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Highly Versatile Strategy for the Production of Telechelic Polyolefins

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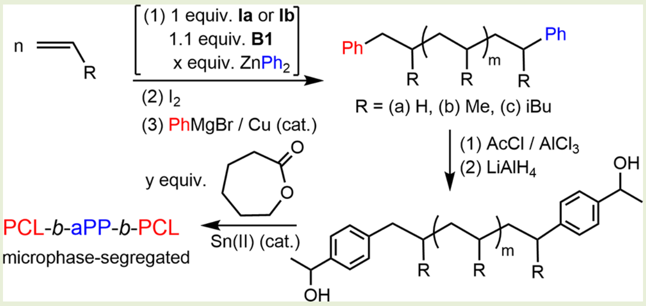
ABSTRACT: A general and versatile synthetic strategy for producing practical quantities of a wide range of phenyl-group-terminated hetero- and homotelechelic semicrystalline polyethenes and amorphous atactic and semicrystalline isotactic poly(α-olefins) is reported. The phenyl groups serve as synthons for functionalities of additional classes of telechelic polyolefins that can be "unmasked" through simple high yielding postpolymerization reactions. A demonstration of the value of these materials as building blocks for structural classes of polyolefin-based synthetic polymers was provided by syntheses of well-defined polyolefin-polyester di- and triblock copolymers that were shown to adopt microphase-segregated nanostructured mesophases in the condensed phase.



Polyolefins are the most widely produced class of polymers worldwide, valued for their low cost and wide range of accessible material properties.[1] At over 250 million metric tons produced globally each year, it is also remarkable that the existing large variety of types and "grades" of polyolefins all come from a very small set of industrially relevant olefin monomers through continuous advances made with transition-metal catalysts, polymerization processes, and reactor designs for tailoring the molar mass, molar mass distribution (MMD), tacticity, and copolymer composition, to name a few.[2] On the downside, the ubiquity and importance of polyolefins to society has now been a large contributor to the increasing global plastic waste problem.[3] In response, there is a critical need for the design and development of "next generation" polyolefins that are more amenable to chemical and mechanical recycling or that can aid in the processing of combined plastic waste streams by serving as blend compatibilizers and property modifiers.[4] For this purpose, telechelic polyolefins, which possess reactive functionalities at each of the polymer chain ends, are an ideal target for potentially providing access to well-defined block copolymers that are comprised of two or more dissimilar block domain types. Unfortunately, in contrast to well-established categories of telechelic polymers obtained through step-growth polymerization (e.g., polyesters, polyamides, and polyurethanes), the polymer science and technology of telechelic polyolefins are surprisingly still largely unexplored areas.[5] Ideally, a general strategy for obtaining telechelic polyolefins should be able to provide control over (1) molar mass, (2) MMD, as defined by the breadth, skewness, and modality (e.g., monomodal, bimodal, or multimodal), (3) tacticity, with this parameter ranging from being stereorandom (i.e., atactic) to highly stereoregular (e.g., isotactic), (4) a broad structural scope of polymerizable olefin monomers, (5) a highly versatile range of end-group functionalities, and most importantly, (6) the ability to generate practical quantities of these telechelic polyolefin products from readily available and inexpensive reagents and standard reactor and polymerization techniques.[6−8] Indeed, finding a viable solution to the challenge of meeting *all of these goals* for the production of telechelic polyolefins is so difficult that, to the best of our knowledge, it has never been achieved.[9−15] Herein, we now report a general and highly versatile strategy for the production of semicrystalline telechelic α,ω-bis(phenyl)-terminated polyethene and either amorphorus, atactic or semicrystalline, isotactic α,ω-bis-(phenyl)-terminated poly(α-olefins) via (stereomodulated) living coordinative chain transfer polymerization (LCCTP) using a group 4 metal ion-pair initiator, and excess equivalents of diphenylzinc (ZnPh$_2$) as a chain transfer agent (CTA), followed by reactive quench with molecular iodine (I$_2$) and Cu-catalyzed phenylation according to Scheme 1. We further demonstrate that the phenyl group in these polyolefins can serve as a synthon for an extensive array of different functionalities that can be "unmasked" by industrially relevant, high-yielding transformations, such as the electrophilic aromatic substitution and reduction chemistry reported in the present study. Finally, the synthetic utility of these new classes of telechelic polyolefins is established through the synthesis of well-defined polyolefin-*block*-poly(ε-caprolactone)

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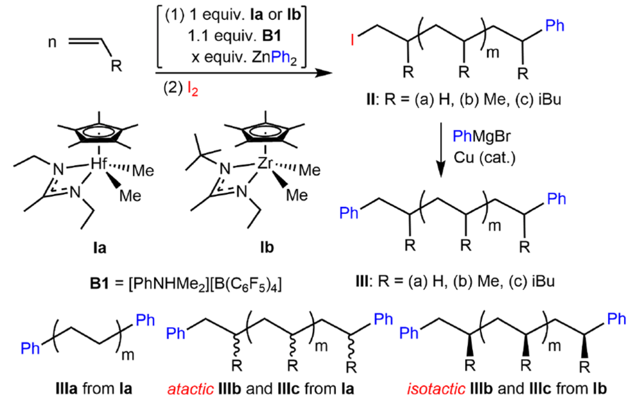
Scheme 1. Production of Hetereotelechelic α-Iodo, ω-Phenyl-Terminated (II) and Homotelechelic α,ω-Bis(phenyl)-Terminated (III) Polyolefins



di- and triblock copolymers that adopt different microphase-segregated periodic mesophases in the condensed phase.

The Sita group has previously reported extensively on the (stereomodulated) living coordinative chain transfer polymerization (LCCTP) of ethene, propene, higher-carbon-numbered linear and branched α-olefins and α,ω-nonconjugated dienes to produce a wide variety of new classes of polyolefins with tunable DP$_n$, dispersity $Đ$, and MMD profile.[2b,16] As presented in Scheme 1, this LCCTP process utilizes a cyclopentadienyl, amidinate (CPAM) group 4 metal complex of the general formula, $(\eta^5\text{-C}_5\text{R}_5)[(N,N)\text{-}\kappa^2\text{-N(R}^1)\text{C(R}^2)\text{N(R}^3)]\text{M(CH}_3)_2$ (M = Zr, Hf) (**I**), as a preinitiator that is "activated" in situ with a stoichiometric equivalent of the dimethylanilinium borate, $[\text{PhNH(CH}_3)_2][\text{B(C}_6\text{F}_5)_4]$ (**B1**), to generate an ion-pair initiator. In the presence of excess equivalents of a main-group-metal alkyl, such as diethylzinc (ZnEt$_2$) or triethylaluminum (AlEt$_3$), serving as a chain transfer agent (CTA), polymerization proceeds through rapid and reversible polymeryl group (chain) transfer between a population of active transition-metal propagating species and a much larger population of main-group-metal "surrogate" chain growth centers. Under the condition where the magnitudes of the rate and rate constant for reversible chain transfer, ν_{CT} and k_{CT}, are much greater than those for propagation through migratory insertion at the transition metal center, ν_p and k_p, respectively, all the active and surrogate species appear to undergo chain growth at the same rate. As such, all the desired features of a living polymerization process can still be achieved.[17,18] However, the scalability of providing practical quantities of new polyolefin materials through LCCTP is now largely dependent on the cost associated with the relatively inexpensive main-group-metal CTA being employed that, in the case of ZnEt$_2$ and AlEt$_3$, are available in commodity (rail car) volumes. Most importantly, upon reactive quenching with molecular iodine (I$_2$), LCCTP can provide a quantitative yield of the corresponding iodo-terminated polyolefin product, which can then be used as a precursor to a much greater spectrum of end-group functionalized polyolefins (x-PAOs) via well-established and high yielding synthetic transformations.[19]

Although reactive quenching of LCCTP provides a means by which to place a functional group on the terminating end of the polymer chain, this still leaves open the question of how best to establish another functional group at the initiating end for production of either hetereotelechelic ($\alpha \neq \omega$) or homotelechelic ($\alpha = \omega$) α,ω-difunctional polyolefins. Conceivably, this goal could be accomplished by employing a CTA bearing a functional group; however, given the highly reactive nature of the transition-metal initiator and propagating species involved in LCCTP, viable choices for the design and synthesis of such functionalized main-group organometallics are severely limited.[20] Hence, as a general synthetic strategy for the production of telechelic polyolefins, we sought a CTA that would not only be chemically compatible, but that further meets the requirements of being readily (commercially) available, structurally well-defined, highly efficient in reversible chain transfer, and highly versatile in providing access to a range of end-group functionality. Toward this goal, we have recently reported that a stoichiometric excess of commercially available ZnPh$_2$ can be used as a highly effective CTA in the LCCTP of a wide variety of α-olefin monomers to provide the corresponding phenyl-terminated poly(α-olefins).[21] In this report, we now document that ZnPh$_2$-mediated LCCTP can be extended as a general strategy for the scalable production of the hetereotelechelic α-iodo, ω-phenyl-terminated and homotelechelic α,ω-bis(phenyl)-terminated polyolefins, **II** and **III**, respectively, according to Scheme 1 and the results of Table 1.

To begin, in a preliminary investigation of the LCCTP of ethene using the CPAM hafnium dimethyl complex **Ia** in combination with **B1** to form the initiator and excess equivalents of either ZnEt$_2$ or diisopropylzinc [Zn(iPr)$_2$] as CTA, polymerizations were performed at 25 °C and quenched with an acidic workup upon observation of initial precipitation of PE from solution.[16b] In the present work, we have now determined that an optimum yield and an increase in the range of accessible M_n (DP$_n$) values for **IIa** are obtained at the elevated temperature of 50 °C when using ZnPh$_2$ as CTA under otherwise identical conditions (cf. run 1, Table 1: M_n = 1.0 kDa, $Đ$ = 1.20, yield = 3.9 g).[22] The level of phenyl group termination in this sample of **IIa** was determined to be 99% by ^{1}H NMR (800 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C)

Table 1. Hetereotelechelic Polyolefins (II) Obtained by LCCTP Using ZnPh$_2$ as CTA and Reactive Quench with I$_2$[a]

run	II	I	M[b] (equiv)	ZnPh$_2$[d] (equiv)	yield (g)	M_n[e] (kDa)	$Đ$[e]	T_g[f] (°C)	T_m[f] (°C)	*mmmm*[g] (%)
1	I-PE-Ph (**IIa**)	**Ia**	E (nd)[c]	20	3.9	1.0	1.20	nd	102	
2	I-aPP-Ph (***a*-IIb**)	**Ia**	P (nd)[c]	40	11.8	14.0	1.08	−7		nd
3	I-aPMP-Ph (***a*-IIc**)	**Ia**	4M1P (713)	10	4.3	6.2	1.08	19		nd
4	I-iPP-Ph (***i*-IIb**)	**Ib**	P (nd)[c]	5	4.3	9.9	1.30	−10	100	55
5	I-iPP-Ph (***i*-IIb′**)	**Ib**	P (nd)[c]	10	3.5	4.9	1.18	−16	71	36
6	I-iPMP-Ph (***i*-IIc**)	**Ib**	4M1P (1188)	10	1.4	11.2	2.23	18	219	nd

[a] For details of polymerization conditions for each run, see SI. [b] E = ethene, P = propene, 4M1P = 4-methyl-1-pentene. [c] Gaseous monomer held constant at 5 psi. [d] Relative to **I**. [e] Determined by GPC using polystyrene standards (1,2,4-trichlorobenzene, 135 °C for **IIa** and **IIc**; THF, 40 °C for **IIb**). [f] Determined by DSC. [g] Determined by ^{13}C{^{1}H} NMR (200 MHz, 1,1,2,2-tetrachloroethane-d_2, 90 °C).

spectroscopy, which when compared to the theoretical value, confirms the high effectiveness of ZnPh$_2$ as a CTA in which both phenyl groups participate in exchange with the transition-metal initiator or propagator. High temperature size exclusion chromatography (HT-SEC) provided further support for the living character of this LCCTP process by revealing a narrow, monomodal MMD with a *Đ* value of 1.20.[22]

Given the C_s-symmetric nature of **Ia**, propagation with an α-olefin monomer (i.e., R ≠ H) has previously been shown to proceed in a stereorandom fashion, and reactive quenching with I$_2$ is accordingly expected to provide a high yield of the corresponding atactic α-iodo, ω-phenyl poly(α-olefin) product ***a*-II** of Scheme 1.[16,19] The results presented in Table 1 for runs 2 and 3 confirmed this expectation with proof of the production of atactic α-iodo, ω-phenyl polypropene (I-aPP-Ph, ***a*-IIb**) and atactic α-iodo, ω-phenyl poly(4-methyl-1-pentene) (I-aPMP-Ph, ***a*-IIc**) when propene and 4-methyl-1-pentene were, respectively, employed as the α-olefin monomer.[22] In each case, a very narrow and monomodal MMD was established by ambient-temperature SEC, while ^{13}C NMR spectroscopy confirmed an atactic microstructure that renders these materials amorphous with only a glass transition temperature, T_g, being observed by differential scanning calorimetry (DSC; see Table 1).[22,23]

As further detailed with the results of runs 4 and 5 of Table 1, we also now report the first example of stereomodulated LCCTP of propene that was achieved using varying excess equivalents of ZnPh$_2$ as a CTA in combination with the chiral (racemic) C_1-symmetric CPAM zirconium dimethyl complex **Ib** as preinitiator and the borate **B1** as co-initiator (see Scheme 1).[24] More specifically, under LCCTP conditions, rapid and reversible chain transfer that occurs between the two enantioforms of the transition-metal propagating species and the main-group-metal surrogates serves to introduce a level of incorporation of racemic (*r*) dyad stereoerrors as a function of the relative rates of chain transfer vs stereoselective (isoselective) propagation.[16e,g,23,24] Hence, an increase in the initial ZnPh$_2$/**Ib** ratio should lead to a decrease in both M_n and %*mmmm*, which is observed (cf. run 4 vs run 5, Table 1). Note also that the magnitude of %*mmmm* has a direct impact on the melting transition temperature, T_m, of the two different ***i*-IIb** and ***i*-IIb′** products. Finally, to round out this initial set of heterotelechelic polyolefins, the stereoselective LCCTP of 4-methyl-1-pentene (4M1P) as the α-olefin monomer using excess equivalents of ZnPh$_2$ as CTA and the **Ib**/**B1** initiator combination was conducted to provide an excellent yield of α-iodo, ω-phenyl-terminated isotactic poly(4-methyl-1-pentene) (***i*-IIc**) according to run 6 of Table 1. Curiously, both the SEC and HT-SEC determined MMD of this material is uncharacteristically broad and multimodal with a *Đ* value of 2.23 (see Figure S100), even though this LCCTP is living by all other criteria. We currently believe that this feature is an artifact arising from incomplete solubilization of the highly crystalline iPMP within the limited solvents that can be used in this analytical method. Isotactic poly(4-methyl-1-pentene) (iPMP) is a commercially important high-melting thermoplastic with a T_m of 250 °C that has been known for some time since first being reported by Natta and co-workers in 1956.[25,26] However, in spite of this and the fact that 4M1P is readily available through alkali-metal-catalyzed dimerization of inexpensive propene, the synthesis and systematic investigation of other stereochemical grades of PMP have been surprisingly almost absent from the literature.[27] Recently, the Sita group has shown the value of end-group functionalized aPMP for providing the amorphous hydrophobic domain of amphiphilic sugar−polyolefin conjugates that adopt thermotropic canonical double gyroid and noncanonical Frank-Kasper A15 and σ phases in the condensed state.[19a,c,d] It is of some interest, therefore, to explore the properties and synthetic utility of heterotelechelic and telechelic PMP of varying stereoregularity in the future.

With respect to the goal of telechelic polyolefins, as noted previously, the phenyl end group is attractive as a synthon that can be used to expand the range of end-group functionality through a host of postpolymerization processes. Accordingly, we sought to establish the high-yielding conversion of the hetereotelechelic polyolefins **II** into the corresponding α,ω-bis(phenyl)-terminated homotelechelic products **III**. As shown in Scheme 2 and Table 2, this goal was easily achieved in each case through Cu-catalyzed phenylation of the iodo end group using commercial phenyl magnesium halide (Grignard) reagents in tetrahydrofuran (THF) or toluene solution at an elevated temperature.[22,28] In this preliminary investigation, only the synthesis and characterization of Ph-PE-Ph (**IIIa**), atactic Ph-aPP-Ph (***a*-IIIb**), isotactic Ph-iPP-Ph (***i*-IIIb**), atactic Ph-aPMP-Ph (***a*-IIIc**), and isotactic Ph-iPMP-Ph (***i*-IIIc**) are being reported, but there is no conceivable limitation on extending this methodology to a much broader range of telechelic poly(α-olefins). It is also important to point out here that, in the case of telechelic **IIIa**, each polymer chain is symmetric with respect to possessing two identical benzyl (PhCH$_2$) end groups. In contrast, for any telechelic poly(α-olefin), such as **IIIb** and **IIIc**, the two benzylic carbon atoms are now differentiated, with the initiating one being tertiary due to originating from 1,2-migratory insertion of monomer, while the terminating one is secondary as the result of phenylation (see Scheme 1).[29] While this structural difference between the two benzylic positions is not anticipated to have any significant effect on the rate of electrophilic substitution of the aromatic rings, it is possible that one could make use of this fact to develop selective orthogonal transformations of one benzylic position over the other in the future. Finally, identical benzyl end groups for **III** would presumably arise if noncommercially available dibenzylzinc (ZnBn$_2$) is employed as the CTA, and we are investigating this hypothesis.

Scheme 2. Synthesis of Acetophenone-Terminated (IV and VI) and Benzylalcohol-Terminated (V and VII) Polyolefins

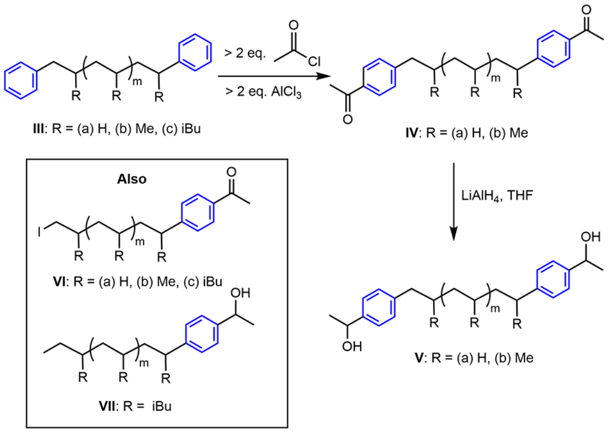


Table 2. Telechelic Polyolefins, III–V, and Hetereotelechelic Polyolefins, VI and VII, via Postpolymerization Reactions[a]

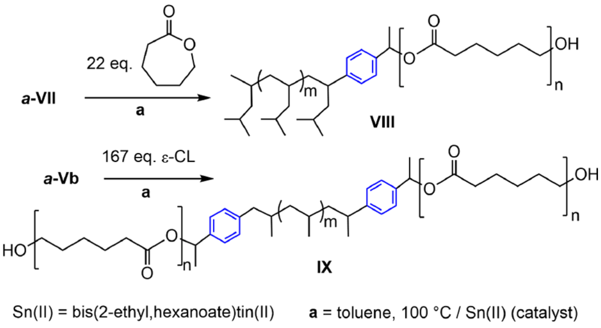
initial[b]	reagents	final[b]	% yield	M_n[c] (kDa)	Đ[c]	T_g[d] (°C)	T_m[d] (°C)
I-PE-Ph (**IIa**)	PhMgCl	Ph-PE-Ph (**IIIa**)	>99	1.0	1.18	nd	104
Ph-PE-Ph (**IIIa**)	AcCl/$AlCl_3$	AcPh-PE-PhAc (**IVa**)	99	0.8	1.30	nd	107
AcPh-PE-PhAc (**IVa**)	$LiAlH_4$	HOBn-PE-BnOH (**Va**)	>99	0.8	1.27	nd	110
I-aPP-Ph (***a*-IIb**)	PhMgBr	Ph-aPP-Ph (***a*-IIIb**)	88	14.0	1.08	−6	
Ph-aPP-Ph (***a*-IIIb**)	AcCl/$AlCl_3$	AcPh-aPP-PhAc (***a*-IVb**)	95	13.6	1.11	−9	
AcPh-aPP-PhAc (***a*-IVb**)	$LiAlH_4$	HOBn-aPP-BnOH (***a*-Vb**)	>99	13.7	1.11	−7	
I-iPP-Ph (***i*-IIb**)	PhMgBr	Ph-iPP-Ph (***i*-IIIb**)	61	9.8	1.30	−10	98
Ph-iPP-Ph (***i*-IIIb**)	AcCl/$AlCl_3$	AcPh-iPP-PhAc (***i*-IVb**)	>99	6.9	1.43	−10	101
AcPh-iPP-PhAc (***i*-IVb**)	$LiAlH_4$	HOBn-iPP-BnOH (***i*-Vb**)	>99	7.6	1.45	−7	102
I-iPP-Ph (***i*-IIb′**)	PhMgBr	Ph-iPP-Ph (***i*-IIIb′**)	76	5.1	1.21	−16	72
Ph-iPP-Ph (***i*-IIIb′**)	AcCl/$AlCl_3$	AcPh-iPP-PhAc (***i*-IVb′**)	>99	4.2	1.27	−12	65
AcPh-iPP-PhAc (***i*-IVb′**)	$LiAlH_4$	HOBn-iPP-BnOH (***i*-Vb′**)	98	4.0	1.64	−9	73
I-aPMP-Ph (***a*-IIc**)	PhMgBr	Ph-aPMP-Ph (***a*-IIIc**)	88	5.5	1.20	28	
I-iPMP-Ph (***i*-IIc**)	PhMgBr	Ph-iPMP-Ph (***i*-IIIc**)	81	12.7	3.84	19	219
I-PE-Ph (**IIa**)	AcCl/$AlCl_3$	I-PE-PhAc (**VIa**)	97	0.9	1.23	nd	105
I-aPP-Ph (***a*-IIb**)	″	I-aPP-PhAc (***a*-VIb**)	96	14.5	1.07	−7	
I-iPP-Ph (***i*-IIb**)	″	I-iPP-PhAc (***i*-VIb**)	98	8.9	1.33	−9	96
I-iPP-Ph (***i*-IIb′**)	″	I-iPP-PhAc (***i*-VIb′**)	>99	4.0	1.30	−18	70
I-aPMP-Ph (***a*-IIc**)	″	I-aPMP-PhAc (***a*-VIc**)	>99	5.9	1.10	14	
I-iPMP-Ph (***i*-IIc**)	″	I-iPMP-PhAc (***i*-VIc**)	97	12.1	2.28	21	218
I-aPMP-PhAc (***a*-VIc**)	$LiAlH_4$	aPMP-BnOH (***a*-VII**)	>99	6.3	1.20	26	

[a] For experimental details of each transformation, see the SI. [b] AcPh = p-C_6H_4–C(O)CH_3, BnOH = p-C_6H_4–CH(OH)CH_3. [c] Determined by SEC using polystyrene standards (1,2,4-trichlorobenzene, 135 °C for **IIa** and **IIc**; THF, 40 °C for **IIb**). [d] Determined by DSC.

Friedel–Crafts (FC) acylation of phenyl side chains of polystyrene using acetyl chloride (AcCl) in combination with aluminum trichloride ($AlCl_3$) as a Lewis acid catalyst has previously been reported as a strategy for introducing *para*-acetophenone groups [AcPh = p-C_6H_4-C(O)CH_3].[29] As Scheme 2 and the results of Table 2 further reveal, similar FC acylation of the series of *α*,*ω*-bis(phenyl)-terminated telechelics, **IIIa**, ***a*-IIIb**, and ***i*-IIIb**, proceeded with near quantitative yield in each case to correspondingly provide AcPh-PE-PhAc (**IVa**), AcPh-aPP-PhAc (***a*-IVb**), and AcPh-iPP-PhAc (***i*-IVb** and ***i*-IVb′**) [AcPh = p-C_6H_4-C(O)CH_3]. All these telechelic polyolefins were then reduced in high yield using lithium aluminum hydride ($LiAlH_4$) in THF to provide the respective telechelic *α*,*ω*-bis(benzylalcohol)-terminated polyolefins, HOBn-PE-BnOH (**Va**), HOBn-aPP-BnOH (***a*-Vb**), and HOBn-iPP-BnOH (***i*-Vb** and ***i*-Vb′**) [BnOH = p-C_6H_4–C(OH)CH_3] according to Scheme 2. It is notable that the trends in T_m values for each of the telechelic polypropenes within the two series of different isotacticity remain constant (cf., last column of Table 2 for ***i*-IIIb** to ***i*-Vb** and ***i*-IIIb′** to ***i*-Vb′**). As a final consideration, we were interested in determining if FC acylation could also be successfully carried out with the heterotelechelic *α*-iodo, *ω*-phenyl-terminated polyolefins, **IIa–c**, and this proved to be the case as the results of Table 2 attest. In this regard, the observed high degree of chemical inertness of the iodo functional group of **II** to the FC acylation reaction conditions was unexpected, but it might now also provide the foundation for synthetic transformations leading to other classes of hetereotelechelic polyethene and poly(*α*-olefins). Finally, the iodo terminal group can be easily removed by hydride reduction using $LiAlH_4$ as demonstrated with the conversion of I-aPMP-PhAc (***a*-VIc**) to aPMP-BnOH (***a*-VII**) according to the last row of Table 2 and Scheme 2.

With a variety of end-group functionalized (x-PAO), heterotelechelic (y-PAO-x), and homotelechelic polyolefin (x-PAO-x) precursors now available in practical quantities, we were interested in determining their synthetic utility for the design and production of well-defined amphiphilic di- and triblock copolymers, and specifically, those that might undergo microphase segregation.[30] Toward this end, there is considerable interest in the development of polyethene-*block*-poly(*ε*-caprolactone) (PE-*b*-PCL) block copolymers that can potentially serve as compatibilizers for polyethene/polyester blends.[31] Since these previous materials possess two different types of semicrystalline block domains, in the present work, we sought to increase the knowledge base by pursuing the synthesis and characterization of the thermotropic phase behavior of well-defined PAO-*b*-PCL block copolymers that incorporate an amorphous, atactic poly(*α*-olefin) domain of varying T_g value. Scheme 3 presents syntheses of the di- and triblock copolymers, aPMP-*b*-PCL (**VIII**) and PCL-*b*-aPP-*b*-PCL (**IX**) that were achieved through the Sn(II)-catalyzed ring-opening polymerization of excess equivalents of *ε*-caprolactone using aPMP-BnOH (***a*-VII**) and HOBn-aPP-BnOH (***a*-Vb**), respectively, as macroinitiators. Characterization of these materials using a suite of analytical and

Scheme 3. Synthesis of Polyolefin-*block*-poly(*ε*-caprolactone) Di- and Triblock Copolymers



spectroscopic tools confirmed, among other things, the expected structural composition, molar mass, MMD, block mole fractions, and thermal phase transitions (cf., for **VIII**: M_n = 7.1 kDa, $Đ$ = 1.26. f_{PCL} = 0.24, T_g = 16 °C, T_m = 87 °C; and for **IX**: M_n = 23.5 kDa, $Đ$ = 1.36, f_{PCL} = 0.35, T_g = −4 °C, T_m = 54 °C).[22] Importantly, as presented in Figure 1, the immiscible nature of the PAO and PCL block domains manifest in strong microphase-segregated morphologies in the condensed phase with periodic nanostructures that are consistent with the PCL mole fraction (f_{PCL}).[30] Thus, for **VIII**, a body centered cubic (BCC) spherical mesophase is observed in sub-100 nm-thick ultrathin films by phase-sensitive tapping mode (ps-tm) AFM, and within the bulk by variable temperature small-angle-X-ray-scattering (VT-SAXS), with scattering peaks appearing at q/q^* = 1, $\sqrt{2}$, and $\sqrt{3}$ (q^* = 0.056 Å^{-1}) for a domain spacing of 11.1 nm at 100 °C (see Figure 1a–c). In contrast, for **IX** with a slightly larger f_{PCL} value, the ps-tm AFM of a sample annealed at 200 °C for 18 h and then rapidly quenched in liquid N_2 now revealed a "fingerprint" surface morphology for ultrathin films that is consistent with either a lamellar (LAM) mesophase with the lamellae oriented perpendicular to the surface,[19b] or a hexagonally packed cylindrical (HEX) mesophase in which the cylinders are aligned parallel to the surface (see Figure 1e).[32]

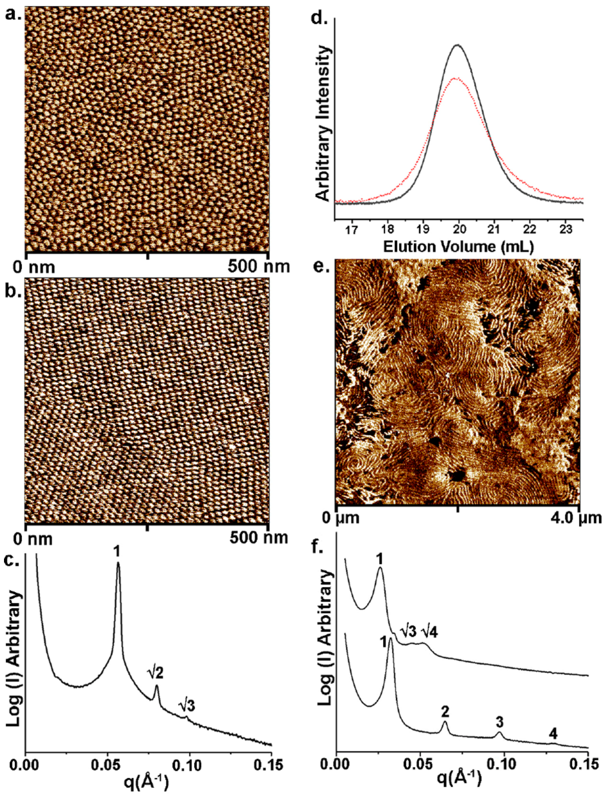


Figure 1. (a) ps-tm AFM phase map of "as cast" from toluene of a 60 nm thick film of the aPMP−PCL diblock **VIII** on a carbon-coated Si (c-Si) substrate. (b) ps-tm AFM phase map of same sample in (a) after thermal annealing at 100 °C for 18 h. (c) 1D SAXS profile of **VIII** obtained at 100 °C. (d) SEC trace (RI detector = black solid line, UV detector = red dotted line) of PCL-aPP−PCL triblock **IX**. (e) ps-tm AFM phase map of a 100 nm thick film of **IX** on a c-Si substrate annealed to 200 °C followed by a rapid quench into liquid N_2. (f) 1D SAXS profile of the LAM phase of **IX** obtained at 80 °C (bottom) and a mixed HEX (major)/LAM (minor) phase observed upon heating the same sample to 200 °C (top).

In fact, VT-SAXS of the bulk confirmed the existence of a LAM phase appearing below 100 °C, with scattering peaks at q/q^* = 1, 2, 3, and 4 (q^* = 0.033 Å^{-1}) that correspond to a domain spacing of 19 nm, and above 150 °C, a HEX phase is seen to emerge with a new set of scattering peaks appearing at q/q^* = 1, $\sqrt{3}$, and $\sqrt{4}$ (q^* = 0.026 Å^{-1}) that are associated with a cylinder-to-cylinder distance, d_c, of 23.7 nm at 200 °C (see Figure 1f). Epitaxial thermotropic LAM → HEX phase transitions are well-known for other classes of di- and triblock copolymers.[30,33] We recognize that other factors, such as overall molar mass of the block copolymers and the nature of the PAO domain (i.e, aPMP vs aPP) are also playing key roles, and accordingly, more thorough investigations of the thermotropic phase behavior of these and other classes of PAO-polyester block copolymers are currently in progress.

Clearly, the results presented in this preliminary report represent only the tip of the iceberg of the extensive investigations and innovations that are now possible for exploring the science and technology of new classes of well-defined polyolefin-based block copolymers that can be easily derived from a broad array of telechelic polyolefins in which the polyolefin domain can be systematically varied in a programmed fashion through the general and versatile synthetic strategy presented herein. Additional results of such studies will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00108.

Experimental details, including complete spectroscopic data (PDF)

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Author Contributions

A.A.B. contributed experimental development of the telechelic PE materials and D.M.F contributed experimental development of all telechelic poly(α-olefins) and block copolymers. C.M.W. contributed the SAXS data collection and analysis of the block copolymers. K.L.B. and L.R.S. contributed to project management, and strategic goals. L.R.S. wrote the manuscript and all coauthors have contributed to the review and revision of the final submission, including the Supporting Information.

Author Contributions

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Notes

The authors declare the following competing financial interest(s): The corresponding author has a financial interest in the university spin-out company, Precision Polyolefins, LLC (PPL). This work did not involve any PPL personnel, funding, or other resources and all new intellectual property has been disclosed in accordance with state and federal requirements.

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(7) Stereoregularity of a poly(α-olefin) can be defined by the relative percent of each possible sequence of adjacent stereocenters for a given number of repeat units, where *m* = meso and *r* = racemic relationships. At the pentad level of analysis, there are 10 possible configuration, with *mmmm* and *rrrr* representing the limiting isotactic and syndiotactic forms.

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