Macromolecules

pubs.acs.org/Macromolecules Article

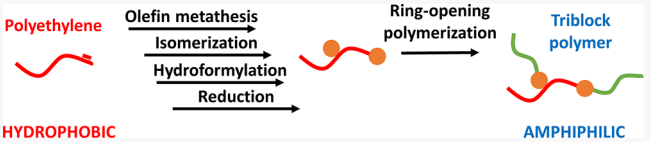
Polyethylene Containing Triblock Copolymers Synthesized by Post-polymerization Functionalization

Tianwei Yan and Damien Guironnet*

Cite This: *Macromolecules* 2020, 53, 4338−4344 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We report the synthesis of amphiphilic triblock copolymers containing a polyethylene block as the center block. The synthetic methodology consists of performing four consecutive post-polymerization reactions on polyethylene to yield a dihydroxyl-terminated polymer. First, a cross-metathesis reaction converts the olefinic end-group of the polyethylene into an α,β-unsaturated ester followed by isomerization of the double bond and then its hydroformylation. This sequence introduces an aldehyde group randomly distributed along the polymer backbone. Finally, the reduction of the aldehyde- and ester-functionalized polymer yields two terminal hydroxyl groups. The methodology was first established using low-molecular-weight model substrates before being performed on a polyethylene with a molecular weight of M_n = 13 kg mol^{-1}. The functionalized polyethylene was used to initiate the ring-opening polymerizations of ε-caprolactone and *tert*-butyl glycidyl ether to yield the corresponding triblock copolymers. Subsequent hydrolysis of the *tert*-butyl groups in the polyether yielded an amphiphilic polymer that formed micelles in water.

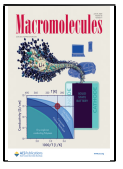


INTRODUCTION

Polyethylene (PE) and block copolymers are two important groups of polymeric materials. On the one hand, polyethylene is the ultimate example of a commodity material as it accounts for almost one-third of the total amount of polymer produced annually.[1−3] On the other hand, block copolymers are specialty materials that are produced on much smaller scales. The unique chemical structures of block copolymers result in characteristic mechanical properties that are unmatched by any other materials.[4−6] The development of living polymerization techniques has significantly simplified the synthesis of block copolymers, and thus, a myriad of research articles on block copolymers are published annually.[7,8] Despite the market dominance of polyethylene, only ∼2% of block copolymers reported in the literature in 2019 contained a polyethylene block.[9] This dissonance between the dominance of polyethylene and its under-representation as a component in block copolymers is the direct result of the difficulty of incorporating polyethylene into block copolymers. The incompatibility of most olefin polymerization catalysts toward functional groups is the cause of this difficulty.[10−12] To work around this barrier, the synthesis of most polyethylene-containing block copolymers in the literature uses monomers other than ethylene. Commonly used techniques to access polyethylene block copolymers include the ring-opening metathesis polymerization of cyclooctene or the anionic polymerization of butadiene, both followed by a post-polymerization hydrogenation step.[13,14] Recently, a new strategy of polyhomologation of ylides to synthesize polyethylene block copolymers has been developed.[15] Polyethylene-containing block copolymers synthesized from ethylene via an insertion polymerization pathway have also been reported. However, these are mostly limited to polyethylene-*block*-polyolefins (propylene or other α-olefins) due to the minimal chemical compatibility of the insertion polymerization catalyst, and only a very scarce number of polyethylene-containing block copolymers with polar blocks have been reported in the literature.[16−22]

Given the limited chemical compatibility of the olefin polymerization catalysts, the synthesis of amphiphilic block copolymer containing polyethylene requires the process to start with the synthesis of an end-group functionalized polyethylene. The telechelic polyethylene is then used as an initiator in a second polymerization (following a different polymerization mechanism) to yield the desired block copolymer. Living ethylene polymerization followed by the subsequent quenching of the reactive alkyl metal complex has been used to synthesize semi-telechelic polyethylene.[23−28] This technique is successful; however, a limited number of living insertion polymerization exist, and the process yields only one functionalized PE chain per metal alkyl group.[29] Two alternative strategies to synthesize larger quantities of semi-telechelic polyethylene are prevalent in the field: a direct synthesis approach, which involves the use of functionalized chain transfer agents during ethylene polymerization;[30−34] or

Received: March 18, 2020
Revised: April 29, 2020
Published: May 14, 2020



https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344

Scheme 1. Synthesis of Branched PCL-*block*-PE-*block*-PCL Triblock Copolymers

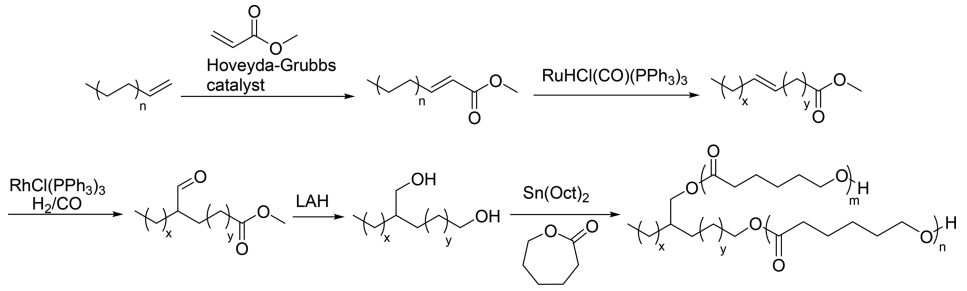


Table 1. Deconjugative Isomerization-Hydroformylation of Model Molecules[a]

model molecule	isomerization %	hydroformylation % with $RhCl(PPh_3)_3$[b]	hydroformylation % with $[Rh(COD)Cl]_2/NBu_3$[b]	hydrogenation %[c]
C8	81	81	83	18
C15	94	94	93	8

[a]Reaction conditions: 1.7 mol % Ru catalyst; 0.5 mol % Rh catalyst, 80 bar syngas, $CO/H_2 = 1$. [b]Total conversion compared from starting C8 or C15, determined by ^1H NMR. [c]Determined by GC.

an indirect synthesis approach, where the ethylene polymerization reaction yields polymer chains having one olefinic end-group (via β-X elimination or chain transfer to the monomer). A post-polymerization reaction converts the olefinic end-group into a more reactive end-group to be used to initiate the synthesis of a second block. The successful implementation of these two approaches has linked polyethylene to many types of polymers including polyesters, polystyrene, polyethers, and polyacrylates.[35−38] These two approaches, however, can only yield semi-telechelic polyethylene, which means that block copolymers can contain the polyethylene block positioned at the polymer chain ends. The requisite end placement of the polyethylene block is a limitation as other placements of the polyethylene block, such as in the center of the block copolymer, would expand the properties achievable by the block copolymer.[4,39,40]

We report a post-polymerization functionalization strategy that yields triblock polymers with the polyethylene located in the center of the macromolecules. The synthesis consists of four consecutive post-polymerization modifications on polyethylene to yield difunctionalized polyethylene. We established the precision of the PE functionalization using a polyethylene oligomer (M_n = 0.8 kg mol^{-1}) as a model substrate before performing the method on larger linear PE. The difunctionalized polyethylenes were ultimately used as macroinitiators for the polymerization of ε-caprolactone and *tert*-butyl glycidyl ether to yield amphiphilic triblock polymers.

RESULTS AND DISCUSSION

Our methodology to synthesize triblock polymer with a polyethylene block in the center consists of performing four consecutive post-polymerization reactions on polyethylene synthesized via an insertion polymerization mechanism. The first reaction is a cross-metathesis reaction of the PE olefinic end-group with an acrylate to introduce an α,β-unsaturated ester at one end of the polyethylene. We and others have previously implemented this technique to quantitatively functionalize polyolefins with molecular weights of up to 100 kg mol^{-1}.[36,41] This reaction converts a polyethylene molecule that initially contained a single functionality (olefin) into a molecule containing two conjugated functionalities (an olefin and an ester). Mecking et al. have recently reported tandem isomerization/alkoxycarbonylation on α,β-unsaturated ester functionalized low-molecular-weight amorphous polyethylene to yield a difunctionalized PE diol, which was subsequently used as a monomer in the step-growth polymerization.[41] Inspired by this work, we developed a tandem isomerization/functionalization strategy to synthesize semicrystalline dihydroxyl polyethylene (Scheme 1). We opted to employ a hydroformylation reaction for the introduction of a reactive end-group and initially focused our attention on the isomerization reaction.

Isomerization and Hydroformylation of Model Compounds. The deconjugative isomerization of α,β-unsaturated carbonyl functionalities is an active topic of research, and for the most part, the α,β-unsaturated carbonyl substrates employed are small molecules.[42−44] Transferring this knowledge to a polymeric substrate led us to postulate that we would not be able to control the location of the double bond after the isomerization reaction. We first probed the efficacy of the isomerization and hydroformylation reactions using low-molecular-weight model substrates. We used a commercially available methyl *trans*-2-octenoate (C8) and methyl 2-pentadecenoate (C15), synthesized through the cross-metathesis reaction of 1-tetradecene with methyl acrylate. These substrates have the same functionalities as the functionalized PE, but their low molecular weights make them compatible with characterization via gas chromatography (GC). Following a literature procedure using $RuHCl(CO)(PPh_3)_3$ as an isomerization precatalyst (1.7 mol %, Table 1), we accomplished the deconjugative isomerization of the α,β-unsaturated esters (Scheme 1).[45] The products of the isomerization reactions were analyzed by ^1H NMR spectroscopy and by GC (Table 1). The reactions were performed for varying lengths of time; however, after 6 h, no change in conversion was observed for either substrate. The presence of a non-negligible amount of unreacted starting material at maximum conversion is consistent with the reaction reaching its thermodynamic equilibrium.[46] The maximum conversion values reached are in good agreement with previously reported isomer distributions at equilibrium, with the isomerization of the shorter unsaturated ester achieving a lower maximum conversion than the longer one under the same reaction conditions (C8: 81% vs C15: 94%, Table 1).[46]

https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344

The products of the isomerization reactions were then subjected to a hydroformylation reaction to introduce an aldehyde functionality. An undesired but common side reaction of the hydroformylation reaction is the hydrogenation of the double bond.[47] This hydrogenation is especially dominant for α,β-unsaturated ester substrates.[48] In our study, this hydrogenation reaction would result in the formation of a monohydroxyl PE instead of the targeted dihydroxyl PE. Another common side reaction with hydroformylation is olefin isomerization, and therefore, attention was given to the regioselectivity of the hydroformylation. We probed two hydroformylation catalysts during this study (Wilkinson's catalyst and $[Rh(COD)Cl]_2/NBu_3$).

We first performed the hydroformylation on the α,β-unsaturated ester as a control experiment. This reaction yielded only minuscule amounts of aldehyde products for the C15 substrate, while a significant amount of the hydrogenation products was observed (66%).[49] Second, we performed the hydroformylation of the isomerized C8 and C15 substrates. The aldehyde contents, determined by GC and NMR, matched the conversion reached by the isomerization conversion (Table 1). These results suggest that the hydroformylation catalyst does not isomerize the double bond significantly as it would have resulted in the formation of the thermodynamically more stable α,β-unsaturated ester and its subsequent hydrogenation. The GC chromatograph of the hydroformylation product shows a large number of aldehyde products being formed (Figures S1 and S2). This result, combined with the chain-length-dependent thermodynamic equilibrium observed for the isomerization, infers a statistical distribution of the aldehyde groups along the alkyl chains. Finally, in an attempt to decrease the number of steps involved in the post-polymerization functionalization strategy, we used $[Rh(COD)Cl]_2/NBu_3$ to perform the tandem hydroformylation/hydrogenation and directly introduce a hydroxymethyl group into the polymer chains.[35] However, residual amounts of phosphine from the isomerization catalyst resulted in the in situ formation of Wilkinson's catalyst, and small amounts of alcohol were detected (<5%, Figure S4).

Overall, this study of the tandem isomerization and hydroformylation of α,β-unsaturated ester using low-molecular-weight substrates suggests that the isomerization reaction will be quantitative when applied to polyethylene. The yield of hydroformylation reaction also matches one of the isomerizations, suggesting that minor isomerization occurs during this step. Finally, this study demonstrates that the hydroxymethyl group introduced from the isomerization/hydroformylation/reduction will be randomly located along the polyethylene backbone.

Functionalization of Polyethylene. Three grades of semicrystalline polyethylene with different molecular weights, *l*-PE, *m*-PE, and *h*-PE, were synthesized and used as substrates (Table 2). Since we exclusively used ^{1}H NMR as a characterization technique to determine the yield of each reaction, we used the low-molecular-weight PE (*l*-PE) to establish the reaction conditions. The low molecular weight and thus higher end-group concentration of this grade enable a more precise determination of the conversion by ^{1}H NMR. The optimized reaction conditions are then directly transposed to medium- and high-molecular-weight PEs (*m*-PE and *h*-PE).

Table 2. Polyethylene Library

		% end-group[a]	
polyethylene grade	M_n (kDa[a])	vinyl	internal
l-PE	0.8	45	55
m-PE	3.3	70	30
h-PE	12.6	82	18

[a]Determined by ^{1}H NMR (d_2-TCE, 600 MHz, 110 °C).

All the three grades of linear polyethylene were first end-functionalized by an olefin cross-metathesis reaction following a reported procedure.[36] The deconjugative isomerization and hydroformylation were then applied to the end-functionalized PE to introduce the aldehyde functionality. Because of the significantly longer alkyl chain of the polymer in comparison to the previously implemented model compounds, we extended the reaction time for the isomerization to reach maximum conversion. At this point, the double bond is presumed to be randomly distributed along the chain. This assumption implies that the methyl groups present along the PE chain (~1 every 100 carbons) do not interfere in the isomerization reaction. The isomerization conversions were determined by NMR using the ratio between the conjugated methyl ester peak and the nonconjugated one ($-COOCH_3$, 3.77 vs 3.70 ppm). The conversion exceeded 95% for all three PE grades. This shift in resonance peaks is also consistent with the disappearance of the original conjugated olefinic proton chemical peaks (7.00 and 5.87 ppm) and the emergence of new resonances corresponding to 1,2-disubstituted olefinic protons (Figure 1, 5.36 to 5.54 ppm). Some small amounts of the trisubstituted olefinic group (5.14 to 5.21 ppm) were also detected (Scheme 2). These were attributed to the product from the methyl branches dispersed along the PE backbone.

The hydroformylation reaction was then performed to convert this isomerized olefin into an aldehyde functionality. The complete disappearance of the olefinic protons demonstrated that the reaction was run to completion for all PE grades (Figure 1). The comparison of the integral of the aldehyde proton (9.62 ppm) to the ester protons (3.70 ppm) suggests that the hydroformylation was quantitative and that little to no olefin hydrogenation occurred. Part of the aldehyde group appeared to have been hydrogenated into alcohol during the hydroformylation, resulting in a small peak at 3.58 ppm on the ^{1}H NMR spectra corresponding to a hydroxymethyl proton on the middle of the PE backbone. Finally, the ester introduced through the olefin metathesis reaction and the aldehyde introduced through the hydroformylation reaction were simultaneously reduced using lithium aluminum hydride (LAH) to yield the desired dihydroxyl polyethylene. The complete disappearance of the methyl ester and aldehyde protons establishes that the reduction reached completion. The product also showed new hydroxymethyl protons ($-CH_2OH$, δ = 3.68 and 3.58 ppm, Figure 1) that we attributed to the linear alcohol at one chain end (from the ester reduction) and the internal β-branched alcohol (from the aldehyde reduction), respectively. We performed this post-polymerization strategy on all three grades of PE. The overall yields for the three consecutive post-polymerization reactions were higher than 90% and reached 95% for the more challenging *h*-PE (Table 3). We noted that the molecular weights of the polymers determined by end-group analysis (^{1}H NMR) increased for each step of the post-polymerization functionalization. This increase was more significant for the low-molecular-weight PE than for the higher-molecular-weight PE (Table 3). We attributed this effect to the precipitations performed at each

https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344

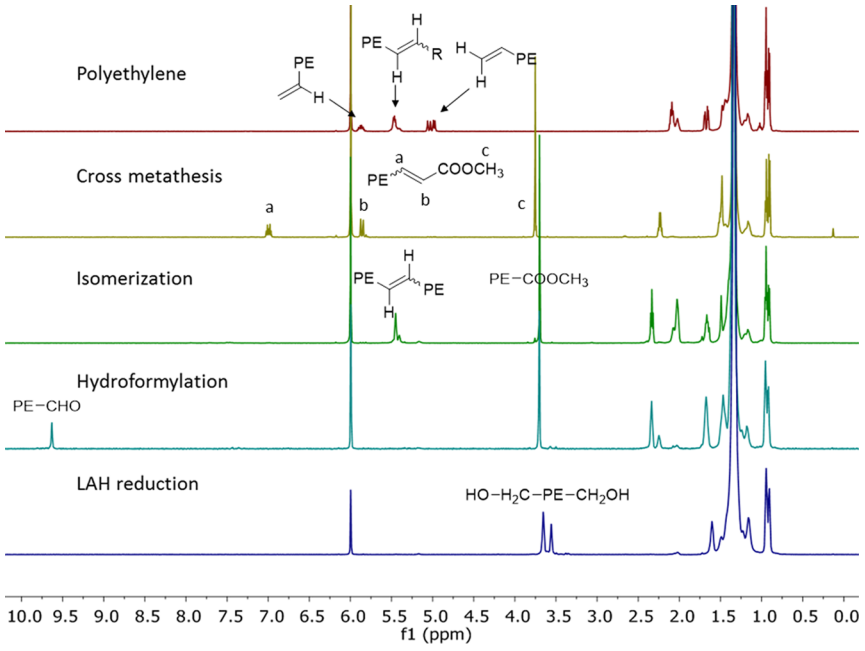


Figure 1. ^{1}H NMR spectra for the synthesis of the HO-PE-OH from l-PE branched triblock copolymer from *l*-HDPE (Table 3, *l*-PE, d_2-TCE, 600 MHz, 110 °C).

Scheme 2. Trisubstituted Internal Olefin Due to Methyl Branches on the PE Backbone

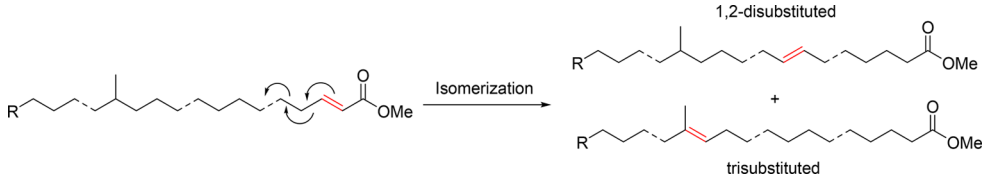


Table 3. Synthesis of Difunctionalized PE

polyethylene grade	parameter	starting PE	olefin metathesis	isomerization	hydroformylation	reduction
l-PE	% conv.		98	97	95	>99
	overall % conv.		98	95	90	90
	M_n (kg mol^{-1})	0.8	0.9	1.0	1.0	1.1
m-PE	% conv.		99	97	95	>99
	overall % conv.		99	96	91	91
	M_n (kg mol^{-1})	3.3	3.8	4.0	4.5	4.6
h-PE	% conv.		>99	>98	97	>99
	overall % conv.		>99	98	95	95
	M_n (kg mol^{-1})	12.6	13.0	13.1	13.6	13.9

Table 4. Ring-Opening Polymerization

polyethylene grade	starting PE M_n (kg mol^{-1})	monomer	monomer conversion %	theoretical M_n (kg mol^{-1})	experimental M_n (kg mol^{-1})[a]	$Đ$
l-PE	1.1	ε-CL	85	9.8	9.7 (12.5)	1.11
l-PE	1.1	*t*BuGE	98	23.1	23.5 (8.9)[b]	1.15
m-PE	4.6	ε-CL	45	10.8	9.3	n.d.
h-PE	13.9	ε-CL	48	25.5	19.6	n.d.

[a]Reaction conditions: xylenes, 105 °C, $[\varepsilon\text{-CL}]_o$ = 1 M, 0.2 equiv. of $Sn(Oct)_2$. Or toluene, 70 °C, $[t\text{BuGE}]_o$ = 2.4 M, 0.7 equiv. of KHMDS and 18-crown-6. Determined by ^{1}H NMR using end-group analysis. Values in parentheses are determined by GPC in THF versus polystyrene standards. [b]The discrepancy between the GPC and NMR values is attributed to the impossibility to identify the linker groups in the ^{1}H (see the Supporting Information for more details).

step of the process that inevitably result in the loss of some of the lowest-molecular-weight fractions of the distribution.

Ring-Opening Polymerization of Cyclic Ester and Ether. The PE diols were used as macroinitiators for the ring-opening polymerization of ε-caprolactone catalyzed by $Sn(Oct)_2$ and the ROP of glycidyl *tert*-butyl ether catalyzed by KHMDS.[26] These catalysts were selected for their temperature stability as the ROP requires to be performed at high

https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344

temperatures where the polyethylene macroinitiators are soluble. ^{1}H NMR spectroscopy of the isolated block copolymer showed full consumption of the macroinitiators with the disappearance of the PE hydroxymethyl signals from 3.4 to 3.8 ppm and the appearance of a single sharp triplet at 3.7 ppm corresponding to the PCL hydroxymethyl end-group (Figure S14). The degree of polymerization of the PCL blocks was determined using the PCL hydroxymethyl end-group and PCL repeat units. These values match the theoretical values based on ε-CL conversion and polymer loadings (Table 4) confirming that only a small amount of monofunctional PE was present in the reaction mixture (monofunctional PE-OH would result in a twice longer PCL block). GPC analysis of the block copolymers showed a bimodal distribution with a combined dispersity ($Đ$ = 1.11, Figure 2). Deconvolution of

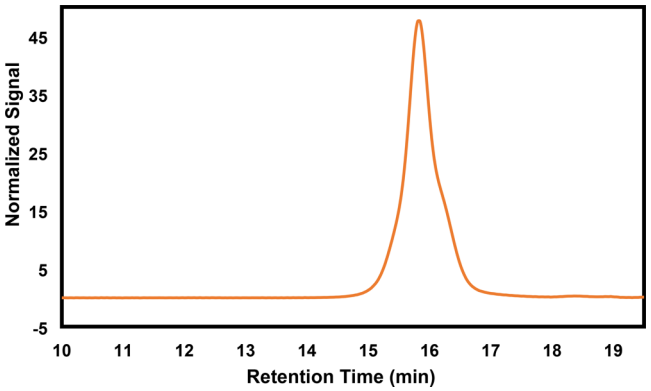
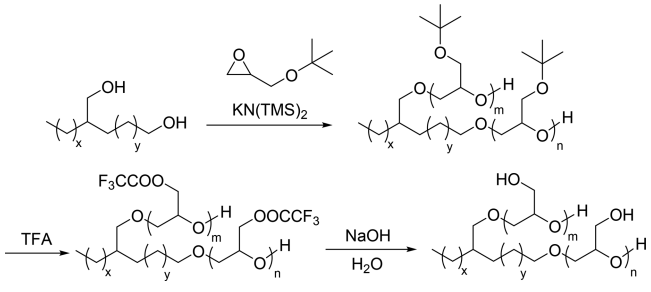


Figure 2. GPC trace for the ROP of ε-CL initiated by *l*-PE diol (xylenes, 105 °C, $[\varepsilon\text{-CL}]_o$ = 1 M, 0.2 equiv. of $Sn(Oct)_2$). M_n = 12.5 kg/mol, dispersity = 1.11.

the GPC traces suggests the presence of 10% diblock copolymer, which is consistent with the overall yield of the post-polymerization functionalization (Table 3, *l*-PE). The combination of NMR and GPC validates that we successfully synthesized triblock copolymers with PE as the center block.

Additionally, we performed the anionic ROP of *tert*-butyl glycidyl ether with *l*-PE diol to yield the corresponding poly(*tert*-butyl glycidyl ether)-*block*-poly(ethylene)-*block*-poly(*tert*-butyl glycidyl ether). The ROP was followed by a hydrolysis step to yield a water-soluble block copolymer (Scheme 3). The amphiphilic nature of the triblock copolymer was illustrated by its water solubility and the formation of large micelles in water (Z-average particle size ~310 nm).

Scheme 3. Synthesis of Poly(glycidol)-*block*-PE-*block*-poly(glycidol)



CONCLUSIONS

We have developed a post-polymerization functionalization strategy for the synthesis of polyethylene-containing triblock copolymers where the polyethylene is the central block. Our approach consists of first performing ethylene polymerization in the absence of any chain transfer agents to yield semicrystalline polyethylene having an olefinic end-group. We then introduced an α,β-unsaturated ester group at one end of the polymer using the olefin cross-metathesis reaction of this semi-telechelic polyethylene with an acrylate. The olefinic group of this α,β-unsaturated ester is then deconjugated (isomerization reaction) before undergoing hydroformylation to introduce an aldehyde functionality along the polymer backbone. Finally, the reduction of the aldehyde and ester groups yields a dihydroxyl functionalized polyethylene. This dihydroxyl functionalized polyethylene initiated the ROP of ε-caprolactone and *tert*-butyl glycidyl ether to produce triblock copolymers containing the polyethylene block in the center. Ultimately, the block copolymer synthesized with *t*BuGE was hydrolyzed to yield an amphiphilic polymer that forms micelles in water.

While this methodology consists of performing four consecutive reactions on the polyethylene starting material, the overall yield of the reaction is higher than 90% for the three grades of polyethylene used (PE with different molecular weights). The implementation of mostly catalytic reactions (at the exception of the reduction step) enables the synthesis of gram quantities of functional polyethylene at once.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00627.

Experimental procedures, NMR spectra, GC chromatogram, GPC chromatogram, and DLS profiles (PDF)

AUTHOR INFORMATION

Corresponding Author

Damien Guironnet − *Department of Chemical and Biomolecular Engineering, University of Illinois Urbana−Champaign, Urbana, Illinois 61801, United States;* orcid.org/0000-0002-0356-6697; Email: guironne@illinois.edu

Author

Tianwei Yan − *Department of Chemical and Biomolecular Engineering, University of Illinois Urbana−Champaign, Urbana, Illinois 61801, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.0c00627

Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Funding

The authors thank the NSF CBET 17-06911 for funding.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Major funding for the 500 MHz Bruker CryoProbe was provided by the Roy J. Carver Charitable Trust (Muscatine, Iowa; Grant #15-4521) to the School of Chemical Sciences NMR.

■ REFERENCES

(1) Shamiri, A.; Chakrabarti, M.; Jahan, S.; Hussain, M.; Kaminsky, W.; Aravind, P.; Yehye, W. The Influence of Ziegler-Natta and Metallocene Catalysts on Polyolefin Structure, Properties, and Processing Ability. *Materials* **2014**, *7*, 5069−5108.
(2) Baier, M. C.; Zuideveld, M. A.; Mecking, S. Post-Metallocenes in the Industrial Production of Polyolefins. *Angew. Chem., Int. Ed.* **2014**, *53*, 9722−9744.
(3) Stürzel, M.; Mihan, S.; Mülhaupt, R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116*, 1398−1433.
(4) Bates, C. M.; Bates, F. S. 50th Anniversary Perspective : Block Polymers—Pure Potential. *Macromolecules* **2017**, *50*, 3−22.
(5) Bates, F. S.; Fredrickson, G. H. Block Copolymer Thermodynamics: Theory and Experiment. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557.
(6) Bates, F. S.; Fredrickson, G. H. Block Copolymers—Designer Soft Materials. *Phys. Today* **1999**, *52*, 32−38.
(7) Coessens, V.; Pintauer, T.; Matyjaszewski, K. Functional Polymers by Atom Transfer Radical Polymerization. *Prog. Polym. Sci.* **2001**, 337−377.
(8) Braunecker, W. A.; Matyjaszewski, K. Controlled/Living Radical Polymerization: Features, Developments, and Perspectives. *Prog. Polym. Sci.* **2007**, *32*, 93−146.
(9) Number of Publications in 2019: Search 'Block Copolymer' and 'Block Copolymer AND Polyethylene NOT Oxide NOT Glycol' Respectively in Web of Science. Search Performed on 01/29/2020.
(10) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169−1204.
(11) Nakamura, A.; Ito, S.; Nozaki, K. Coordination−Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109*, 5215−5244.
(12) Chen, C. Designing Catalysts for Olefin Polymerization and Copolymerization: Beyond Electronic and Steric Tuning. *Nat. Rev. Chem.* **2018**, *2*, 6−14.
(13) Wang, Y.; Hillmyer, M. A. Polyethylene-Poly(L-Lactide) Diblock Copolymers: Synthesis and Compatibilization of Poly(L-Lactide)/Polyethylene Blends. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2755−2766.
(14) Martinez, H.; Ren, N.; Matta, M. E.; Hillmyer, M. A. Ring-Opening Metathesis Polymerization of 8-Membered Cyclic Olefins. *Polym. Chem.* **2014**, *5*, 3507.
(15) Alshumrani, R. A.; Hadjichristidis, N. Well-Defined Triblock Copolymers of Polyethylene with Polycaprolactone or Polystyrene Using a Novel Difunctional Polyhomologation Initiator. *Polym. Chem.* **2017**, *8*, 5427.
(16) Xu, J.; Eagan, J. M.; Kim, S.-S.; Pan, S.; Lee, B.; Klimovica, K.; Jin, K.; Lin, T.-W.; Howard, M. J.; Ellison, C. J.; et al. Compatibilization of Isotactic Polypropylene (IPP) and High-Density Polyethylene (HDPE) with IPP−PE Multiblock Copolymers. *Macromolecules* **2018**, *51*, 8585−8596.
(17) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining Polyethylene and Polypropylene: Enhanced Performance with PE/IPP Multiblock Polymers. *Science* **2017**, *355*, 814−816.
(18) Zhang, K.; Ye, Z.; Subramanian, R. Synthesis of Block Copolymers of Ethylene with Styrene and N-Butyl Acrylate via a Tandem Strategy Combining Ethylene "Living" Polymerization Catalyzed by a Functionalized Pd-Diimine Catalyst with Atom Transfer Radical Polymerization. *Macromolecules* **2008**, *41*, 640−649.
(19) Frauenrath, H.; Balk, S.; Keul, H.; Höcker, H. First Synthesis of an AB Block Copolymer with Polyethylene and Poly(Methyl Methacrylate) Blocks Using a Zirconocene Catalyst. *Macromol. Rapid Commun.* **2001**, *22*, 1147−1151.
(20) Atiqullah, M.; Hossain, M. M.; Kamal, M. S.; Al-Harthi, M. A.; Khan, M. J.; Hossaen, A.; Hussain, I. Crystallization Kinetics of PE-b-Isotactic PMMA Diblock Copolymer Synthesized Using SiMe2(Ind)-2ZrMe2 and MAO Cocatalyst. *AIChE J.* **2013**, *59*, 200−214.
(21) Desurmont, G.; Tanaka, M.; Li, Y.; Yasuda, H.; Tokimitsu, T.; Tone, S.; Yanagase, A. New Approach to Block Copolymerization of Ethylene with Polar Monomers by the Unique Catalytic Function of Organolanthanide Complexes. *J. Polym. Sci. Part A:Polym. Chem.* **2000**, *38*, 4095−4109.
(22) Song, X.; Yu, L.; Shiono, T.; Hasan, T.; Cai, Z. Synthesis of Hydroxy-Functionalized Cyclic Olefin Copolymer and Its Block Copolymers with Semicrystalline Polyolefin Segments. *Macromol. Rapid Commun.* **2017**, *38*, 1600815.
(23) Briquel, R.; Mazzolini, J.; Le Bris, T.; Boyron, O.; Boisson, F.; Delolme, F.; D'Agosto, F.; Boisson, C.; Spitz, R. Polyethylene Building Blocks by Catalyzed Chain Growth and Efficient End Functionalization Strategies, Including Click Chemistry. *Angew. Chem., Int. Ed.* **2008**, *47*, 9311−9313.
(24) Sita, L. R. Ex Uno Plures ("Out of One, Many"): New Paradigms for Expanding the Range of Polyolefins through Reversible Group Transfers. *Angew. Chem. Int. Ed.* **2009**, *48*, 2464−2472.
(25) Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **2013**, *113*, 3836−3857.
(26) Han, C. J.; Lee, M. S.; Byun, D. J.; Kim, S. Y. Synthesis of Hydroxy-Terminated Polyethylene via Controlled Chain Transfer Reaction and Poly(Ethylene-b-Caprolactone) Block Copolymer. *Macromolecules* **2002**, *35*, 8923−8925.
(27) Baier, M.; Wöll, D.; Mecking, S. Diffusion of Molecular and Macromolecular Polyolefin Probes in Cylindrical Block Copolymer Structures As Observed by High Temperature Single Molecule Fluorescence Microscopy. *Macromolecules* **2018**, *51*, 1873−1884.
(28) Chenal, T.; Olonde, X.; Pelletier, J. F.; Bujadoux, K.; Mortreux, A. Controlled Polyethylene Chain Growth on Magnesium Catalyzed by Lanthanidocene: A Living Transfer Polymerization for the Synthesis of Higher Dialkyl-Magnesium. *Polymer* **2007**, *48*, 1844−1856.
(29) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. Living Alkene Polymerization: New Methods for the Precision Synthesis of Polyolefins. *Prog. Polym. Sci.* **2007**, *32*, 30−92.
(30) Amin, S. B.; Marks, T. J. Versatile Pathways for in Situ Polyolefin Functionalization with Heteroatoms: Catalytic Chain Transfer. *Angew. Chem., Int. Ed.* **2008**, *47*, 2006−2025.
(31) Hyatt, M. G.; Guironnet, D. Silane as Chain Transfer Agent for the Polymerization of Ethylene Catalyzed by a Palladium(II) Diimine Catalyst. *ACS Catal.* **2017**, *7*, 5717−5720.
(32) Hyatt, M. G.; Guironnet, D. Introduction of Highly Tunable End-Groups in Polyethylene via Chain-Transfer Polymerization Using a Cobalt(III) Catalyst. *Organometallics* **2019**, *38*, 788−796.
(33) Kay, C. J.; Goring, P. D.; Burnett, C. A.; Hornby, B.; Lewtas, K.; Morris, S.; Morton, C.; McNally, T.; Theaker, G. W.; Waterson, C.; et al. Polyolefin−Polar Block Copolymers from Versatile New Macromonomers. *J. Am. Chem. Soc.* **2018**, *140*, 13921−13934.
(34) Wang, X.; Nozaki, K. Selective Chain-End Functionalization of Polar Polyethylenes: Orthogonal Reactivity of Carbene and Polar Vinyl Monomers in Their Copolymerization with Ethylene. *J. Am. Chem. Soc.* **2018**, *140*, 15635−15640.
(35) Yan, T.; Walsh, D. J.; Qiu, C.; Guironnet, D. One-Pot Synthesis of Block Copolymers Containing a Polyolefin Block. *Macromolecules* **2018**, *51*, 10167−10173.
(36) Walsh, D. J.; Su, E.; Guironnet, D. Catalytic Synthesis of Functionalized (Polar and Non-Polar) Polyolefin Block Copolymers. *Chem. Sci.* **2018**, *9*, 4703−4707.
(37) Goring, P. D.; Morton, C.; Scott, P. End-Functional Polyolefins for Block Copolymer Synthesis. *Dalton Trans.* **2019**, *48*, 3521.

https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344

(38) Keyes, A.; Alhan, H. E. B.; Ordonez, E.; Ha, U.; Beezer, D. B.; Dau, H.; Liu, Y.-S.; Tsogtgerel, E.; Jones, G. R.; Harth, E. Olefins and Vinyl Polar Monomers: Bridging the Gap for Next Generation Materials. *Angew. Chem., Int. Ed.* **2019**, *58*, 12370−12391.
(39) Xu, Y.; Thurber, C. M.; MacOsko, C. W.; Lodge, T. P.; Hillmyer, M. A. Poly(Methyl Methacrylate)-Block-Polyethylene-Block-Poly(Methyl Methacrylate) Triblock Copolymers as Compatibilizers for Polyethylene/Poly(Methyl Methacrylate) Blends. *Ind. Eng. Chem. Res.* **2014**, *53*, 4718−4725.
(40) Buggy, N. C.; Du, Y.; Kuo, M.-C.; Ahrens, K. A.; Wilkinson, J. S.; Seifert, S.; Coughlin, E. B.; Herring, A. M. A Polyethylene-Based Triblock Copolymer Anion Exchange Membrane with High Conductivity and Practical Mechanical Properties. *ACS Appl. Polym. Mater.* **2020**, *2*, 1294−1303.
(41) Liu, Y.; Dong, K.; Beller, M.; Mecking, S. Selective Long-Range Isomerization Carbonylation of a Complex Hyperbranched Polymer Substrate. *ACS Catal.* **2018**, *8*, 9232−9237.
(42) Sommer, H.; Juliá-Hernández, F.; Martin, R.; Marek, I. Walking Metals for Remote Functionalization. *ACS Cent. Sci.* **2018**, *4*, 153−165.
(43) Vasseur, A.; Bruffaerts, J.; Marek, I. Remote Functionalization through Alkene Isomerization. *Nat. Chem.* **2016**, *8*, 209−219.
(44) Romano, C.; Fiorito, D.; Mazet, C. Remote Functionalization of α,β-Unsaturated Carbonyls by Multimetallic Sequential Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 16983−16990.
(45) Wakamatsu, H.; Nishida, M.; Adachi, N.; Mori, M. Isomerization Reaction of Olefin Using RuClH(CO)(PPh3)3. *J. Org. Chem.* **2000**, *65*, 3966−3970.
(46) Witt, T.; Häußler, M.; Kulpa, S.; Mecking, S. Chain Multiplication of Fatty Acids to Precise Telechelic Polyethylene. *Angew. Chem., Int. Ed.* **2017**, *56*, 7589−7594.
(47) Franke, R.; Selent, D.; Börner, A. Applied Hydroformylation. *Chem. Rev.* **2012**, *112*, 5675−5732.
(48) Vilches-Herrera, M.; Domke, L.; Börner, A. Isomerization − Hydroformylation Tandem Reactions. *ACS Catal.* **2014**, *4*, 1706−1724.
(49) Tanaka, M.; Hayashi, T.; Ogata, I. Diphosphine−Rhodium Complex-Catalyzed Hydroformylation of α,β-Unsaturated Esters. *Bull. Chem. Soc. Jpn* **1977**, *50*, 2351−2357.

https://dx.doi.org/10.1021/acs.macromol.0c00627
Macromolecules 2020, 53, 4338−4344