RSC Advances

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

ARTICLE

New Synthetic Strategy Targeting Well-defined α,ω-Telechelic Polymethylenes with Hetero Bi-/Tri-Functionalities via Polyhomologation of Ylides Initiated by New Organic Boranes Based on Catecholborane and Post Functionalization

Fang Xu,[a,b] Peng Dong,[a,b] Kun Cui,[b] Shi-Zheng Bu,[b] Jin Huang,[b] Guang-Yu Li,[b] Tao Jiang,[a,†] Zhi Ma[b,†]

A series of well-defined α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities were synthesized by a tandem strategy combining polyhomologation of ylides initiated by new organic boranes based on catecholborane with post functionalization using end-capping reagents and esterification. The chain structures of such polymers were attested by ^{1}H NMR spectra, FT-IR and GPC. The functionality can reach up to 100%, and the molecular weights of the obtained polymers showed a range from 870 to 12080 g/mol remaining narrow distribution (Đ = 1.04-1.12).

Polyolefins are known to be cost effective and good performing materials used in a broad range of commodity applications. Despite this great popularity, the ready introduction of reactive groups into these nonpolar materials is still an important target. Up to now, a significant amount of research has been directed to introduce of polar or functional group into polyolefin backbone to dramatically improve the properties of polyolefins, such as crystallinity, elasticity, adhesion and compatibility with other materials, thus widen the field of application.[1-8] In addition, these functional polyolefins are also a starting point for other more complex structures, like block copolymers, graft copolymers, and more complex polymer brushes.[9-15]

Main-chain-end functional polyolefins are highly desired materials, due to their beneficial properties. Many different pathways exist for the synthesis of these materials, each with its own advantages and drawbacks. Then, the recent progress in the main-chain-end functional polyolefins was reviewed with emphasis on its design and synthesis by four methodologies: 1) the chain transfer reaction in the olefin polymerization;[16-22] 2) the coordinative living olefin polymerization;[23-25] 3) the anion living polymerization;[26-28] 4) the polyhomologation of ylides.[29-35]

Telechelic polymers have an important economic position because of their possible applications as cross-linkers, chain extenders and building blocks.[36] However, in the relevant reports of main-chain-end functionalization, there is rare telechelic polyolefins which are macromolecules possessing two well-defined reactive functional groups situated at the chain termini. Some great achievements dealing with the synthesis of α,ω-telechelic polyolefins can be found in the literature.[20-23,27,31,32,37-42] Carboxy-telechelic poly(cyclooctene)s (M_n=1,760-23,200 g/mol, Đ = 1.77-2.49) were prepared by including a symmetric acyclic alkene during ring-opening metathesis polymerization (ROMP) of cyclooctene. Building further on this foundation, carboxy-telechelic polyethylene was obtained by hydrogenation.[38] Dihydroxy-terminal poly(propylene)s (M_n=8,300-10,400 g/mol, Đ = 1.06-1.14) were successfully synthesized in a broad range of functionality of 50-100% by a living polymerization using L_2TiCl_2 [L: C_6F_5N=CH(2-O-C_6H_3-3-^{t}Bu)]/methylaluminoxane (MAO) and functionalized a-olefins, H_2C=CH$(CH_2)_9$-OSiMe$_3$.[24] D'Agosto, Boisson and coworkers produced PE-Mg-PE intermediate by catalysing chain growth (CCG) on magnesium using $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ in combination with a dialkyl magnesium as chain transfer agent (CTA). Then heterobifunctional telechelic polyethylenes with a vinyl α end group and a -I, -SC(S)NEt$_2$ group at the ω-chain end were obtained in high functionality of 96% and 87% (M_n = 1,500 and 1,550 g/mol, Đ = 1.14 and 1.15). Divinyl-end-functionalized polyethylene was further used as a reactant for the design of a vast range of homotelechelic polyethylenes on the basis of thiol-ene chemistry.[20,43] Telechelic Zn-metalated polyolefins,

[a.] College of Chemical Engineering and Materials Science, Tianjin University of Science & Technology, Tianjin, 300457, People's Republic of China
[b.] Key Laboratory of Synthesis and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic China
† Corresponding authors: Prof. Zhi Ma (mazhi728@sioc.ac.cn) and Prof. Tao Jiang (jiangtao@tust.edu.cn)
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

whose molecular weights were controllable over a wide range, were obtained via CCG on multinuclear alkylene zinc compounds. And the Zn-terminated telechelics served as a polymer precursor for further reactions could be converted into a variety of telechelic functionalized polyolefins (M_n = 1,990 and 7,950 g/mol, Đ = 1.46-1.78).[39]

Polyhomologation, recently developed by Shea,[29] is a borane-initiated living polymerization of ylides leading to linear polymethylenes (PM) with controlled molecular weight, low polydispersity, well-defined structures and high functionality of chain-end (~100%). The telechelic polymethylenes have potential applications as high value-added standard sample of polymer and model polymer with a variety of chain-end functional groups. Functionality at the α-chain end arose from the substituents on the trialkylborane initiator which could be prepared by hydroboration of functional α-olefins or by direct synthesis. ω-Hydroxy polymethylenes were prepared by a polyhomologation-oxidation sequence. Thus, α-vinyl/benzylamino/(p-methoxyphenyl)-ω-hydroxylpolymethylene were obtained and the molecular weight showed a range from 500 to 13,200 g/mol remaining narrow distribution (Đ = 1.01-1.19).[32,33,44] By using the same method, Alkayal and Hadjichristidis prepared α-anthracene-ω-hydroxy polymethylene (M_n = 5,600 g/mol, Đ = 1.14).[41] According to reports in the literature, some organic boranes, such as $BH_3 \cdot SMe_2$, $BF_3 \cdot OEt_2$, B-alkyl-9-borabicyclo[3.3.2]nonanes (9-BBN), trialkylborane, thexylborane and 1-boraadamantane·THF were regularly chosen as the initiators of polyhomologation.[45,46,47] Among of the organic boranes, catecholborane has unique structural features, the boron atom is part of a planer five-membered ring and hence its steric requirements are much less than other reagents such as 9-BBN.[48] The regioselectivity observed for $BH_3 \cdot THF$ in the hydroboration of alkenes is influenced by both steric and electronic effects. Interestingly, catecholborane is less sensitive to the electronic influenced of a phenyl substituent. And hydroboration of alkenes with catecholborane shows a stereoselectivity comparable to that observed for $BH_3 \cdot THF$. Moreover, some of borane reagents are not enough stable, they can't undergo rapid and reversible disproportionation such as dialkoxyboranes. With catecholborane, where π-bonding between boron and oxygen, displays remarkable stability. At the same time, the existence of π-bonding also reduces reactivity relative to BH_3 or alkylboranes. But with catecholborane, oxygen is bound to a benzene ring, this increased rate of hydroboration is expected since the oxygen 2p electrons can resonate into the benzene ring.[49-51] Consequently, π-bonding between oxygen and boron is less important. A sample of catecholborane could stored for over one year at 0-5°C showed no detectable loss in hydride activity by GC analysis. In general, catecholborane is worthy to be employed in the synthesis of new initiators for polohomologation of ylides.

In this paper, firstly, new organic intiators produced by hydroboration of diene/triene compounds using catecholborane were employed in the polyhomologation of dimethylsulfoxnium methylide. Then the post functionalization

of the polymers obtained above was in situ performed using end-capping reagents. Alternatively, the esterification of the terminal hydroxyl group of α,ω-telechelic polymethylenes with succinic anhydride was carried out aiming at carboxyl-terminated polymethylene. Using this strategy, a series of well-defined α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities can be synthesized. And such polymers are expected to show high functionality up to 100%, and a broad range of molecular weights with narrow distribution (Đ < 1.2).

Experimental section

Materials

All manipulations involving air- and/or moisture sensitive compounds were carried out in a nitrogen-filled dry box or using Schlenk techniques. Toluene (Sinopharm Chemical Reagent Co., Ltd, ≥ 99.5%) was refluxed over sodium and distilled under nitrogen before use. Divinylbenzene (DVB, Alfa Aesar, 80%) and 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TAIC, Aldrich, 98%) were dissolved by toluene, and degassed with nitrogen prior to use. Sodium hydride (Beidouxing Company, Tianjin, 95%) was stirred in n-hexane 6h and standing for 1h, then n-hexane drew off by a needle, in this way washed three times with n-hexane, dried in a vacuum, and stored under nitrogen. Trimethylsulfoxonium iodide (Acros Organics, 98%), benzyltributylammonium chloride (TCI, > 98%), dichloromethane (Sinopharm Chemical Reagent Co., Ltd, ≥ 99.5%), celite-545 (Acros), trimethylamine N-oxide dehydrate (TAO, J&K, 98%), phenolphthalein (Acros, 98.5%), catecholborane (Aldrich, 1.0M in THF), iodine (Sinopharm Chemical Reagent Co., Ltd, > 99.8%), 4-(Dimethylamino)pyridine (DMAP, Aldrich, 99%), succinic anhydride (Aldrich, 99%), and tetraethylthiram disulfide (Aldrich, ≥ 97%) were used as received.

First, dimethylsulfoxonium methylide was synthesized in a similar procedure described in literature[44] using trimethylsulfoxonium iodide in ion-exchange reaction with benzyltributylammonium chloride and sodium hydride in the deprotonation of trimethylsulfoxonium chloride. Dimethylsulfoxonium methylide is established by quenching an aliquot in water, using of phenolphthalein as a colored reagent and titrating with standardized hydrochloric acid solution.

Synthesis of Functional Polymethylene (FG-PM-OH)

In a typical procedure to obtain a new organic borane, DVB (or TAIC) (1.5 equiv, 1.5 mmol) was freeze-dried three times in liquid nitrogen, and then dried toluene (20 mL) were introduced into a nitrogen-purged, 50 mL, round-bottom flask equipped with a stirring bar. The solution was cooled to 0°C, adding dropwise of catecholborane solution (1 equiv, 1 mmol), then was stirred at 80°C for 3 h. Such reaction mixture was added slowly via syringe under nitrogen protection to ylide solution (265.4 mmol or 663.6 mmol) to run the polyhomologation in a similar procedure as described in our previous work[10,11] at 80°C for 40 min, then added TAO (2

Journal Name

ARTICLE

equiv, 2.0 mmol) in the oxidation of carbon-boron bond at 90°C. After 6 h, the resulting mixture was poured into a large amount of methanol under magnetic stirring. The functional polymethylene (**FG-PM-OH**, FG=Functional Group) was collected by filtration, washed with methanol several times, and dried overnight at 40°C under vacuum. **R$_1$-PM-OH** (product 1, FG=R$_1$, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 6.62-6.74 (m, **CH$_2$=CH-**), 5.59-5.72, 5.09-5.20 (m, **CH$_2$**=CH-), 3.60(t, -**CH$_2$**-OH), 2.60 (m, CH$_2$=CH-C$_6$H$_4$-**CH$_2$**-), 1.64 (m, -**CH$_2$**-CH$_2$-OH), 1.04-1.59 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 3250 (O-H), 2920 (C-H), 1602 (C=C), 1508 (C=C), 1467 (C-H), 1050 (C-O), 720 (-(CH$_2$)$_n$-, n≥4) cm^{-1}. **R$_2$-PM-OH** (product 2, FG=R$_2$, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 5.8-6.0 (m, **CH$_2$=CH-**), 5.11-5.32 (m, **CH$_2$**=CH-), 4.48 (t, CH2=CH-**CH$_2$**-), 3.86 (m, N-**CH$_2$**-(CH$_2$)$_n$-), 3.60 (t, -**CH$_2$**-OH), 1.69 (m, -**CH$_2$**-CH$_2$-OH), 1.13-1.63 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 3560 (O-H), 2918 (C-H), 1697 (C=O), 1464 (C-H), 1319 (C-N), 1054 (C-O), 720 (-(CH$_2$)$_n$-, n≥4) cm^{-1}.

Synthesis of FG-PM-COOH by Esterification Reaction

In a typical procedure, FG-PM-OH, succinic anhydride (4 equiv of succinic anhydride compared to FG-PM-OH), DMAP (0.5 equiv) and dried toluene (60 mL) were added to a reaction flask, and the mixture was stirred at 80°C for 16 h under nitrogen. The final polymer was precipitated into methanol, washed with methanol, and dried under vacuum. **R$_1$-PM-COOH** (product 3, FG=R$_1$, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 6.63-6.74 (m, **CH$_2$=CH-**), 5.60-5.74, 5.11-5.22 (m, **CH$_2$**=CH-), 4.12 (t, -**CH$_2$**-OC(O)-), 2.55-2.72 (m, CH$_2$=CH-C$_6$H$_4$-**CH$_2$**-, -OC(O)-**CH$_2$**-**CH$_2$**-COOH), 1.60 (m, -**CH$_2$**-CH$_2$-OC(O)-), 1.09-1.52 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 2918 (C-H), 1735 (C=O), 1472 (C-H), 1159 (C-O-C), 720 (-(CH$_2$)$_n$-, n≥4) cm^{-1}. **R$_2$-PM-COOH** (product 4, FG=R$_2$, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 5.8-6.0 (m, **CH$_2$=CH-**), 5.11-5.32 (m, **CH$_2$**=CH-), 4.47 (t, CH2=CH-**CH$_2$**-), 4.09 (t, -**CH$_2$**-OC(O)-), 3.86 (m, N-**CH$_2$**-(CH$_2$)$_n$-), 2.60 (t, -OC(O)-**CH$_2$**-**CH$_2$**-COOH), 1.65 (m, -**CH$_2$**-CH$_2$-OC(O)-), 1.13-1.63 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 2918 (C-H), 1739 (C=O), 1464 (C-H), 1163 (C-O), 1319 (C-N), 720 (-(CH$_2$)$_n$-, n≥4) cm^{-1}.

Synthesis of PM-I

In a typical polymerization, ylide solution (379.2 mmol) was added to a nitrogen-purged reaction flask equipped with a stirring bar, then added catecholborane solution (0.9 mmol) at room temperature, and the resulting mixture was stirred under nitrogen at 80°C for 40 min. Cooling to room temperature, an iodine solution (4 equiv of I$_2$ compared to catecholborane solution, in 15 mL of dried toluene) was added, and the resulting mixture was stirred under the condition of dark for 3 h. The polymer was precipitated in methanol under nitrogen atmosphere and collected by filtration, washed with methanol several times, and dried under vacuum. **PM-I** (product 5, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 3.10 (t, -**CH$_2$**-I), 1.75 (m, -**CH$_2$**-CH$_2$-I), 1.24-1.44 (m, -(**CH$_2$**)$_n$-), 0.87-0.97 (m, **CH$_3$**-)

ppm. FT-IR (KBr): 2918 (C-H), 1473 (C-H), 720 (-(CH$_2$)$_n$-, n≥4), 560 (C-I) cm^{-1}.

Synthesis of FG-PM-I

In a similar procedure, DVB (or TAIC) (1.5 equiv, 1.5 mmol) was freeze-dried three times in liquid nitrogen, and then dried toluene (20 mL) was introduced into a nitrogen-purged, 50 mL, round-bottom flask equipped with a stirring bar. The solution was cooled to 0°C, adding dropwise of catecholborane solution (1 equiv, 1 mmol), and then was stirred at 80°C for 2 h. In the polyhomologation, such reaction mixture was added slowly via syringe to ylide solution (183.2 mmol or 379.2 mmol) at 80°C for 40 min. After cooling to room temperature, an iodine solution (4 equiv of I$_2$ compared to catecholborane solution, in 15 mL of dried toluene) was added, and the resulting mixture was stirred under the condition of dark for 3 h. The resulting mixture was then poured into a large amount of methanol under nitrogen atmosphere. After filtration and washing several times with methanol, the precipitate polymer was collected and dried under vacuum. **R$_1$-PM-I** (product 6, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 6.60-6.77 (m, **CH$_2$=CH-**), 5.62-5.79, 5.11-5.28 (m, **CH$_2$**=CH-), 3.09 (t, -**CH$_2$**-I), 2.60 (m, CH$_2$=CH-C$_6$H$_4$-**CH$_2$**-), 1.62 (m, -**CH$_2$**-CH$_2$-I), 1.01-1.52 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 2918 (C-H), 1602 (C=C), 1508 (C=C), 1464 (C-H), 720 (-(CH$_2$)$_n$-, n≥4), 560 (C-I) cm^{-1}. **R$_2$-PM-I** (product 7, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 5.82-5.99 (m, **CH$_2$=CH-**), 5.10-5.37 (m, **CH$_2$**=CH-), 4.49 (d, CH$_2$=CH-**CH$_2$**-), 3.90 (t, N-**CH$_2$**-(CH$_2$)$_n$-), 3.09 (t, -**CH$_2$**-I), 2.01 (m, -**CH$_2$**-CH$_2$-I), 1.15-1.54 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 2915 (-CH$_2$-), 1739 (C=O), 1470 (C-H), 1319 (C-N), 718 (-(CH$_2$)$_n$-, n≥4), 535 (C-I) cm^{-1}.

Synthesis of FG-PM-SC(S)NEt$_2$

In a similar procedure as described above, DVB (or TAIC) (1.5 equiv, 1.5 mmol) and dried toluene (20 mL) were introduced into a nitrogen-purged, round-bottom flask equipped with a stirring bar. The solution was degassed with nitrogen for 30 min and cooled to 0°C, then added catecholborane solution (1 equiv, 1 mmol), stirred at 80°C for 2 h. In the polyhomologation, the reaction mixture was added slowly via syringe to ylide solution (61.0 or 900.6 mmol) at 80°C for 40 min, then tetraethylthiram disulfide was added. After 4 h, the reaction mixture was poured in methanol. The precipitated polymer was filtered off, washed several times with methanol and dried under vacuum. **R$_1$-PM-SC(S)NEt$_2$** (product 8, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 6.57-6.76 (m, **CH$_2$=CH-**), 5.62-5.74, 5.10-5.26 (m, **CH$_2$**=CH-), 3.88 (m, -N(**CH$_2$**CH$_3$)$_2$), 3.36 (t, **CH$_2$**-S), 2.60 (m, CH$_2$=CH-C$_6$H$_4$-**CH$_2$**-), 1.01-1.56 (m, -(**CH$_2$**)$_n$-) ppm. FT-IR (KBr): 2918 (C-H), 1601 (C=C), 1509 (C=C), 1466 (C-H), 1413 (C=S), 1208 (C-N), 720 (-(CH$_2$)$_n$-, n≥4) cm^{-1}. **R$_2$-PM-SC(S)NEt$_2$** (product 9, see Scheme 1): ^{1}H NMR 400 MHz (1,2-dichlorobenzene-d$_4$, 80°C), δ: 5.80-5.99 (m, **CH$_2$=CH-**), 5.09-5.34 (m, **CH$_2$**=CH-), 4.47 (d, CH$_2$=CH-**CH$_2$**-), 3.88 (t, N-**CH$_2$**-(CH$_2$)$_n$-, -N(**CH$_2$**CH$_3$)$_2$), 3.36 (t, -**CH$_2$**-S-), 1.67 (m, -**CH$_2$**-CH$_2$-S-), 1.05-1.61 (m, -(**CH$_2$**)$_n$-), 0.93 (t, -

N(CH$_2$**CH$_3$**)$_2$) ppm. FT-IR (KBr): 2918 (C-H), 1697 (C=O), 1464 (C-H), 1416 (C=S), 1319 (C-N), 720 (-(CH$_2$)$_n$-, n≥4), 560 (C-I) cm^{-1}.

Polymer Characterization

^{1}H NMR and ^{13}C NMR spectra of polymers were obtained on a Bruke AV 400 spectrometer (400 MHz) at 80°C with 1, 2-dichlorobenzene-d$_4$ as the solvent. Molecular weights and distributions (M_w/M_n) of polymers were determined by high-temperature gel permeation chromatography using a Waters Alliance GPC2000 equiped with three types of Styragel columns (Styragel HT5, Styragel HT4 and Styragel HT3) a Waters 2410 differential refractometer RI (refractive index) detector relative to linear polyethylenes standards. GPC was performed at 135°C using 1, 2, 4-trichlorobenzene as eluent at a flow rate of 0.92 mL min^{-1}. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. Thermal analyses of polymers were performed on a different scanning calorimeter (Perkin Elmer Pyris 1). The sample was heated to 130°C at 10°C min^{-1}, maintained at 130°C for 5 min, and cooled to 10°C at 10°C min^{-1} followed by reheating to 130°C at 10°C min^{-1}. The thermogram of the samples was recorded during the second heating run. The instrument was calibrated with the melting points of indium.

Results and Discussion

Recently, we developed a new system of polyhomologation combining with catecholborane/alkenes/sulfur ylides to synthesize α,ω-telechelic polymethylenes. The synthetic approach involved three steps: a) the reaction of alkenes with catecholborane; b) an in situ polyhomologation of dimethylsulfoxonium methylide; c) the post functionalization using TAO/I$_2$/disulfiram as end-capping reagents.
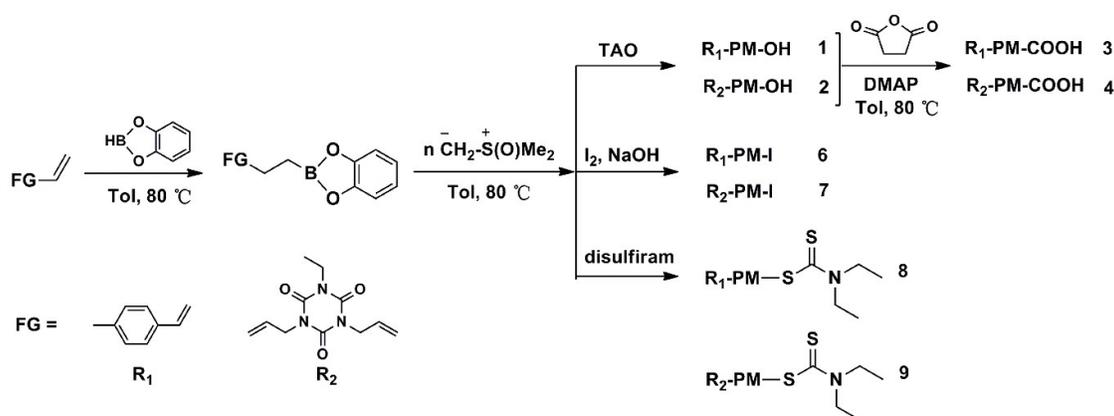
Scheme 1 Synthesis of α,ω-telechelic polymethylenes with bi-/tri-functionalities

First of all, catecholborane was chosen to hydroborate diene/triene to form novel organic borane initiators for polyhomologation. Such new initiators have one C-B bond and two B-O bonds, but there is no literature reported that the polyhomologation could be realized or not by inserting methylene group between B-O bond. So an experiment was designed. The reaction of excessive benzaldehyde with catecholborane overnight at room temperature was carried out after hydroboration workup.

The reaction of benzaldehyde with catecholborane, which will form three B-O bonds,[52] must ensure that the catecholborane was reacted completely, otherwise it will react with ylide to obtain polymethylene. Excessive amounts of benzaldehyde reacted with ylide will generate styrene oxide instead of polymers. In the polyhomologation process, reaction time was extended to an hour because the bond strength of B-O bond is stronger than C-B bond. After the reaction, a small amount of liquid was taken out and added to distilled water. When a few drops of phenolphthalein were added, such solution turned red meaning the presence of residual ylide. Then the resulting mixture was poured into a large amount of methanol under magnetic stirring, there was no polymer precipitated. So it could be supposed that the B-O bond formed by hydroboration of catecholborane with aldehyde, unlike B-H and B-C bond in boranes can not initiate the polyhomologation of ylides in such case. Therefore, using this synthetic strategy (Scheme 1), only one carbon backbone of polymethylene was constructed. While, in the system of 9-BBN, a polymer mixture namely one α,ω-telechelic polymethylenes containing hetero terminal groups and the other one containing homo terminal groups with double molecular weight was formed. It was difficult to separate such polymer mixture into pure α,ω-telechelic polymethylenes with homo- and hetero bi-/tri-functionalities, respectively, by normal precipitation and purification. So, the catecholborane was a good candidate to realize the synthesis of α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities in high purity and employed in all cases of this work.

The synthesis of α,ω-telechelic polymethylenes based on polyhomologation is illustrated in Scheme 1. As already mentioned in the literature,[27,32] the peak at about 0.94 ppm was assigned to protons of methyl branches, this possible

resulted from the competitive of dimethylsulfoxium ethylene during the polyhomologation process. The compositional ratio of methylidene and ethylidene in the polymer backbone can be expressed by eq 1 according to ^{1}H NMR analysis.

$$[M]/[E]=\{[(CH_2+CH)-(CH_3)/3]/2\}/[(CH_3)/3] \qquad (1)$$

The characteristics of the obtained α,ω-telechelic polymethylenes are summarized in Table 1. The terminal functionalities of 77-100% can be reached in different reaction system targeting various α,ω-telechelic polymethylenes. The molecular weights of the obtained polymers can be controlled in a range from 870-12080 g/mol remaining narrow distribution (Đ = 1.04-1.12). Product 1, 2, 6 and 7 all showed a monomodal distribution in the GPC curves (Figure 1). The incidence of the -CH(CH_3)- group from NMR analysis in the polymer is relatively low. The melting temperatures and crystallinities of polymers have a range from 49.8-118.0°C and 11.5-60.7%, respectively.

Table 1 Characteristics of α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities

Product	1	2	5	6	7	8	9
$M_{n,GPC}$(g/mol)	3740	9210	5340	2600	5520	870	12080
Đ	1.04	1.12	1.04	1.08	1.04	1.06	1.05
$M_{n, ^1H\ NMR}$(g/mol)	4200	9270	6320	2760	6270	980	14040
[M]/[E][a]	40.03	57.86	53.01	43.94	12.45	13.47	50.76
F(%)[b]	100	100	90	100	100	93	77
T_m(℃)[c]	112.4	116.0	118.0	49.8	61.2	75.8	113.2
X_c(%)[c]	54.0	57.1	60.7	12.9	20.0	11.5	47.4

[a] The relative amount of -CH_2 to -CH(CH_3) group in the polymer was calculated by ^{1}H NMR; [b] The functionality was calculated by ^{1}H NMR F(%)=integral area of -**CH_2**OH/(integral area of -**CH_2**OH + integral area of -**CH_2**-FG)×100%; [c] Melting temperatures (T_m) were determined by DSC measurement and X_c (crystallinity) were calculated from X_c (%) = (ΔH_m/Δ$H°_m$) ×100%, Δ$H°_m$= 293 J/g for HDPE.[53]
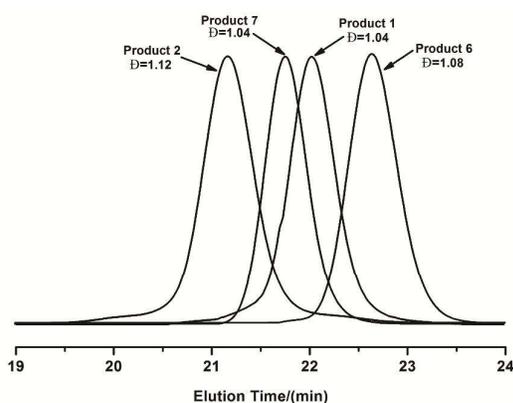
Figure 1 GPC trace curves of hydroxyl/iodine-terminated polymethylenes

An oxidative work-up of C-B bond provides the corresponding alcohols. Other reported examples of oxidative work up of the C-B bonds that are produced during polyhomologation allowed the synthesis of hydroxyl terminated polymethylene.[33] In the field of polyolefin functionalization, in order to get more functional groups at the chain ends, chemical modification were widely used.[20,26,40,42-44] In this paper, it was achieved by esterification reaction.[54-56]

The chemical structure of product 1 (**R_1-PM-OH**) was confirmed by ^{1}H NMR spectrum as shown in Figure 2(a). The characteristic resonances of carbon-carbon double bonds at the polymethylene chain end (-CH=CH_2) can be clearly observed at 6.62-6.74, 5.59-5.72, 5.09-5.20 ppm. The resonance of the methylene group adjacent to the −OH group appeared at 3.60 ppm. And the triplet peak at 2.60 ppm is assigned to methylene protons next to the styryl group. The integral ratio of signals at peak a and peak c is close to the theoretical value of 1:1. Hence, all the results described above revealed that St-PM-OH was obtained efficiently. Product 3 (**R_1-PM-COOH**) was analyzed by ^{1}H NMR spectroscopy (Figure 2(b)) and compared to the product 1. The integral ratio of peak at 3.6 ppm and peak f' is 1:4.07 which give the functionality of 80%. The triplet peak assigned to methylene protons next to the oxygen atom was shifted to 4.12 ppm (-CH_2O-) and the triplet peak at 2.58 ppm for methylene protons between two carbonyl groups (-OCO-CH_2-CH_2-COOH) was formed. This result was also observed by FT-IR, the peak of O-H at 3250 cm^{-1} has disappeared, and the peak of C=O and C-O-C stretching vibration absorption had formed respectively at 1735 and 1159 cm^{-1}. And the peaks at 1509 and 1602 cm^{-1} proved the existence of the benzene ring.
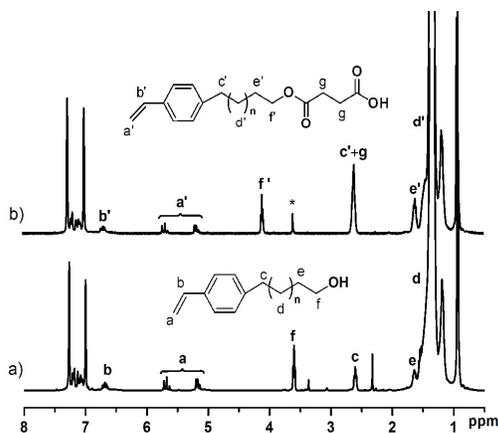
Figure 2 ^{1}H NMR spectra of a) **R$_1$-PM-OH** and b) **R$_1$-PM-COOH**
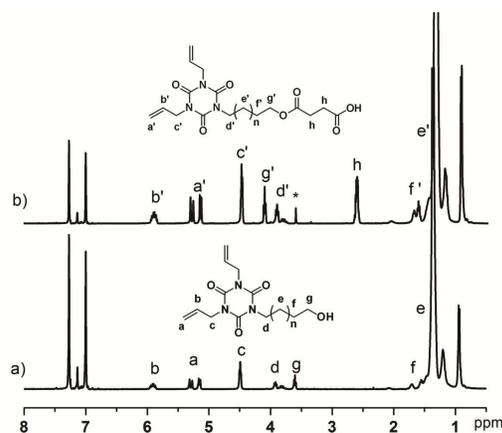
Figure 3 ^{1}H NMR spectra of a) **R$_2$-PM-OH** and b) **R$_2$-PM-COOH**

The ^{1}H NMR spectrum of **R$_2$-PM-OH** (Product 2), as shown in Figure 3(a), confirmed its chain structure. The chemical shifts at 5.80-6.00 and 5.11-5.32 ppm were assigned to protons of double bond at the polymethylene chain end (-CH=CH$_2$). And the peak at 4.48 and 3.86 ppm were respectively assigned to methylene protons next to the carbon-carbon double bond and the TAIC group (TAIC-CH$_2$-). The peak of methylene protons next to the hydroxyl group was assigned at 3.60 ppm (-CH$_2$-OH). **R$_2$-PM-COOH** (product 4), as shown in Figure 3(b), the triplet peak assigned to methylene protons next to the oxygen atom was shifted to 4.12 ppm (-CH$_2$O-), and the peak at 2.58 ppm for methylene protons between two carbonyl groups (-OCO-CH$_2$-CH$_2$-COOH) was formed. The integral ratio of peak at 3.6 ppm and peak g' is 1:9.2. According to this data, functionalization rate could be calculated (90%). FT-IR analysis showed that the peak of O-H at 3560 cm^{-1} disappeared and the absorption peaks of C=O and C-O-C stretching vibration appeared at 1739 and 1163 cm^{-1}, respectively. Hence, all the information described above indicated that the -OCO-CH$_2$-CH$_2$-COOH segment had been connected with PM segment.

Reaction of alkene with catecholborane is very slow at room temperature. So the hydroboration reactions of DVB and

TAIC were carried out a relatively high temperature (80°C). To make sure that the catecholborane was consumed entirely, which could react with ylide, the molar ratio of DVB or TAIC to catecholborane more than 1:1 was provided, preventing the formation of hydroxyl-terminated PM (PM-OH) byproduct. The polymers **R$_1$-PM-OH** and **R$_2$-PM-OH** were obtained in high yield (94% and 96%), high functionalities of 100% and narrow molecular weight distribution (Đ=1.04 and 1.12).

Iodo compounds/polymers are efficient transfer agents in radical polymerization because of the ability of the iodine atom as a good leaving atom. D'Agosto, Boisson and coworkers found that high functionalities (up to 97%) were obtained by a simple addition of I$_2$ on PE-Mg-PE right after the ethylene polymerization step and the iodo terminated polymethylenes can be further transformed to -C=C-, -N$_3$- and -NH$_2$, etc. [20,57-59] Therefore, the trial on post functionalization of ylide polyhomologation by directly introducing I$_2$ as end-capping reagent was performed. **PM-I** (product 5), as control polymer, was obtained and analyzed by ^{1}H NMR. The peak of methylene protons next to the iodine atom was assigned at 3.10 ppm (-CH$_2$-I). And the integral ratio of peak d to c was 1:1, showed the successful synthesis of PM-I. Meanwhile, there are some methyl groups in the side chains, so the integral ratio of peak d to a was more than 1:3. The integral ratio of peak at 3.6 ppm to peak d was 1:8.93. In order to avoid the oxidation of C-B bond to form hydroxyl terminal group, the precipitation of polymerization mixture should be manipulated under nitrogen atmosphere to achieve higher functionality (*ca.* 90%).
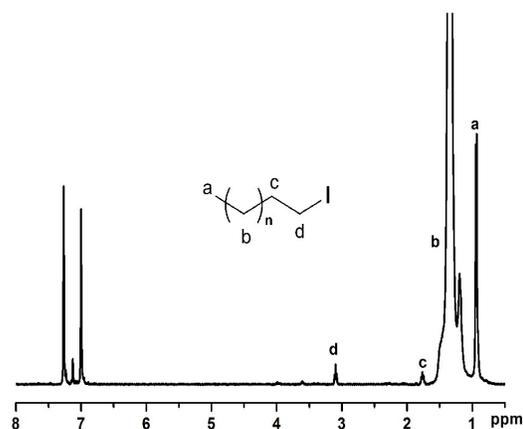
Figure 4 ^{1}H NMR spectrum of **PM-I**
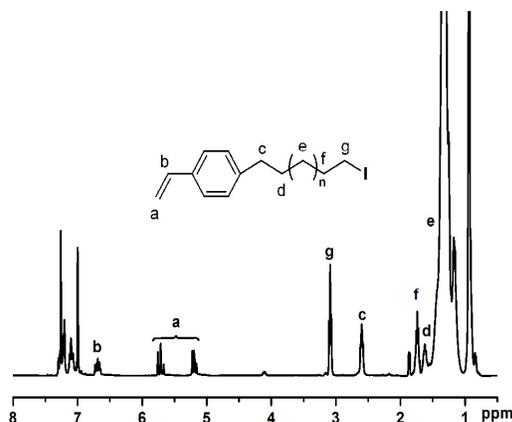
Figure 5 ^{1}H NMR spectrum of **R$_1$-PM-I**

The chain structure of **R$_1$-PM-I** (product 6) was confirmed by ^{1}H NMR spectrum. The characteristic resonances of styryl unit in the St-PM-I can be observed at 7.30-7.05 ppm(-phenyl-) and 6.60-6.77, 5.62-5.79, 5.11-5.28 ppm (-CH=CH$_2$). The resonance of the methylene group adjacent to the iodine group appeared at 3.09 ppm. And the triplet peak at 2.60 ppm was assigned to methylene protons next to the styryl group. Furthermore, by ^{13}C NMR analysis, the chemical shifts at 123.79 and 134.46 ppm indicated the presence of carbon atoms in carbon-carbon double bond. This result was also observed by FT-IR, the peak of C-I stretching vibration absorption had formed at 560 cm^{-1}. And the peaks at 1508 and 1601 cm^{-1} proved the existence of the benzene ring.
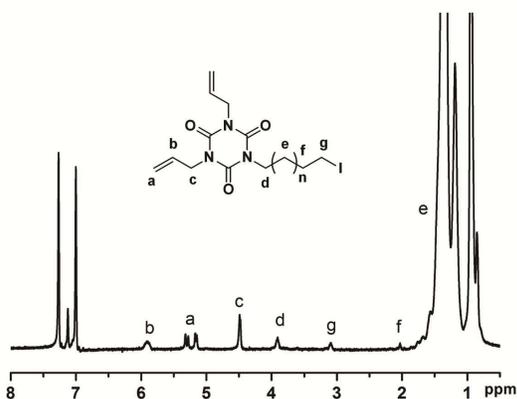
Figure 6 ^{1}H NMR spectrum of **R$_2$-PM-I**

The polymer **R$_2$-PM-I** (product 7) was analyzed by ^{1}H NMR spectroscopy (Figure 6). The triplet peak at 4.49 ppm was assigned to methylene protons next to the nitrogen atom (-CH$_2$N-). And the peak at 3.90 ppm was assigned to methylene protons next to the TAIC group (TAIC-CH$_2$-). The peak of methylene protons next to the iodine atom was assigned at 2.01 ppm (-CH$_2$-I). And FT-IR spectra showed that the peak of C-I stretching vibration absorption had formed at 560 cm^{-1}.

High functionalities (up to 100%) were obtained by a simple addition of I$_2$ (in toluene) after the polyhomologation

step. In addition, it was found to be necessary to add a small amount of sodium hydroxide, and limit the temperature (<20°C). Regardless of the temperature, FG-PM-I was only obtained in moderate yields (60%~70%) in the absence of sodium hydroxide which probably act as an efficient catalyst in the reaction of organoboranes with iodine.[60]

The ^{1}H NMR spectrum (Figure 7) feature signals corresponding to terminal group resonances, along with those assigned to protons of -CH$_2$S- and -N(CH$_2$CH$_3$)$_2$ of **R$_1$-PM-SC(S)NEt$_2$** (product 8). The integral ratio of signals at peak f and peak g is 1:3, the ideal ratio showed the successful synthesis of **R$_1$-PM-SC(S)NEt$_2$**. The integral ratio of peak at 3.6 ppm to peak f is 1:12.5, and this determined the functionalization rate (93%). The FT-IR spectrum of **R$_1$-PM-SC(S)NEt$_2$** revealed absorbance at 1413 cm^{-1}, which is characteristic of the dithiocarbamate C=S stretching mode. And the peaks at 1509 and 1602 cm^{-1} proved the existence of the benzene ring.
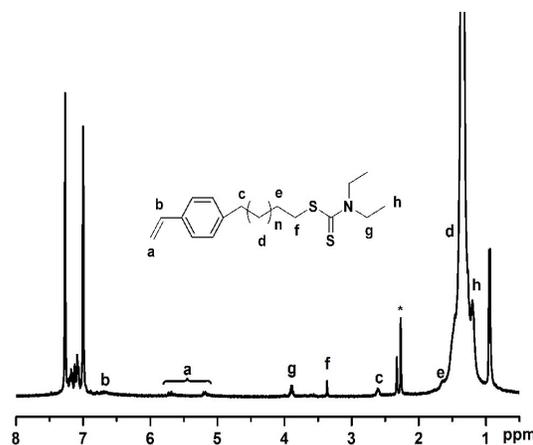
Figure 7 ^{1}H NMR spectrum of **R$_1$-PM-SC(S)NEt$_2$**
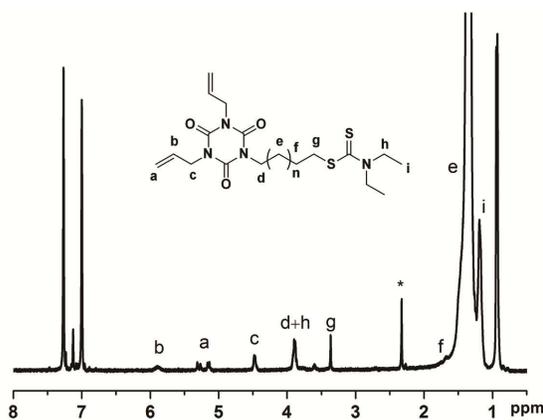
Figure 8 ^{1}H NMR spectrum of **R$_2$-PM-SC(S)NEt$_2$**

The characteristic peaks had indicated in the ^{1}H NMR spectrum of **R$_2$-PM-SC(S)NEt$_2$** (product 9, in Figure 8). The presence of a triplet at 3.36 ppm corresponds to a methylene adjacent to sulfur atom. The FT-IR spectrum revealed

absorbance at 1698 and 1319 cm^{-1}, which are characteristics of the C=O and C–N stretching mode. The integral ratio of peak at 3.6 ppm to peak g was 1:3.34. Although a good functionality was obtained (77%), the optimization of reaction and post-treatment conditions will be studied targeting higher functionality.

Conclusions

We have synthesized a series of α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities via a tandem strategy. Firstly, new organic boranes with one or two -CH=CH$_2$ groups were prepared by the hydroboration of DVB or TAIC using catecholborane and initiated in situ the polyhomologation of ylides. Subsequently, the post functionalization were carried out directly in the reaction system above-mentioned using end-capping reagents such as TAO, I$_2$ and tetraethylthiramdisulfide to achieve terminal -OH, -I and –SC(S)NEt$_2$, respectively, containing one or two -CH=CH$_2$ on the other chain end at the same time. The -COOH terminal groups was obtained by esterification of -OH with succinic anhydride. The terminal functionalities of 77-100% can be reached in different reaction system targeting various α,ω-telechelic polymethylenes. The molecular weights of the obtained polymers can be controlled in a broad range from 870 to 12,080 g/mol remaining narrow distribution (Đ = 1.04-1.12). Further research works on the functionalization via obtaining more functional groups (azide, amine, thiol, etc) and employing a variety of "click" reactions was expected to develop the categories of functional polymethylene-based homo-/co-polymers.

Acknowledgements

Notes and references

1   T. C. Chung, *Prog. Polym. Sci.*, 2002, 27, 39
2   J. Y. Dong, Y. L. Hu, *Coord. Chem. Rev.*, 2006, 250, 47
3   M. J. Yanjarappa, S. Sivaram, *Prog. Polym. Sci.*, 2002, 27, 1347
4   R. Godoy Lopez, F. D'Agosto, C. Boisson, *Prog. Polym. Sci.*, 2007, 32, 419
5   Y. L. Zhao, L. Wang, A. G. Xiao, H. J. Yu, *Prog. Polym. Sci.*, 2010, 35, 1195
6   M. Hong, Y. G. Li, B. X. Li, Y. S. Li, *Macromol. Rapid Commun.*, 2012, 33, 998
7   N. M. G. Franssen, J. N. H. Reek, B. de Bruin, *Chem. Soc. Rev.*, 2013, 42, 5809
8   C.-C. Chang, T. Emrick, *Macromolecules*, 2014, 47, 1344
9   J. D. Wang, J. H. Horton, G. J. Liu, Sun-Yeol Lee, K. J. Shea, *Polymer*, 2007, 48, 4123
10 J. Z. Chen, K. Cui, S. Y. Zhang, P. Xie, Q. L. Zhao, J. Huang, L. P. Shi, G. Y. Li, Z. Ma, *Macromol. Rapid Commun.*, 2009, 30, 532
11 J. Li, Q. L. Zhao, J. Z. Chen, L. Li, J. Huang, Z. Ma, Y. W. Zhong, *Polym. Chem.*, 2010, 1, 164
12 Y. Zhao, X. B. Shi, H. Y. Gao, L. Zhang, F. M. Zhu, Q. Wu, *J. Mater. Chem.*, 2012, 22, 5737
13 H. F. Zhang, N. Alkayal, Y. Gnanou, N. Hadjichristidis, *Chem. Commun.*, 2013, 49, 8952
14 X. Wang, J. P. Gao, Q. L. Zhao, J. Huang, G. L. Mao, W. Wu, Y. N. Ning, Z. Ma, *J. Polym. Sci. A: Polym. Chem.*, 2013, 51, 2892
15 H. F. Zhang, N. Hadjichristidis, *Macromolecules*, 2016, 49, 1590
16 J.-I. Imuta, N. Kashiwa, *J. Am. Chem. Soc.*, 2002, 124, 1176
17 S. G. Gaynor, *Macromolecules*, 2003, 36, 4692
18 R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Bertin, P. Tordo, *Macromolecules*, 2004, 37, 3540
19 R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gigmes, D. Bertin, *Macromol. Rapid Commun.*, 2006, 27, 173
20 I. German, W. Kelhifi, S. Norsic, C. Boisson, F. D'Agosto, *Angew. Chem. Int. Ed.*, 2013, 52, 3438
21 M. Ciftci, S. Norsic, C. Boisson, F. D'Agosto, Y. Yagic, *Macromol. Chem. Phys.*, 2015, 216, 958
22 R. Ribeiro, R. Ruivo, H. Nsiri, S. Norsic, F. D'Agosto, L. Perrin, C. Boisson, *ACS Catal.*, 2016, 6, 851
23 A. C. Gottfried, M. Brookhart, *Macromolecules*, 2003, 36, 3085
24 H. Makio, T. Fujita, *Macromol. Rapid Commun.*, 2007, 28, 698
25 S. Y. Li, Z. B. Ye, *Macromol. Chem. Phys.*, 2010, 211, 1917
26 T. D. Jones, C. W. Macosko, B. Moon, T. R. Hoye, *Polymer*, 2004, 45, 4189
27 G. Y. Li, M. A. Hillmyer, *Macromolecules*, 2011, 44, 3021
28 S. M. Kimani, S. J. Hardman, L. R. Hutchings, N. Clarke, R. L. Thompson, *Soft Matter*, 2012, 8, 3487
29 K. J. Shea, J. W. Walker, H. Zhu, M. Paz, J. Greaves, *J. Am. Chem. Soc.*, 1997, 119, 9049
30 X. Z. Zhou, K. J. Shea, *J. Am. Chem. Soc.*, 2000, 122, 11515
31 C. E. Wanger, J.-S. Kim, K. J. Shea, *J. Am. Chem. Soc.*, 2003, 125, 12179
32 C. E. Wanger, A. A. Rodriguez, K. J. Shea, *Macromolecules*, 2005, 38, 7286
33 J. Luo, K. J. Shea, *Acc. Chem. Res.*, 2010, 43, 1420
34 J. Luo, F. F. Lu, K. J. Shea, *ACS Macro Lett.*, 2012, 1, 560
35 R. B. Zhao, K. J. Shea, *ACS Macro Lett.*, 2015, 4, 584
36 M. A. Tasdelen, M. U. Kahveci, Y. Yagci, *Prog. Polym. Sci.*, 2011, 36, 455
37 W. T. Lin, H. Niu, T. C. Chung, J. Y. Dong, *J. Polym. Sci. A: Polym. Chem.*, 2010, 48, 3534
38 L. M. Pitet, M. A. Hillmyer, *Macromolecules*, 2011, 44, 2378
39 H. Makio, T. Ochiai, J.-I. Mahri, K. Takeda, T. Shimazaki, Y. Usui, S. Matsuura, T. Fujita, *J. Am. Chem. Soc.*, 2013, 135, 8177
40 Y. J. Zhang, H. Y. Li, J. Y. Dong, Y. L. Hu, *Polym. Chem.*, 2014, 5, 105
41 N. Alkayal, N. Hadjichristidis, *Polym. Chem.*, 2015, 6, 4921
42 Y. Li, Y. J. Zhang, Q. Li, H. Y. Li, S. R. Zheng, Y. L. Hu, *Macromol. Chem. Phys.*, 2015, 216, 569
43 S. Norsic, C. Thomas, F. D'Agosto, C. Boisson, *Angew. Chem. Int. Ed.*, 2015, 54, 4631
44 B. B. Busch, M. M. Paz, K. J. Shea, C. L. Sttaiger, J. M. Stoddard, J. R. Walker, X. Z. Zhou, H. Zhu, *J. Am. Chem. Soc.*, 2002, 124, 3636
45 K. J. Shea, *Chem. Eur. J.*, 2000, 6, 1113
46 C. E. Wagner, K. J. Shea, *Org. Lett.*, 2001, 3, 3063
47 J. Bai, K. J. Shea, *Macromol. Rapid Commun.*, 2006, 27, 1223
48 H. C. Brown, J. Chandrasekharan, *J. Org. Chem.*, 1983, 48, 5080
49 H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.*, 1971, 93, 1816
50 H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.*, 1975, 97, 5249
51 C. F. Lane, G. W. Kabalka, *Pergamon Press*, 1976, 32, 981
52 C. C. Chong, R. Kinjo, *ACS Catal.*, 2015, 5, 3238
53 K. Musikabhumma, T. P. Spaniol, J. Okuda, *J. Mol. Catal. A: Chem.*, 2003, 192, 223
54 Y. G. Li, Y. Q. Zhang, D. Yang, J. H. Hu, G. L. Lu, X. Y. Huang, *J. Polym. Sci. A: Polym. Chem.*, 2010, 48, 2084
55 Y. L. Cai, Y. Q. Tang, S. P. Armes, *Macromolecules*, 2004, 37, 9728
56 J. T. Xu, L. Tao, J. Q. Liu, V. Bulmus, T. P. Davis, *Macromolecules*, 2009, 42, 6893

RSC Advances Accepted Manuscript

57 G. David, C. Boyer, J. Tonnar, B. Ameduri, P. Lacroix-Desmazes, B. Boutevin, *Chem. Rev.*, 2006, 106, 3936

58 R. Briquel, J. Mazzolini, T. L. Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson, R. Spitz, *Angew. Chem. Int. Ed.*, 2008, 47, 9311

59 J. Mazzolini, I. Mokthari, R. Briquel, O. Boyron, F. Delolme, V. Monteil, D. Bertin, D. Gigmes, F. D'Agosto, C. Boisson, *Macromolecules*, 2010, 43, 7495

60 H. C. Brown, M. W. Rathke, M. M. Rogić, J. Am. Chem. Soc., 1968, 90, 5038

RSC Advances Accepted Manuscript

New Synthetic Strategy Targeting Well-defined α,ω-Telechelic Polymethylenes with Hetero Bi-/Tri-Functionalities via Polyhomologation of Ylides Initiated by New Organic Boranes Based on Catecholborane and Post Functionalization

Fang Xu,[a,b] Peng Dong,[a,b] Kun Cui,[b] Shi-Zheng Bu,[b] Jin Huang,[b] Guang-Yu Li,[b] Tao Jiang,[a,†] Zhi Ma[b,†]

Diverse well-defined α,ω-telechelic polymethylenes with hetero bi-/tri-functionalities were synthesized by a tandem strategy combining polyhomologation with post functionalization using end-capping reagents and esterification.