Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Polymer Chemistry RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received ,
Accepted

DOI: 10.1039/x0xx00000x

www.rsc.org/

Living cationic polymerization and polyhomologation: an ideal combination to synthesize functionalized polyethylene-polyisobutylene block copolymers

Hefeng Zhang,[a] Sanjib Banerjee,[b] Rudolf Faust[b]* and Nikos Hadjichristidis[a]*

[a] King Abdullah University of Science and Technology (KAUST), Division of Physical Sciences & Engineering, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal, 23955-6900, Kingdom of Saudi Arabia
[b] Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854, United States
Corresponding author, Email: nikolaos.hadjichristidis@kaust.edu.sa

A series of hydroxyl-terminated polyisobutylene-*b*-polyethylene (PIB-*b*-PE-OH) copolymers were synthesized by combining living cationic polymerization and polyhomologation. Allyl-terminated PIBs, synthesized by living cationic polymerization, were hydroborated with $BH_3\cdot THF$ to produce 3-arm boron-linked stars, PIB_3B, which served as macroinitiators for the *in situ* polyhomologation of dimethylsulfoxonium methylide. The resulting 3-arm star block copolymers, $(PIB\text{-}b\text{-}PE)_3B$, were oxidized/hydrolysed to afford PIB-*b*-PE-OH. Characterization of all intermediates and final products by high temperature gel permeation chromatography (HT-GPC) and proton nuclear magnetic resonance spectroscopy (^1H NMR) revealed the well-defined character of the copolymers. The thermal properties of the copolymers were studied by differential scanning calorimetry (DSC).

Introduction

Polyethylene (PE) is one of the most important polymeric materials with many applications in our daily life ranging from packaging to artificial joints and bulletproof vests. Although PE is an "old" polymer it is still challenging to synthesize well-defined PE-based polymeric materials in order to expand the applications.[1]

Polyhomologation, (alkyl)borane initiated polymerization of ylides, discovered by Shea et al, has emerged as a powerful methodology to synthesize well-defined PE-based materials.[2] This approach is achieved by two consequent steps: i) formation of an "ate" complex between the ylide (monomer) and the alkylborane (initiator), followed by ii) intramolecular 1,2-migration of the methylene groups from the ylide into the three alkyl branches of borane with the simultaneous elimination of dimethyl sulfoxide. After quantitative consumption of the ylide, a boron-linked PE 3-arm star is generated giving three linear hydroxyl-terminated PE chains by oxidation/hydrolysis. By using this chemistry, a series of well-defined linear, cyclic and star-like PEs have been synthesized, as well as some PE-based copolymers by combining polyhomologation with other living or controlled/living polymerization techniques.[2,3] For example, in our recent work, polyhomologation was successfully combined with anionic polymerization for the synthesis of narrow-dispersed PE-based block copolymers.[3a,4] In this strategy, a bridge molecule, "$BF_3\cdot OEt_2$", was used to quench the living polymeric anion and gave a boron linked 3-arm star which served as a macroinitiator for the *in situ* polyhomologation of the dimethylsulfoxonium methylide. The resulting star-like PE-based block copolymer afforded the linear block copolymer after oxidation and hydrolysis.

Polyisobutylene (PIB)-*b*-PE would be an interesting amorphous-crystalline block copolymer that would self-assemble in nonpolar medium. Accordingly, low molecular weight PIB-*b*-PE could have potential application as a wax crystallization modifier. In the present work, living cationic polymerization and polyhomologation were combined to synthesize hydroxyl-terminated polyisobutylene-*b*-polyethylene block copolymers (PIB-*b*-PE-OH).

Results and discussion

Allyl-terminated PIBs (PIB-allyls) were synthesized by living cationic polymerization followed by *in-situ* functionalization with allyltrimethylsilane (see experimental section, ESI).[5] All three PIB-allyls showed narrow and symmetric peaks in gel permeation chromatography (GPC) (Figure 1). The existence of terminal allyl group was confirmed by the characteristic chemical shifts at δ = ~5.9 and ~5.1 ppm of vinyl protons ($-C\boldsymbol{H}{=}C\boldsymbol{H}_2$) revealed by the proton nuclear magnetic resonance spectroscopy (^1H NMR) (Figure 2). Furthermore, the comparison of the area of these peaks to those at δ = 1.3-1.0 ppm of methyl protons ($-C\boldsymbol{H}_3$) was used to calculate the molecular weight of PIBs. The thermal properties studied by differential scanning calorimetry (DSC) indicated that, when the molecular weight of PIB is increased from 1070 to 3640 g/mol, the glass transition temperatures (T_g) increased from -87 to -70 °C (Figure 3). The small feature appeared in the DSC traces of $PIB_{2.7k}$ and $PIB_{3.6k}$ at around -40 °C is attributed to unstable baseline. The molecular characteristics of the three PIB-allyls were shown in Table 1.

Table 1. Molecular characteristics of PIB-allyls synthesized by living cationic polymerization

Sample	$M_{n\ RI}$ [a] (g/mol)	PDI[a]	$M_{n\ NMR}$ [b] (g/mol)	T_g [c] (°C)
$PIB_{1.1k}$-allyl	1040	1.24	1070	-87
$PIB_{2.7k}$-allyl	2670	1.22	2660	-74
$PIB_{3.6k}$-allyl	3750	1.24	3640	-70

[a] Determined by high temperature gel permeation chromatography (HT-GPC) (1,2,4-trichlorobenzene, 150 °C, PS standards, RI:

refractive index); [b.] Calculated from ^{1}H NMR spectra (toluene-d_8, 80 °C); [c.] Measured by DSC under nitrogen atmosphere (N_2) (10 °C/min, second heat cycle).

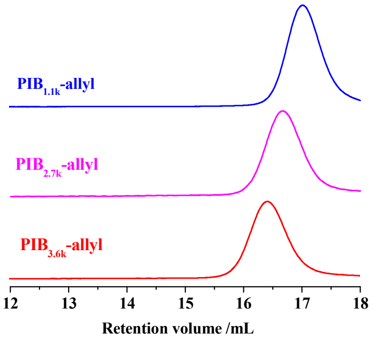


Figure 1. HT-GPC traces of the three PIB-allyls, synthesized by living cationic polymerization, in 1,2,4-trichlorobenzene at 150 °C. All peaks are negative but shown in positive style for better presentation

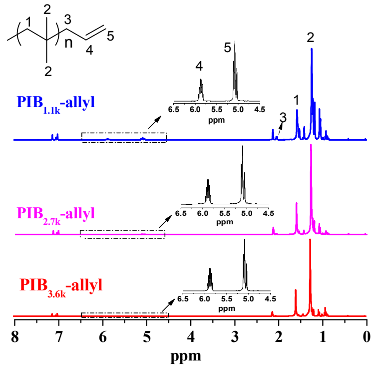


Figure 2. ^{1}H NMR spectra of the three PIB-allyls (toluene-d_8, 80 °C)

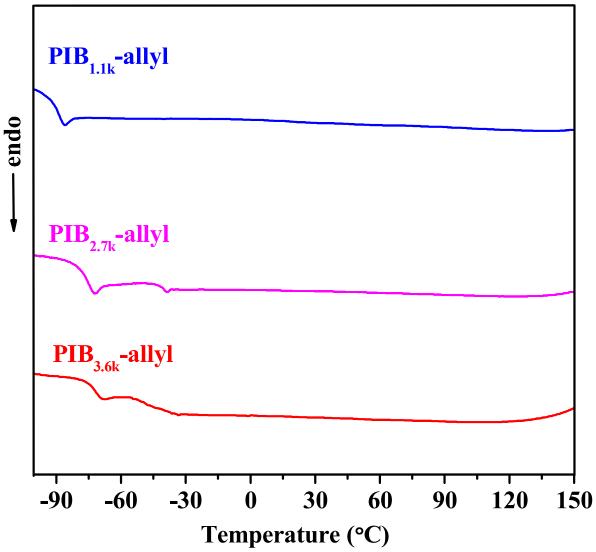
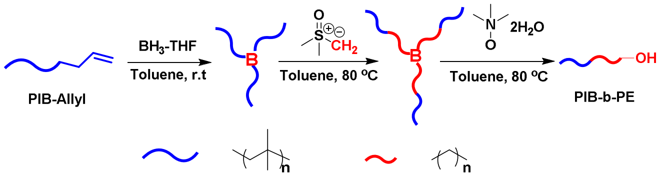


Figure 3. DSC traces of the three PIB-allyls (N_2, 10 °C/min, second heat cycle)

To synthesize the PIB-*b*-PE-OH copolymer, the PIB-allyl was hydroborated with BH_3·THF complex resulting in a boron-linked 3-arm star, $(PIB)_3B$. The borane moiety in the core served as a trifunctional initiator for the polyhomologation of dimethylsulfoxonium methylide (Scheme 1). After polyhomologation a $(PIB\text{-}b\text{-}PE)_3B$ 3-arm star was generated which by oxidation/hydrolysis afforded a linear diblock copolymer with a hydroxyl group at the chain-PE-end, PIB-*b*-PE-OH. It should be pointed out that a smaller than stoichiometric amount of BH_3·THF complex was used in order to avoid the presence of boron-hydrogen group (R_2BH or RBH_2) during polyhomologation. These boranes can also initiate the polyhomologation of the ylide leading to neat polyethylenes which are difficult to separate from PIB-*b*-PE-OH copolymers. As a result, the final product is a mixture of PIB-*b*-PE-OH and excess PIB-allyl. Moreover, the existence of impurities existing in PIB-allyl or introduced during the experiment could deactivate both BH_3·THF and alkylborane species formed during hydroboration. Consequently, fractionation is required to improve the purity of the final PIB-*b*-PE-OH. The crude product (mixture of PIB homopolymer and PIB-*b*-PE-OH) was dissolved in hot toluene giving a clear and transparent homogeneous solution. After cooling down to room temperature, the solution turned cloudy due to the aggregation of the PE block. The aggregated (precipitated) PIB-*b*-PE-OH was separated from the PIB solution by centrifugation.

Since boranes are very sensitive to air the amount of the macroinitiator PIB_3B is less than that calculated from the amount of BH_3·THF complex used, consequently the molecular weight of PE block is higher than expected. To exactly control the molecular weight of PE block, the real concentration of PIB_3B should be determined. A blank polyhomologation was performed to reveal the accurate concentration (see experimental section and Figure S1 and S2, ESI). Using the real concentration of the PIB_3B, a series of well-defined PIB-*b*-PE-OHs were synthesized with controlled molecular weights (Table 1).



Scheme 1. General reactions for the synthesis of PIB-*b*-PE-OH by combining living cationic polymerization and polyhomologation

The successful synthesis of PIB-*b*-PE-OHs was monitored by HT-GPC (Figure 4 and Figure S3-S4, ESI). Taking $PIB_{3.6k}$-*b*-$PE_{9.3k}$ as an example, after polyhomologation a new peak appears in the high molecular range in the GPC trace indicating the formation of PIB-*b*-PE-OH (Figure 4). The second peak at low molecular range corresponds to the excess/unreacted PIB which subsequently was completely removed by fractionation (Figure 4). By using the same fractionation process, all block copolymers were successfully purified (Figure S3 and S4 in ESI).

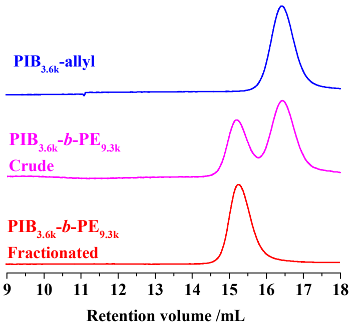


Figure 4. Monitoring the synthesis of $PIB_{3.6k}$-*b*-$PE_{9.3k}$ by HT-GPC in 1,2,4-trichlorobenzene at 150 °C. All peaks are negative but shown in positive style for better presentation

The successful synthesis was further demonstrated by ^{1}H NMR spectroscopy (Figure 5). Taking again the same polymer $PIB_{3.6k}$-*b*-

$PE_{9.3k}$ as an example it is clear that after hydroboration and polyhomologation, a new peak at δ = 1.37 ppm ($-CH_2-$) appeared indicating the formation of PE block. The complete disappearance of the terminal vinyl groups ($-C\boldsymbol{H}=C\boldsymbol{H}_2$) in PIB-allyl (peaks at δ = ~5.9 and ~5.1 ppm) also indicates the quantitative fractionation efficiency (Figure 5, left image). The molecular weight of the PE block was calculated from the ^1H NMR spectra (Figure 5, right image) by comparison of the peaks at δ = 1.25 ($-C\boldsymbol{H}_2-$) and 1.5 ppm ($-C\boldsymbol{H}_3$) of PIB block with the peaks at δ = 1.37 ppm ($-C\boldsymbol{H}_2-$) of PE block. The existence of the terminal hydroxyl group was clearly confirmed by the appearance of a new peak at δ = 3.39 ppm ($-C\underline{\boldsymbol{H}}_2-OH$). Similar results were found in all the PIB-*b*-PE-OH block copolymers (Figure S5 and S6, Table 2).

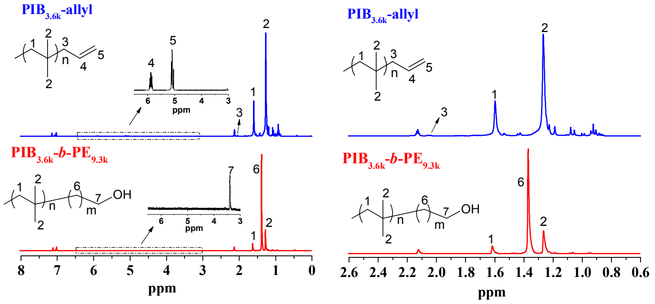


Figure 5. Monitoring the synthesis of $PIB_{3.6k}$-*b*-$PE_{9.3k}$ by ^1H NMR spectroscopy (toluene-d_8, 80 °C) (left: full spectra; right: after zooming)

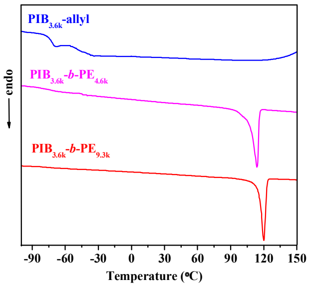


Figure 6. DSC traces of the $PIB_{3.6k}$-*b*-PEs (N_2, 10 °C/min, second heat cycle)

Table 2. Molecular characteristics of PIB-*b*-PE-OHs

Sample	$M_{theor.}$	$M_{n\,RI}$ [a] (g/mol)	PDI[a]	$M_{n\,NMR}$ [b] (g/mol)	T_g [c] (°C)	T_m [c] (°C)	X_c [c] (%)
$PIB_{1.1k}$-*b*-$PE_{1.8k}$	/[d]	3 300	1.28	2 800	-86	106.7	40.0
$PIB_{1.1k}$-*b*-$PE_{2.0k}$	3 200	3 050	1.50	3 000	-78	109.1	26.7
$PIB_{2.7k}$-*b*-$PE_{3.5k}$	/[d]	8 160	1.37	6 100	-76	115.4	30.1
$PIB_{2.7k}$-*b*-$PE_{6.1k}$	8 300	5730	1.21	8 760	-85	120.8	61.0
$PIB_{2.7k}$-*b*-$PE_{7.8k}$	10 000	12 870	1.42	10 400	-71	124.3	59.6
$PIB_{2.7k}$-*b*-$PE_{10.7k}$	13 000	9 480	1.30	13 360	-43	125.1	42.1
$PIB_{3.6k}$-*b*-$PE_{4.6k}$	/[d]	9 920	1.20	8 170	-77	113.8	42.4
$PIB_{3.6k}$-*b*-$PE_{9.3k}$	11 800	16 020	1.20	12 900	-74	120.0	54.8

[a] Determined by HT-GPC (1,2,4-trichlorobenzene, 150 °C, PS standards); [b] Calculated from ^1H NMR spectra (toluene-d_8); [c] Measured by differential scanning calorimetry (DSC) under nitrogen atmosphere (N_2) (10 °C/min, second cycle), the crystallinity degree (X_c) is calculated by using the equation of $X_c = \Delta H_m/(\Delta H_m^+ \times w_{PE})$, where ΔH_m^+ of 288 kJ/kg is the enthalpy of fusion of 100% crystalline PE,[6] and w_{PE} the weight ratio (%) of PE block calculated from ^1H NMR spectra; [d] Sample synthesized for determining the real concentration of macroinitiator, PIB_3B.

The thermal properties of the block copolymers PIB-*b*-PE-OHs were studied by DSC (Figure 6 and S7-S9, ESI). The peak corresponding to the melting temperature of PE block was found in all copolymers. Unsurprisingly, the T_m increases with the molecular weight of PE block. For example, $PIB_{3.6k}$-*b*-$PE_{9.3k}$ (120.0 °C) has a higher Tm than that of $PIB_{3.6k}$-*b*-$PE_{4.6k}$ (113.8 °C) as shown in Figure 6. On the other hand, the glass transition temperature of the PIB block is strongly influenced by the PE block giving an obscured transition between -90 and -70 °C (Figure S7, ESI). The irregular peaks at the range from -40 to -50 °C are attributed to the unstable baseline.

Conclusions

An efficient strategy combining living cationic polymerization and polyhomologation was developed to synthesize well-defined PIB-*b*-PE-OH block copolymers. The successful synthesis was confirmed by HT-GPC and ^1H NMR measurements and the thermal properties of the block copolymers were studied by DSC. This strategy opens routes for the synthesis of novel PE-based polymeric materials. In addition, the terminal hydroxyl group can be used to introduce more blocks by using appropriate polymerization techniques (ROP, ATRP, RAFT, etc) or coupling reactions (e.g. click and chlorosilane chemistry).

Notes

The experimental section as well as additional HT-GPC, ^1H NMR and DSC results can be found in supporting information.

References

1. Malpass, D. B. *Introduction to Industrial Polyethylene: Properties, Catalysts, and Processes.* **2010**, John Wiley & Sons, Inc. Hoboken, NJ, USA.
2. a) Shea, K. J.; Busch, B. B.; Paz, M. M. *Angew. Chem., Int. Ed.* **1998,** *37*, 1391-1393; b) Wagner, C. E.; Kim, J.-S.; Shea, K. J. *J. Am. Chem. Soc.* **2003,** *125*, 12179-12195; c) Shea, K. J.; Lee, S. Y.; Busch, B. B. *J. Org. Chem.* **1998,** *63*, 5746-5747; d) Luo, J.; Shea, K. J. *Acc. Chem. Res.* **2010,** *43*, 1420-1433; e) Busch, B. B.; Paz, M. M.; Shea, K. J.; Staiger, C. L.; Stoddard, J. M.; Walker, J. R.; Zhou, X.; Zhu, H. *J. Am. Chem. Soc.* **2002,** *124*, 3636-3646; f) C. E. Wagner, A. A. Rodriguez, K. J. Shea. *Macromolecules* **2005**, *38*, 7286-7291; g) J. M. Stoddard, K. J. Shea. *Organometallics* **2003**, *22*, 1124-1131; h) B. B. Busch, C. L. Staiger, J. M. Stoddard, K. J. Shea. *Macromolecules* **2002**, *35*, 8330-8337; i) Zhou, X.; Shea, K. J. *Macromolecules* **2001**, *34*, 3111-3114
3. a) Zhang, H.; Alkayal, N.; Gnanou, Y.; Hadjichristidis, N. *Macromol. Rapid Commun.* **2014,** *35*, 378-390; b) Li, Q.; Zhang, G.; Chen, J.; Zhao, Q.; Lu, H.; Huang, J.; Wei, L.; D'agosto, F.; Boisson, C.; Ma, Z. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 511-517; c) Yuan, C.; Lu, H.; Li, Q.; Yang, S.; Zhao, Q.; Huang, J.; Wei, L.; Ma, Z. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 2398-2405; d) Xue, Y.; Lu, H.; Zhao, Q.; Huang, J.; Xu, S.; Cao, S.; Ma, Z. *Polym. Chem.* **2013,** *4*, 307-312; e) Chen, J. Z.; Cui, K.; Zhang, S. Y.; Xie, P.; Zhao, Q. L.; Huang, J.; Shi, L. P.; Li, G. Y.; Ma, Z. *Macromol. Rapid Commun.* **2009,** *30*, 532-538.
4. Zhang, H.; Alkayal, N.; Gnanou, Y.; Hadjichristidis, N. *Chem. Commun.* **2013,** *49*, 8952-8954.
5. Ivan, B.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 89-104
6. B. Wunderlich, Macromolecular Physics II, Academic Press, New York, 1973

Table of Content

Living cationic polymerization and polyhomologation: an ideal combination to synthesize functionalized polyethylene-polyisobutylene block copolymers