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Well-defined polyethylene molecular brushes by polyhomologation and ring opening metathesis polymerization

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A novel strategy using polyhomologation and ring opening metathesis polymerization (ROMP) has been developed for the synthesis of well-defined polyethylene (PE) molecular brushes. Polyhomologation was used to afford an OH-terminated PE, which after transformation to norbornyl PE macromonomer was submitted in ROMP. Kinetics of ROMP of PE macromonomer was studied by *in situ* ^{1}H NMR monitoring. The brush structure has been proved by HT-GPC, ^{1}H NMR and DSC results.

Access to well-defined (high degree of structural, molecular weight and compositional) polyethylenes (PEs) and PE-based copolymers is necessary in order to elucidate the structure-property relationships, which are very important to understand the behavior and improve the performance of one of the most important industrial polymer (PE).[1]

Recently, Shea developed a polymerization methodology leading to hydroxyl-terminated PE.[2] The general mechanism involves the formation of an organoboron zwitterionic complex between the ylide (monomer) and a trialkylborane (initiator) which break down by intermolecular 1,2-migration. As a consequence, the $-CH_2$ groups are randomly inserted one by one (C1 polymerization in contrast to the used C2 polymerization) into one of the three branches of the initiator leading to a 3-arm polymethylene (or polyethylene) star. The resulting star is subsequently oxidized/hydrolyzed to afford hydroxyl-end-capped linear PEs with low polydispersities.[2e] The end-functionalized PE can be used directly as initiator for the ring opening polymerization of cyclic esters[3] or transformed to atom transfer radical polymerization (ATRP)[4] and RAFT[5] macroinitiator to afford block copolymers.[6]

In a previous paper, we reported a novel one-pot methodology combining anionic polymerization and polyhomologation through a "bridge" molecule ($BF_3 \cdot OEt_2$) for the synthesis of PE-based block copolymers.[7] The macroanion, for example polystyrenyllithium, reacts with the coupling agent, "bridge" molecule, to afford a 3-arm star with boron function point which served as initiator for polyhomologation. The final product is an OH-PE-based block copolymer.

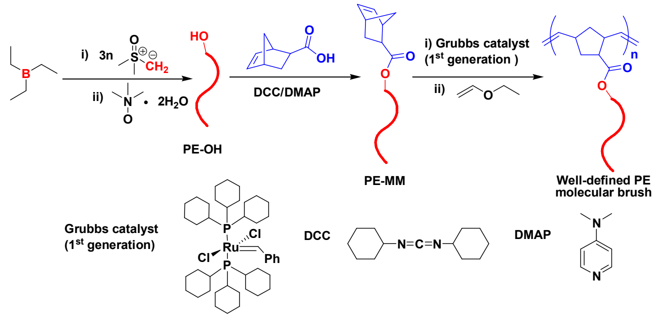
The narrow-distributed PEOH obtained by polyhomologation also provides possibility to construct more complex architectures such as well-defined molecular brushes which has not been reported so far. To synthesize well-defined molecular brushes, the "grafting through" strategy (also known as macromonomer strategy)[8] is a better choice than the other two methods of "grafting-from" and "grafting-onto" since ensures better control over both the backbone and branches.[9] Up to date, there were only a few examples dealing with the synthesis of (meth)acrylate-terminated PE macromonomer (PE-MM)[10] and their conventional free,[10a] atom transfer (ATRP)[10b, 10c] or nitroxide mediated (NMP)[10d] radical copolymerizations with common monomers mostly styrene and (meth)acrylates. For example, a methacrylate-terminated PE macromonomer synthesized by coordination polymerization and further end-group functionalization has been copolymerized with styrene by ATRP affording the corresponding comb-like copolymers.[10c]

Herein we report a "grafting through" strategy, for the first time, to synthesize well-defined PE-based polymacromonomers (molecular brushes) by combining polyhomologation and ROMP (Scheme 1). The ROMP of norbornyl PE-MM was chosen because of its excellent performance in the synthesis of molecular brushes due to the high polymerizability of norbornene moieties driven by the high ring strain.[11] Recently, this method has been employed to polymerize norbornyl-terminated syndiotactic polypropylene macromonomers.[12]

The general reactions for the synthesis of PE molecular brush are given in Scheme 1. First the hydroxyl-terminated PE was prepared by polyhomologation of dimethylsulfoxonium methylide using triethylborane as initiator followed by reaction of the PE-OH with *5*-norbornene-*2*-carboxylic acid. In a second step the norbornyl PE was polymerized by ROMP in the presence of Grubbs catalyst (1st generation).

As an example, the synthesis of PE_{1620}-MM is given. After esterification of the PE-OH with 5-norbornene-2-carboxylic acid, the high temperature gel permeation chromatography (HT-GPC) peak was slightly moved to high molecular weight range while keeping its narrow-dispersed profile (Figure S1). The successful esterification was confirmed by the characteristic absorption peak of the ester group at 1730 cm^{-1} in the FTIR (Fourier transform infrared spectroscopy) spectrum

(Figure S2). Furthermore, the ^{1}H NMR (nuclear magnetic resonance) chemical shift at δ = 3.5 ppm [-CH_2O-] (H_a) disappeared and a new peak at δ = 4.0 ppm [-CH_2OCO-] (H_a') corresponding to the ester group appeared proving the quantitative transformation from the hydroxyl to ester group (Figure 1). It should be noted that quantitative functionality is needed in order to avoid the purification of the norbornyl macromonomer from its precursor PE-OH, which is an extremely difficult procedure. Using the same method, two other norbornyl PEs have been also prepared (Table 1).



Scheme 1 General reactions for the synthesis of well-defined PE molecular brushes through "grafting through" strategy by combining polyhomologation and ROMP

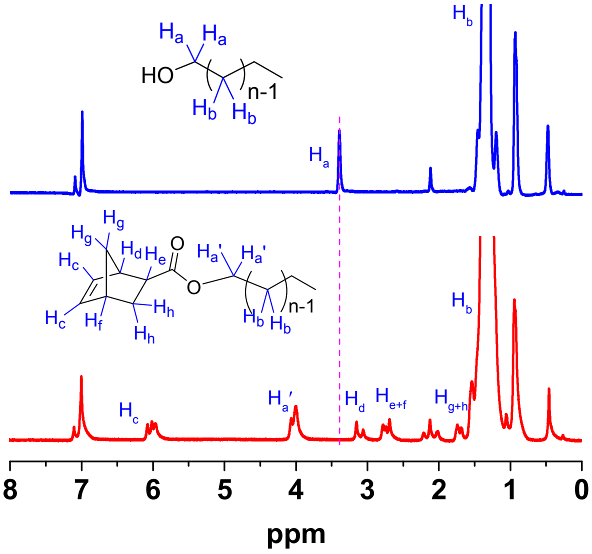


Figure 1 The quantitative transformation of PE_{1500}-OH to the PE_{1620}-MM confirmed by ^{1}H NMR results (toluene-*d8*, 80 °C)

The Grubbs catalyst (1st generation) was employed to initiate the ROMP of the norbornyl PE-MMs and thus to afford the corresponding PE molecular brushes. High conversions (≥95%) have been revealed by HT-GPC in all three PE-MMs (Table 1). As an example, Figure 2 showed HT-GPC traces of PE molecular brush of $Poly(PE_{760})_{63}$ (PDI = 1.18)

For the kinetics study, the polymerization of PE_{1620}-MM was carried out in a NMR tube using toluene-*d8* as solvent and monitored *in situ* by ^{1}H NMR (Figure 3, full spectra were shown in Figure S3). By adding catalyst, the cyclic vinyl protons peak (H_a) in PE-MM at δ = 5.9 - 6.1 ppm was decreasing and a new resonance peak appeared at δ = 5.2 - 5.7 ppm caused by the release of high ring strain of norbornene moiety indicating the ROMP process. The area ratios of these two peaks (H_a and H_a') were used to calculate conversions of the macromonomer. 90 min later, the polymerization was completed with a conversion of > 99%. The kinetic plots revealed a quasi linear relationship between Log$[M_0]/[M]$ and polymerization time (Figure S4).

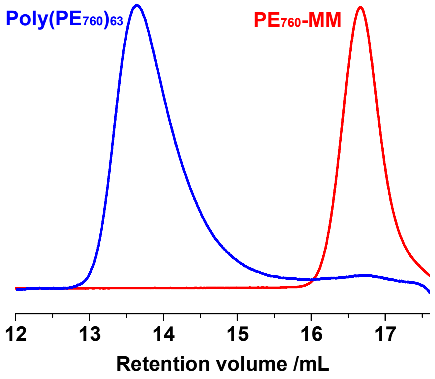


Figure 2 The successful ROMP of PE_{760}-MM resulting in well-defined PE molecular brush monitored by HT-GPC (TCB, 150 °C, the negative peaks caused by negative *dn*/*dc* of PE were shown in a positive style for better comparison)

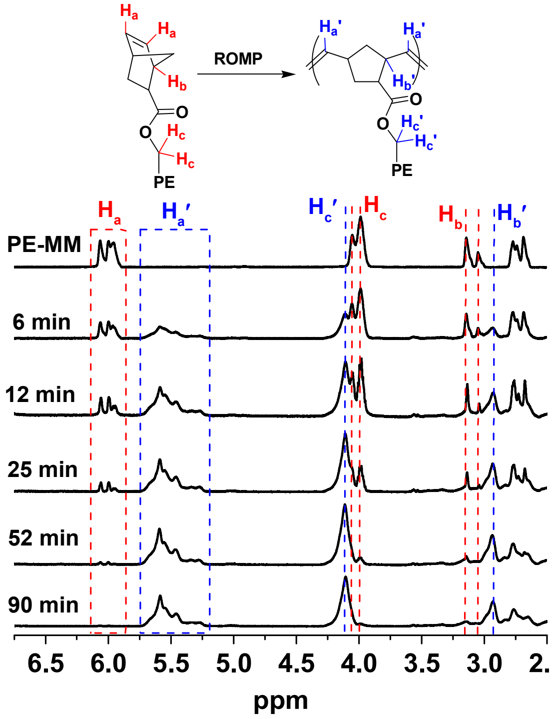


Figure 3 ROMP of norbornyl PE-MM monitored by *in situ* ^{1}H NMR (toluene-*d8*, 80 °C, PE_{1620}-MM : Grubbs 1st generation catalyst = 30 : 1 in mol, $c_{PE\text{-}MM}$ = 33 mg/mL)

All the PE molecular brushes showed much lower intrinsic viscosities than the corresponding linear PEs in solution calculated from Mark-Houwink-Sakurada equation (TCB, 150 °C) (Table 1 and Figure S5) due to their compact structure. Furthermore, the DSC measurements of the PE molecular brushes revealed a higher melting temperature (T_m) and lower crystallinity than the corresponding PE-MMs (Table 1 and Figure 4). It is assumed that the higher T_m is due to the double (span) molecular weight in the brush structure, since at this range of molecular weight the T_m is very sensitive. The lower crystallinity can be attributed to the difficulty of packing caused by the brush structure.

Table 1 PE molecular brushes synthesized by combining polyhomologation and ROMP

PE brushes[a]	PE-MM				PE molecular brushes									
	M_n[b] (g/mol)	PDI[c]	T_m[d] (°C)	X_c[e] (%)	$M_{n,theor.}$[f] (g/mol)	$M_{w,\ obs.}$[g] (g/mol)	PDI[g]	DP[h]	*Conv.*[i] (%)	dn/dc[j] (mL/g)	$IV_{Linear.}$[k] (dL/g)	IV_{brush}[j] (dL/g)	T_m[d] (°C)	X_c[e] (%)
Poly(PE_{760})$_{63}$	760	1.05	76.6	47.8	58 800	50 600	1.18	63	98	0.086	0.43	0.12	83.8	35.5
Poly(PE_{1350})$_{66}$	1 350	1.07	100.2	48.6	142 500	141 000	1.38	66	95	0.088	0.98	0.16	104.3	39.3
Poly(PE_{1620})$_{34}$	1 620	1.10	100.7	41.2	57 200	60 200	1.17	34	96	0.088	0.49	0.10	101.8	39.5
Poly(PE_{1620})$_{107}$	1 620	1.10	100.7	41.2	172 800	190 600	1.26	107	96	0.088	1.25	0.18	100.9	37.8

[a] The PE molecular brushes were named as Poly(PE_m)$_n$, where m referred the M_n of PE-MM and n was the average number of PE arms in each brush molecule; [b] M_n of PE-MM was calculated from ^{1}H NMR spectra (toluene-*d8*, 80 °C); [c] PDI of PE-MM was measured on HT-GPC calibrated by PS standards; [d] Determined by DSC (N_2 atmosphere, 10 °C/min, second heat cycle); [e] Calculated by $X_c = \Delta H_m/\Delta H_m^+$, where ΔH_m^+ of 288 kJ/kg was the specific enthalpy of melting for 100% crystalline PE;[13] [f] $M_{n\ theor.}$ was calculated by $w_{PE\text{-}MM} \times conv./n_{catalyst}$, where $w_{PE\text{-}MM}$ is the weight of PE macromonomer, *conv.* is the conversion of PE macromomer determined by HT-GPC, $n_{catalyst}$ is the amount of Grubbs catalyst in mole; [g] M_w and PDI of PE molecular brush were determined light scattering equipping with HT-GPC system; [h] DP was calculated from DP = $M_{w,\ PE\ brush}/(M_{n,\ PE\text{-}MM} \times PDI_{PE\text{-}MM})$; [i] Conversions were determined by the peak ratios in the HT-GPC curves (refractive index signal). The conversion calculated by NMR, Figure 3, is almost 100%. The difference from the conversion calculated by GPC is due to the formation of non-OH PEs during polyhomologation[2e], which are invisible by NMR (norbornene free chains) but visible by GPC (Figure S6); [j] Determined by HT-GPC equipped with LS, RI and viscometer detectors; [k] Calculated from the Mark-Houwink-Sakurada equation of $[\eta]_w = 6.61 \times 10^{-5} \times M_w^{0.81}$ which was determined from a linear PE standard (M_w = 131 100 g/mol, PDI = 1.20) by HT-GPC system (TCB, 150°C).

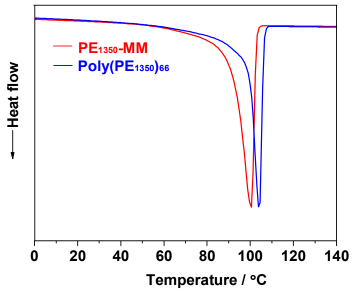


Figure 4 DSC curves of the PE_{1350}-MM and the corresponsive PE brush of Poly(PE_{1350})$_{66}$ (nitrogen atmosphere, 10 °C/min, second heat cycle)

In conclusion, by using polyhomologation and ROMP, a series of well-defined PE molecular brushes have been synthesized for the first time. The brush architecture has been proved by GPC, polymerization kinetics, intrinsic viscosity and DSC. This strategy opens a new horizon for the synthesis of well-defined PE-based brush *homo*(*co*)polymers with complex architectures such as multiblock, star, cyclic, *etc*.

Notes and references

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Electronic Supplementary Information (ESI) available: Experiments details, GPC curves and FTIP spectra of PE-OH and PE-MM, full ^{1}H NMR spectra of *in situ* measurement and Mark-Houwink-Sakurada plots can be found in Supplementary Information. See DOI: 10.1039/c000000x/

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