50/4.5).

Hydroboration of PS₃₈-co-PDVSilOMA₃/polyhomologation by the resultant macroinitiator leads to PE-branched double graft

copolymer PS-co-PDVSilOMA-g-(PE-OH)₂ **13** ($M_{w,GPC-LS} = 218 \times 10^3$, $PDI_{GPC-LS} = 1.35$) (see ESI[†] Fig. S5). High hydroboration efficiency was indicated by the quantitative disappearance of the signal at 5.7–6.2 ppm in ¹H NMR spectra for vinyl protons. The PS backbone is identifiable in NMR spectra (toluene-*d*₈, 25 °C) and the PE fingerprint is much more evident by increasing the temperature up to 80 °C (see ESI[†] Fig. S6).

In conclusion, a novel strategy using the *in situ* synthesized B-thexyl-silaboracyclic moieties with two silicon-connected initiating and one blocked sites for polyhomologation was successfully developed. This general strategy opens a new horizon for the synthesis of PE-based complex macromolecular architectures. Only a few examples are given in this communication, *i.e.* a 4-arm polyethylene star, three PS-PE₂ 3-miktoarm stars and a PE-branched double graft copolymer. Combination of this general strategy with other living and living/controlled polymerization techniques will lead to novel architectures such as multi-arm stars (8, 12, 16-arm), H-shaped, molecular brush copolymers, *etc.*

Notes and references

- (a) P. Galli and G. Vecellio, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 396–415; (b) D. B. Malpass, *Introduction to Industrial Polyethylene: Properties, Catalysts, and Processes*, John Wiley and Sons Ltd, 2010.
- P. S. Chum and K. W. Swogger, *Prog. Polym. Sci.*, 2008, **33**, 797–819.
- (a) L. Leibler, *Prog. Polym. Sci.*, 2005, **30**, 898–914; (b) C. W. Macosko, H. K. Jeon and T. R. Hoyer, *Prog. Polym. Sci.*, 2005, **30**, 939–947; (c) P. J. Phillips, *Polym. Cryst. Rep. Polym. Phys.*, 1990, **53**, 549–604.
- (a) J. Luo and K. J. Shea, *Acc. Chem. Res.*, 2010, **43**, 1420–1433; (b) K. J. Shea, J. W. Walker, H. Zhu, M. M. Paz and J. Greaves, *J. Am. Chem. Soc.*, 1997, **119**, 9049–9050; (c) K. J. Shea, *Chem. – Eur. J.*, 2000, **6**, 1113–1119.
- (a) C. Yuan, H. Lu, Q. Li, S. Yang, Q. Zhao, J. Huang, L. Wei and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2398–2405; (b) Q.-Z. Li, G.-Y. Zhang, J.-Z. Chen, Q.-L. Zhao, H.-C. Lu, J. Huang, L.-H. Wei, F. D’Agosto, C. Boisson and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 511–517.
- (a) H. Lu, Y. Xue, Q. Zhao, J. Huang, S. Xu, S. Cao and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3641–3647; (b) Y. Xue, H. Lu, Q. Zhao, J. Huang, S. Xu, S. Cao and Z. Ma, *Polym. Chem.*, 2013, **4**, 307–312; (c) J. Chen, K. Cui, S. Zhang, P. Xie, Q. Zhao, J. Huang, L. Shi, G. Li and Z. Ma, *Macromol. Rapid Commun.*, 2009, **30**, 532–538; (d) J. Li, Q.-L. Zhao, J.-Z. Chen, L. Li, J. Huang, Z. Ma and Y.-W. Zhong, *Polym. Chem.*, 2010, **1**, 164–167.
- X. Wang, J. Gao, Q. Zhao, J. Huang, G. Mao, W. Wu, Y. Ning and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 2892–2899.
- H. Zhang, Y. Gnanou and N. Hadjichristidis, *Polym. Chem.*, 2014, **5**, 6431–6434.
- (a) K. J. Shea, S. Y. Lee and B. B. Busch, *J. Org. Chem.*, 1998, **63**, 5746–5747; (b) K. J. Shea, B. B. Busch and M. M. Paz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1391–1393.
- (a) C. E. Wagner and K. J. Shea, *Org. Lett.*, 2001, **3**, 3063–3066; (b) C. E. Wagner, J.-S. Kim and K. J. Shea, *J. Am. Chem. Soc.*, 2003, **125**, 12179–12195.
- (a) X.-Z. Zhou and K. J. Shea, *Macromolecules*, 2001, **34**, 3111–3114; (b) K. J. Shea, C. L. Staiger and S. Y. Lee, *Macromolecules*, 1999, **32**, 3157–3158.
- (a) H. Zhang, N. Alkayal, Y. Gnanou and N. Hadjichristidis, *Chem. Commun.*, 2013, **49**, 8952–8954; (b) H. Zhang, N. Alkayal, Y. Gnanou and N. Hadjichristidis, *Macromol. Rapid Commun.*, 2014, **35**, 378–390.
- (a) J. A. Soderquist and A. Hassner, *J. Org. Chem.*, 1983, **48**, 1801–1810; (b) J. A. Soderquist, F.-Y. Shiau and R. A. Lemesh, *J. Org. Chem.*, 1984, **49**, 2565–2569; (c) M. F. Hawthorne, *J. Am. Chem. Soc.*, 1961, **83**, 2541–2544; (d) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, 1972, **94**, 3567–3572; (e) E. Negishi and H. C. Brown, *Synthesis*, 1974, 77–89; (f) H. C. Brown and A. K. Mandal, *J. Org. Chem.*, 1992, **57**, 4970–4976.

