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Access to Polyethylene-Polyester Block Copolymers in Continuous Flow through Single-Step Chain-End-Functionalized Polyethylene

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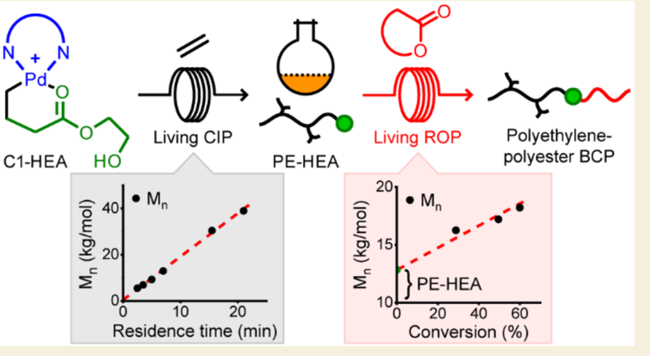

ABSTRACT: Polar polyolefin block copolymer synthesis in continuous flow faces significant challenges due to the nature of the monomers, which require selective polymerization methods for the polymer segments. In this study, we developed a continuous flow strategy by utilizing 2-hydroxyethyl acrylate (HEA) chelated diimine Pd^{II} complex to generate a single-chain-end-functionalized polyethylene (PE-HEA) containing a free OH functionality, which is then employed as a macroinitiator for a ring-opening polymerization (ROP) to form PE-*b*-polyester diblock copolymers. This approach combines two distinct living polymerization processes stepwise, in which a semitelechelic PE is synthesized in the first flow reactor through a single-step living coordination–insertion polymerization (CIP), followed by an ROP in another flow system. This technique avoids a multistep postpolymerization process and ensures the controlled preparation of chain-end-functionalized PE, maintaining a low dispersity (~1.10) throughout a broad range of molecular weights of 5.50 to 38.94 kg/mol, as well as the controlled polymerization of poly(δ-valerolactone) (PVL) with molecular weights of 1.8 to 7.44 kg/mol with a narrow dispersity of ~1.06. With this strategy, a range of distinct polar-PE block copolymers (PE-*b*-PVL) were prepared, in which the PE-HEA functions as a macroinitiator, facilitating a living ROP, yielding block copolymers with extended PVL and polylactide (PLA) segments. This work showcases that a functionalized chelated diimine Pd^{II} complex simplifies the preparation of chain-end-functionalized PE, which then can directly be employed to promote chain extension through ROP, forming polar-PE block copolymers in the flow system.

KEYWORDS: *continuous flow, coordination–insertion polymerization, polyethylene, ring-opening polymerization*

INTRODUCTION

Continuous flow chemistry has rapidly emerged as a transformative platform in modern synthetic and polymer chemistry as it offers unparalleled control over reaction parameters such as pressure, temperature, reaction time (residence), improved safety while dealing with high temperature and pressure reactions.[1−5] Such control over reaction conditions is particularly crucial in polymer synthesis, where the molecular weight, dispersity, and architecture are finely tuned to achieve desired material properties. As an outcome, various types of polymerizations have already been demonstrated over the past decade to benefit from the application of numerous flow systems.[6,7]

In recent years, there has been a growing interest in the application of continuous flow technology to the synthesis of block copolymers (BCPs)—polymers composed of two or more polymer segments or blocks covalently linked in a defined sequence.[8] BCPs have the potential to be utilized as versatile composites and hybrid materials, which are capable of being responsive to various stimuli such as temperature, humidity, pH, redox, magnetic, electric, swelling, and light, and thus ensure unique and improved properties.[9−11] These materials are also associated with self-assembly and are suitable for arranging into nanostructures for applications in numerous fields such as chemistry, nanotechnology, water treatment, environmental applications, medicine, wound healing, solar cells, photocatalysis, and many more.[10−12]

Flow setups are particularly well suited for BCP synthesis, as it allows the preparation of two or more blocks by integrating multiple flow reactors. For instance, the Yoshida group synthesized acrylate BCPs using anionic polymerization at 0 °C and further extended this to mixed BCPs of styrene and methacrylates.[13,14] Photoredox organic atom transfer radical

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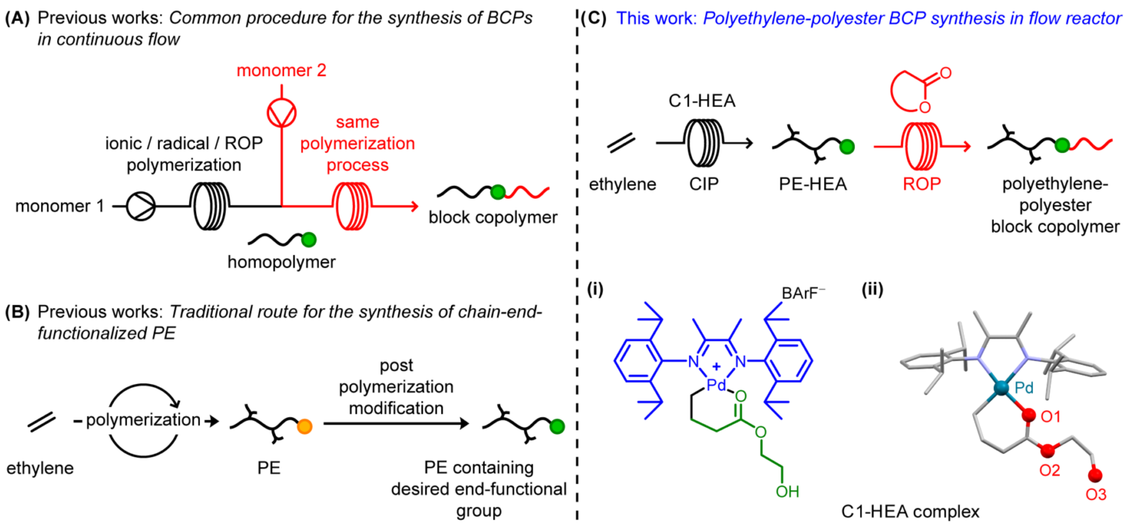

Figure 1. Schematic comparison between previous works and this work. (A) Synthesis of block copolymers (BCPs) in continuous flow using same polymerization process to form both blocks, (B) chain-end-functionalized polyethylene (PE) synthesis through postpolymerization modification to introduce desired end-functionality, and (C) single-step synthesis of chain-end-functionalized PE through coordination−insertion polymerization (CIP) utilized as macroinitiator for further chain extension employing ROP, (i) structure of C1-HEA chelated complex, (ii) X-ray structure of the major isomer found in the C1-HEA complex, the hydrogen atoms and the BArF counterion are omitted for clarity.

polymerization (O-ATRP) was utilized by Miyake and co-workers to form acrylate-methacrylate BCPs.[15] The Junkers group achieved tetrablock quaterpolymers via reversible addition−fragmentation chain transfer (RAFT) polymerization in cascade reactors.[16,17] Guo et al. coupled two flow reactors sequentially for the synthesis of well-defined BCPs of δ-valerolactone and ε-caprolactone through organic and enzymatic catalyzed ring-opening polymerization (ROP) with low dispersity.[18−20] The Pitet group reported ABA-type triblock copolymers through an organocatalyzed ring-opening transesterification polymerization of D, L-lactide utilizing a commercially available hydroxyl-telechelic poly(β-farnesene) as a macroinitiator in an oscillatory flow reactor.[21]

Despite these advantages, the majority of reported flow-synthesized BCPs are limited to blocks derived from monomers of the same family or, less commonly, from different families but still rely on a single polymerization strategy (Figure 1A).[6] The combination of fundamentally distinct polymerization methods in a continuous flow context remains notably scarce. Furthermore, BCPs containing polyethylene (PE) blocks synthesized in continuous flow are extremely rare; only a few examples, such as the polar-polyethylene BCPs, such as PE-*b*-polyacrylates, reported by the Harth group, have been described in the literature.[22]

Although PE is one of the most common and widely used plastic materials, from packaging to construction, due to its remarkable combination of physical and chemical resistance, ease of production, and processability from cost-effective feedstocks, however, in the absence of any polar functionality, it often suffers from limitations associated with inadequate surface properties such as adhesion, dyeability, printability, and compatibility.[23−27] The integration of polar functionality into PE by coupling with distinct polar segments can significantly improve such properties, enabling broader application potential.[28,29] For example, amphiphilic BCPs containing hydrophilic polyester or polyether segments bonded to hydrophobic PE are ideal candidates for the compatibilization of polymer blends and composites, as these materials are able to reduce the interfacial tension and improve adhesion between the immiscible phases.[23,30]

Achieving these types of polar-PE BCPs requires a precise strategy for the synthesis of a chain-end-functionalized PE, serving as a macroinitiator for subsequent divergent polymerization mechanisms. The key methodologies to prepare end-functionalized PE include postmodification of unsaturated chain ends,[31−34] the use of functionalized chain transfer agents (CTA),[35−38] coordinative chain transfer polymerization (CCTP)[39−42] followed by further modification, and olefin metathesis (Figure 1B).[43−46] For instance, in the case of synthesizing amphiphilic polar-PE BCPs, hydroxyl-terminated PEs were prepared via *in situ* chain transfer to organoboranes, alkyl aluminums, or alkyl zincs during ethylene polymerization, followed by oxidation. The Matyjaszewski group synthesized a monohydroxy-terminated PE through a degenerative-transfer coordination polymerization of ethylene by a bis(imino)-pyridineiron/diethylzinc binary catalyst system activated by MAO, followed by oxidation using dry air.[47] Chung and co-workers synthesized PE-*b*-P(ethylene oxide) and PE-*b*-P(ε-caprolactone) through ROP following oxidation and metalation of borane-functionalized PE.[30,48] The Hillmyer group synthesized PE-poly(L-lactide) block copolymer containing two semicrystalline blocks through a combination of anionic polymerization, hydrogenation, and coordination−insertion polymerization (CIP) to prepare PE−OH, followed by ROP of L-lactide.[49] Kim and co-workers prepared PE-*b*-P(ε-caprolactone) following similar strategies involving controlled chain transfer reaction of ethylene.[50] Guironnet et al. employed tandem hydroformylation/hydrogenation of vinyl-terminated PE to yield OH-terminated PE, initiating ε-caprolactone ROP to form a diblock copolymer.[51] The same group reported the synthesis of PE-polyester triblock copolymers via a dihydroxy-terminated PE achieved by performing four consecutive postpolymerization reactions on PE.[52] Duchateau and co-workers synthesized chain-end-functionalized high-density PE (HDPE−OH) and randomly hydroxyl functionalized linear low-density PE (LLDPE−OH) utilizing different synthetic routes, and used them as

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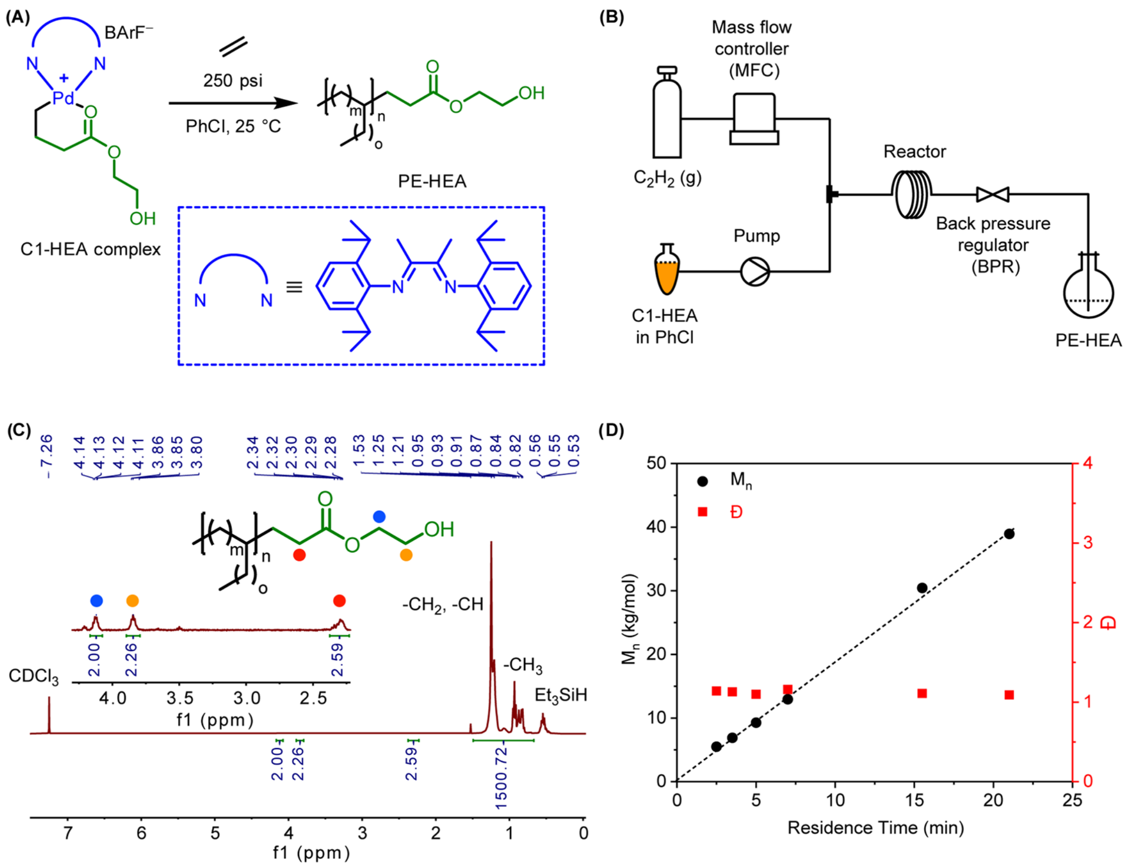

Figure 2. Synthesis of PE-HEA homopolymer in the continuous flow reactor. (A) CIP of ethylene utilizing C1-HEA complex, (B) schematic diagram of the continuous flow reactor for ethylene polymerization, (C) ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of PE-HEA homopolymer, entry 4, Table 1, and (D) M_n vs residence time plot evidenced living polymerization of ethylene (Table 1).

macroinitiators for further ROP to yield PE-polyester block and graft copolymers.[23] Recently, our group developed routes to utilize chelated diimine Pd^{II} complexes to install a versatile active ester group at the PE chain end upon ethylene polymerization. These groups can be transformed to provide PE macroinitiators for ATRP, RAFT, and ROP.[53,54] In this vein, as chelated diimine Pd^{II} complexes have proven to be valuable precursors for the installation of functional chain end units for postmodification routes, a direct integration of initiating units for polymerization is proposed.[55]

Here, we report a continuous flow synthesis of polyethylene-polyester BCPs by integrating CIP of PE and ROP of cyclic esters (Figure 1C). First, we developed a 2-hydroxyethyl acrylate (HEA) chelated diimine Pd^{II} complex (C1-HEA), which was employed as a catalyst in the CIP of ethylene in the flow reactor, resulting in straightforward chain-end-functionalized PE (PE-HEA). This single-step flow synthesis of semitelechelic PE bypassed the postpolymerization modification and purification steps as well as ensured that every polymer chain contains the desired end-functional group, which is crucial for the maximum participation in further polymerization as a macroinitiator. The polar-PE BCPs were then synthesized by the chain extension of PE-HEA through ROP of cyclic esters in another flow setup. Here, the desired BCPs were formed by the stepwise integration of two distinct living polymerization methods, which warranted precise control over both constituent blocks to meet the desired polymeric characteristics.

RESULTS AND DISCUSSION

The chelated diimine Pd^{II} complex (C1-HEA) was synthesized by a single coordination−insertion of 2-hydroxyethyl acrylate to the Pd-Me bond of the C1-precursor, adapting an approach as outlined in the Supporting Information Section 3.3 and Figure S4. Here, the C1-precursor first forms an activated complex (I) upon reaction with NaBArF, which generates a π-acrylate complex (II) in the next coordination step. This species undergoes a 2,1-insertion, affording the four-membered chelate (III). The chelated complex then isomerizes into the five-membered chelate (IV) through β-H elimination and reinsertion (chain walking), which ultimately rearranges to yield the six-membered C1-HEA complex. The predominant formation of a six-membered ring chelate (∼90%) via 2,1-insertion of acrylate over the formation of a five-membered ring chelate (∼10%) through 1,2-insertion was observed in ^{1}H NMR analyses of the obtained products (Figure S1). This result is in agreement with previously reported studies for similar chelated complexes.[53,56] In addition, the structure of the major isomer was also confirmed by X-ray diffraction analysis of the C1-HEA complex after recrystallization by slow diffusion of pentane into a solution of the complex in methylene chloride (CH_2Cl_2, DCM) at −20 °C (Figure 1C (ii)).

The CIP of ethylene was performed in the flow system (Figure 2A,B) using a gas−liquid heterogeneous droplet flow consisting of a C1-HEA complex solution confined by ethylene gas. The polymerization of ethylene exploiting the C1-HEA complex consists of three major steps (Figure S6): (i) chelate opening and coordination of ethylene monomers to the metal center, (ii) migratory insertion, and (iii) chain propagation through successive coordination−insertion of monomer units to form the polymer chain. During this chain propagation, the complex also undergoes chain walking through β-hydride elimination and reinsertion, resulting in a highly branched amorphous polymer microstructure.[57,58] Due to the chelated structure of the complex, semitelechelic polyethylene bearing hydroxyethyl ester moiety (PE-HEA) was directly generated, so that it can act as a macroinitiator for further ROP. In the flow reactor, premature chain transfer was suppressed by exerting a high pressure of 250 psi using a back pressure regulator (BPR) situated at the end of the reactor (Figure 2B). The PE-HEA polymer chain was released only from the metal center upon the addition of Et_3SiH as a quenching reagent, ensuring that each polymer chain incorporated the desired end-functionality, confirmed by the characteristic peaks at 2.30, 3.85, and 4.12 ppm in the ^1H NMR of the purified homopolymer (Figure 2C). A good correlation was observed between the molecular weight determined by GPC (M_n = 12.59 kg/mol, Table 1, entry 4) and the ^1H NMR chain-end analysis (M_n = 10.62 kg/mol, SI Section 7 and eq S1), as well as the absence of olefinic resonances in the range of 5.00−6.00 ppm, indicating high chain-end fidelity in the polymerization. The discrepancy in the molecular weight values is attributed to the use of polystyrene standards for PE analysis.

Table 1. Kinetic Data of Coordination−Insertion Polymerization (CIP) of Ethylene[a]

Entry	Pump flow rate (mL/min)	Vol. of C1-HEA in PhCl (mL)	Res. time (min)[b]	PE-HEA[c] M_n (kg/mol)	PE-HEA[c] $Đ$
1	0.75	22.50	2.5	5.50	1.14
2	0.60	18.00	3.5	6.90	1.13
3	0.45	13.50	5.0	9.28	1.10
4	0.30	9.00	7.0	12.59	1.15
5	0.15	4.50	15.5	30.44	1.11
6	0.10	3.00	21.0	38.94	1.09

[a]Reaction conditions: 2.00 μmol/mL concentration of C1-HEA complex, 3.0 m of reactor length, 6.0 mL/min of ethylene gas flow rate, 250 psi of BPR, 30 min reaction time. [b]Residence time was determined by visual measurement. [c]Molecular weight (M_n) and dispersity ($Đ$) were determined by gel permeation chromatography (GPC) analysis with samples measured in tetrahydrofuran (THF) at 40 °C, calibrated to polystyrene standards.

A kinetic study of PE chain growth based on the residence time, varying the flow rate of the feed solution, was performed to investigate the living ethylene homopolymerization to yield PE-HEA in the flow system (Table 1, Figures 2D and S7). Living polymerization is defined as a chain polymerization in the absence of chain termination, resulting in a linear relationship between the M_n of the polymers and the reaction time with a narrow dispersity ($Đ = M_w/M_n$). In Figure 2D, a linear relationship, following first-order kinetics, between the increase in M_n (5.50 to 38.94 kg/mol) and the increase in residence time (2.5 to 21 min), was observed while maintaining a narrow $Đ$ (~1.10). This observation established the relationship between subsequent monomer propagation for continuing the PE chain growth over the β-hydride elimination and chain transfer. Therefore, we can conclude that the fluid dynamics of the continuous flow are compatible with the living nature of ethylene polymerization, which can produce any desired length of a PE segment by varying the residence time of the reaction solution.

Next, we synthesized poly(δ-valerolactone) (PVL) in another flow setup (Figure S9) through the ROP of δ-valerolactone (δ-VL) in the presence of benzyl alcohol (BnOH) as an initiator at room temperature (summarized in Table 2). Here, we utilized diphenyl phosphate (DPP) as the weak acid organocatalyst because it is commercially available, has low toxicity, and is chemically stable.[59] The concentration of monomer solution was taken as 1.0 M with a ratio of [δ-VL]/[DPP]/[BnOH] = 100/2/1. Under this condition, the Reynolds number (Re) at the start of polymerization was determined to be 26.2 to 3.93 (SI Section 7, eq S2) for the reactions in Table 2, indicating laminar fluid profiles (Re ≤ 2000) in the tubular reactor. Additionally, as polymerization proceeded, the dynamic viscosity of the reaction mixture increased, leading to a decrease in the Reynolds number of the flow system. Therefore, polymerization remained in the laminar regime for the entire reaction duration. In this laminar flow regime, a parabolic flow profile is expected, where the flow streams close to the tube walls have increased residence time compared to the streams in the center of the tube.[60−62] The monomer conversion for a specific residence time in the ROP was determined by ^1H NMR spectra of aliquots of the crude product (Figure S11, SI Section 7, eq S3), and a theoretical $M_{n,theo}$ was calculated from the δ-VL conversion using eq 4 (Section 7 in Supporting Information). The chemical structure of the obtained polymer was assigned through ^1H NMR analysis of the purified PVL (Figure S12). The characteristic

Table 2. Kinetic Data of Ring-Opening Polymerization (ROP) of δ-Valerolactone (δ-VL)[a]

Entry	Pump (1 and 2) flow rate (mL/min)	Vol. of each solution (mL)	Res. time (min)	% conv.[b]	PVL $M_{n,\,theo}$[c] (kg/mol)	PVL $M_{n,\,NMR}$[d] (kg/mol)	PVL $M_{n,\,GPC}$[e] (kg/mol)	PVL $Đ$[e]
1	0.40	12.0	5.0	18.47	1.96	1.98	1.80	1.07
2	0.20	6.0	10.0	35.69	3.68	4.19	3.59	1.06
3	0.13	3.9	15.0	53.98	5.51	5.27	4.79	1.06
4	0.10	3.0	20.0	65.90	6.71	5.98	5.70	1.06
5	0.08	2.4	25.0	77.56	7.87	7.43	6.79	1.07
6	0.06	1.8	30.0	84.06	8.52	7.67	7.44	1.06

[a]Reaction conditions: 1.00 M concentration of δ-VL monomer, [δ-VL]/[DPP]/[BnOH] = 100/2/1, 5 m of reactor length, 40 psi of BPR, 30 min reaction time. [b]Determined by ^1H NMR spectroscopy of crude product. [c]Molecular weight ($M_{n,\,theo}$) was calculated based on the % conversion. [d]$M_{n,\,NMR}$ was calculated from the ^1H NMR of the pure product. [e]$M_{n,\,GPC}$ and $Đ$ were determined by GPC analysis with samples measured in THF at 40 °C calibrated to polystyrene standards.

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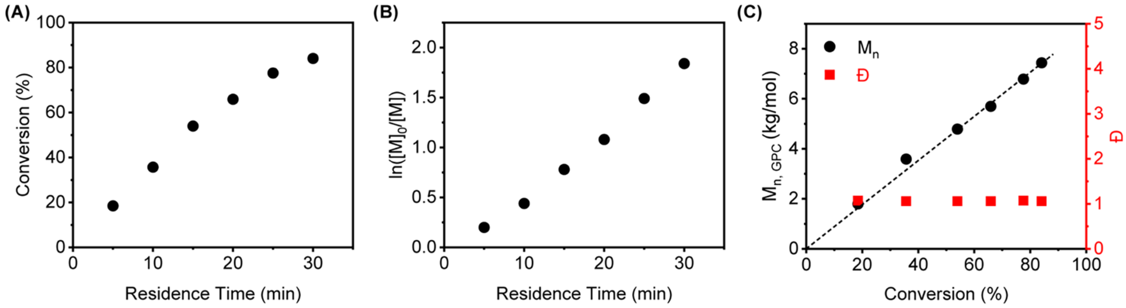

Figure 3. Results from the kinetic study of δ-valerolactone (δ-VL) homopolymerization based on residence time varied with the flow rate of feed solutions (Table 2). (A) Change in conversion with the increase in residence time, (B) the variation of $\ln([M]_0/[M])$ with changes in residence time, and (C) the increase in M_n with increasing % conversion while maintaining narrow $Đ$ evidenced living polymerization of δ-VL.

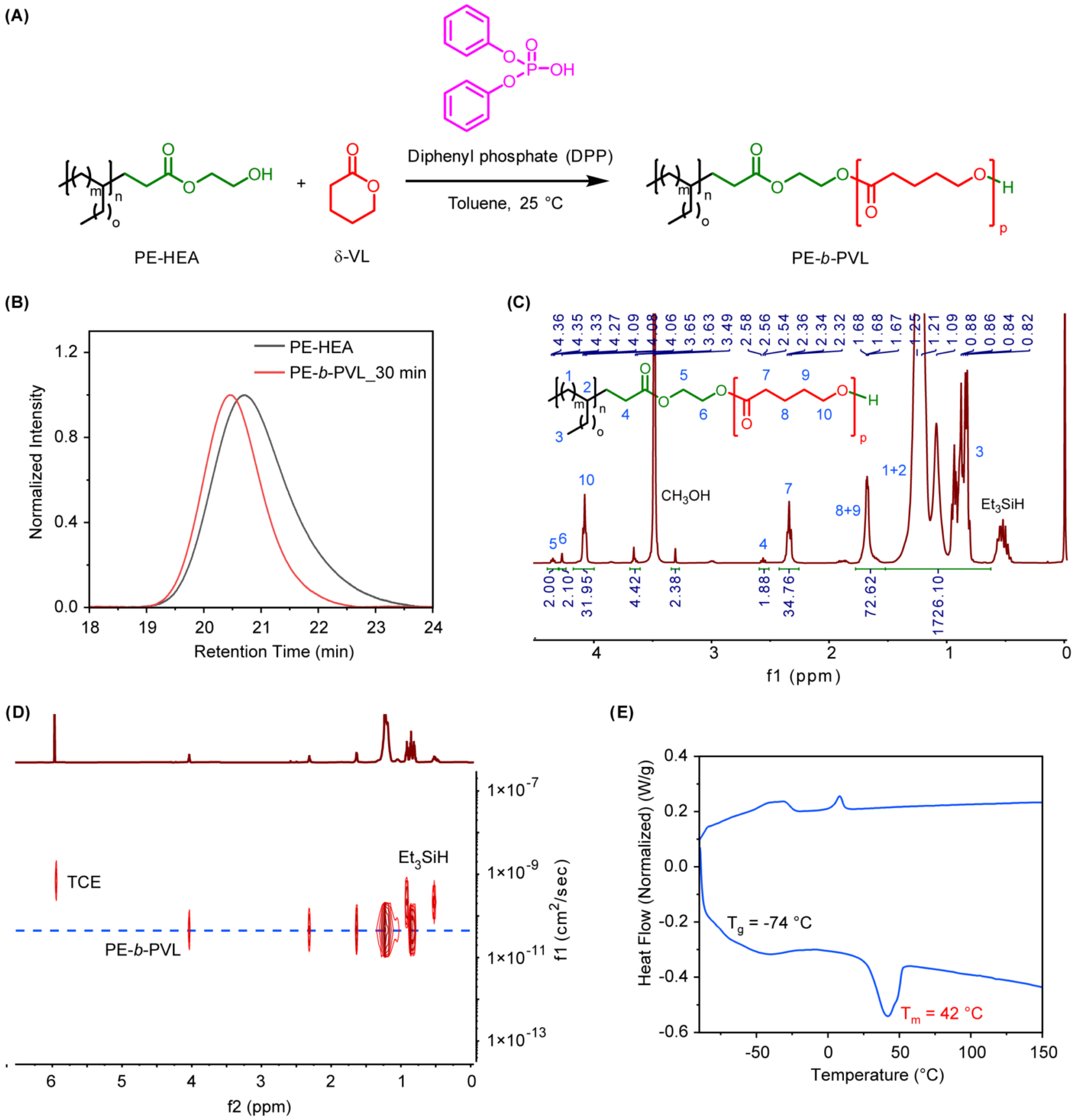

Figure 4. (A) Synthesis of polyethylene-poly(δ-valerolactone) block copolymer (PE-*b*-PVL) in a continuous flow reactor. Characterization of synthesized PE-*b*-PVL (entry 1, Table 3) in the continuous flow reactor. (B) GPC traces of PE-HEA homopolymer and purified PE-*b*-PVL, (C) ^1H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of purified PE-*b*-PVL, (D) DOSY ^1H NMR spectrum of purified PE-*b*-PVL in TCE ($C_2D_2Cl_4$) at 25 °C, and (E) DSC of PE-*b*-PVL purified product.

peaks of the initiator BnOH were observed as the peaks due to the phenyl protons and benzyl protons adjacent to the ester linkage that appeared in the range from 7.32 to 7.39, and 5.19 ppm, respectively. The peak due to the methylene proton

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Table 3. Kinetic Data of Chain Extension through ROP.[a]

		PE-HEA macroinitiator[c]						Polyethylene-*b*-polyester[c]	
Entry	Sample	M_n (kg/mol)	$Đ$	Comonomer	Pump (1 and 2) flow rate (mL/min)	Res. time (min)	% conv.[b]	M_n (kg/mol)	$Đ$
1	PE-*b*-PVL	12.85	1.16	δ-VL	0.133	30	28.84	16.26	1.09
2	PE-*b*-PVL	12.85	1.16	δ-VL	0.089	45	49.60	17.21	1.07
3	PE-*b*-PVL	12.85	1.16	δ-VL	0.067	60	59.98	18.22	1.07
4	PE-*b*-PLA[d]	15.07	1.13	L-LA	0.067	60	20.04	20.38	1.10

[a]Reaction conditions: 0.50 M concentration of δ-VL, [δ-VL]/[DPP]/[PE-HEA] = 100/2/1, 10 m of reactor length, 40 psi of back pressure regulator, 30 min reaction time. [b]Determined by ^{1}H NMR spectroscopy of crude product. [c]M_n and $Đ$ were determined by GPC analysis with samples measured in THF at 40 °C calibrated to polystyrene standards. [d]0.50 M concentration of L-LA, [L-LA]/[DBU]/[PE-HEA] = 100/2/1.

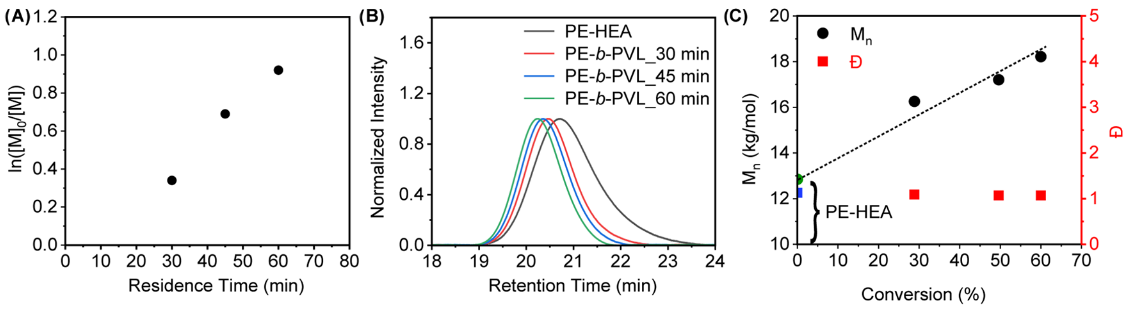

Figure 5. Results from the kinetic study of PE-*b*-PVL polymerization based on residence time varied with the flow rate of feed solutions (entry 1−3, Table 3); (A) variation of ln($[M]_0/[M]$) with the change of residence time, (B) GPC traces of PE-*b*-PVL for different residence times, and (C) M_n vs conversion time plot evidenced living polymerization of δ-VL for the chain extension.

adjacent to the ω-chain end of the hydroxyl group was clearly observed in the range of 3.63 to 3.66 ppm. These observations implied that the δ-VL homopolymerization was initiated from BnOH. In addition, $M_{n,NMR}$ and $M_{n,GPC}$ of the synthesized PVL were determined by ^{1}H NMR spectra (Figure S12, SI Section 7, eq S5) and GPC analysis of purified PVL, respectively. We found that the $M_{n,GPC}$ analyzed by the GPC is in agreement with the $M_{n,theo}$ and $M_{n,NMR}$ of the product.

The kinetic experiment of chain growth in the flow system was carried out to confirm the living nature of the DPP-catalyzed ROP of δ-VL (Table 2). From the kinetic plot shown in Figure 3B, a distinct first-order relationship between the ln($[M]_0/[M]$) and the residence time of the feed solutions was observed, indicating a controlled or living polymerization of δ-VL in the flow reactor. In addition, the molecular weight of the obtained PVL increased linearly from 1.80 to 7.44 kg/mol with the increase of residence time of reactants from 5 to 30 min in the tubular reactor, maintaining almost a constant narrow dispersity (~1.06) (Figure 3C).

After the completion of the kinetic studies of ethylene and δ-VL homopolymerizations, we intended to synthesize PE-*b*-PVL in a similar flow setup that was utilized for δ-VL homopolymerization, illustrated in Figures 4A and S15. Herein, the synthesized PE-HEA through CIP was used as the macroinitiator for the chain extension through ROP in the presence of a DPP catalyst. Since the presence of PE-HEA macroinitiator increases the reaction mixture viscosity, two optimization steps were adapted for the synthesis of BCPs, those were (i) the overall concentration of reaction mixture diluted to halves of δ-VL homopolymerization (i.e., [δ-VL] = 0.5 M) maintaining the ratio [δ-VL]/[DPP]/[PE-HEA] = 100/2/1, and (ii) a 10.0 m tubular reactor was employed instead of 5.0 m to extend the residence time of the reaction mixture even with a moderate flow rate to ensure the better mixing. An aliquot of the crude product was taken off to measure the monomer conversion from the ^{1}H NMR spectra (Figure S16), which was determined as 28.84% for a 30 min residence time with a flow rate of 0.133 mL/min for each pump (Table 1, entry 1). A combination of characterization methods, such as GPC, ^{1}H NMR spectroscopy, ^{1}H diffusion-ordered NMR spectroscopy (DOSY), and differential scanning calorimetry (DSC), was applied to analyze purified PE-*b*-PVL. A GPC trace at higher molecular weight (M_n = 16.26 kg/mol) was observed for the purified BCP (Figure 4B), clearly indicating an increase in molecular weight from 12.85 kg/mol due to the chain extension of PE-HEA macroinitiator to form PE-*b*-PVL. The ^{1}H NMR spectra of the purified BCP displayed all the characteristic peaks of the PE-HEA macroinitiator and the newly formed PVL block, with a noticeable downfield shift observed for the methylene protons of HEA adjacent to the ester linkage (Figure 4C). The ^{1}H DOSY NMR analysis of purified PE-*b*-PVL (Figure 4D) depicted signals corresponding to the PE segment (1.25 to 0.83 ppm) and the PVL segment (4.08, 3.48, and 2.34 ppm), which were aligned in a single diffusion coefficient, confirming that both polymer segments were covalently bonded to each other. To further confirm that homo PE can be detected in a mixture containing BCPs and a rather small molecular weight difference, a purified BCP sample was spiked with PE-HEA to demonstrate the suitability of the analytical method. The PE-HEA could be clearly identified with a slightly higher diffusion coefficient (Figure S17). Finally, the purified BCP was subjected to DSC analysis (Figure 4E) and a glass transition temperature (T_g) in the range of PE block at −74 °C was observed, accompanied by a melting temperature (T_m) of the PVL block at 42 °C, indicating the presence of two heterogeneous phases in the same polymeric matrix. All these findings collectively validate the successful integration of two different homopolymer segments to form a BCP synthesized through two different polymerization methods.

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A kinetic investigation was also conducted for the chain extension of the PE-HEA macroinitiator (M_n = 12.85 kg/mol) to form the PE-*b*-PVL through ROP of δ-VL (Table 3, entries 1−3). In this case, an increase in residence time of the reaction mixture from 30 to 60 min in the tubular reactor increased the monomer δ-VL conversion from 28.84% to 59.98% in the polymerization reactions (Figure S18), maintaining a first-order kinetic relationship between the $\ln([M]_0/[M])$ and the residence time of the feed solutions (Figure 5A). The M_n of the purified BCPs obtained from the GPC analyses also preserved a linear relationship with the monomer conversion (Figure 5C), which evidenced the living nature of chain extension of PE-HEA through the ROP in the flow reactor.

To explore the versatility and monomer scope of our flow synthesis, PE-*b*-polylactide (PLA) was synthesized by the chain extension of PE-HEA macroinitiator through ROP of L-lactide (L-LA) monomer in the same flow setup utilized for PE-*b*-PVL synthesis (Table 3, entry 4, and Figure S19). Here, we introduced a change, using THF as the solvent, because L-LA has comparatively better solubility in THF. In this case, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is used as a catalyst for the ROP of L-LA, where the initial monomer concentration [L-LA] was 0.5 M, maintaining the ratio [L-LA]/[DBU]/[PE-HEA] = 100/2/1. An aliquot of the crude product was taken to determine the monomer conversion and was analyzed by ^{1}H NMR (Figure S20), which was 20% at 60 min residence time. The formation of BCP was confirmed by GPC, ^{1}H NMR spectroscopy, and ^{1}H DOSY NMR analysis of purified PE-*b*-PLA. The GPC for the purified BCP indicated the increase of M_n from 15.07 to 20.38 kg/mol due to the chain extension of the PE-HEA macroinitiator to form PE-*b*-PLA (Figure S21). The ^{1}H NMR spectra of purified PE-*b*-PLA portrayed all characteristic peaks of the PE-HEA macroinitiator and the newly formed PLA block (Figure S22). The ^{1}H DOSY NMR analysis of purified BCP displayed a single resonance, whereas the signals corresponding to the PE segment (1.25−0.83 ppm) and the PLA segment (5.17 and 1.59 ppm) were aligned in a single diffusion coefficient, confirming that both polymer segments were covalently bonded to each other to form a block architecture (Figure S23).

CONCLUSION

In summary, we designed and developed a 2-hydroxyethyl acrylate chelated diimine Pd^{II} complex aiming to synthesize a OH-chain-end-functionalized PE for conducting a sequential ROP with cyclic esters. A single-step continuous flow synthesis of this semitelechelic PE was achieved by the utilization of gas−liquid heterogeneous droplet flow in the tubular reactor. The living nature of the ethylene homopolymerization was established by the kinetic study of the chain growth of PE-HEA with the increase of the residence time of the feed solutions. Another distinct flow reactor was employed for the organocatalyzed ROP of ester monomers, and the kinetic investigation of the ROP of δ-VL verified the living polymerization. Finally, the polyethylene-polyester BCPs with δ-VL and L-LA monomers were synthesized in the continuous flow by the chain extension of PE-HEA as the macroinitiator. This methodology allows the utilization of living polymerizations for both segments of the polar-PE BCPs assuring the fine-tuning of the constituent block compositons, broadening their application in the advanced material sciences.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.5c01094.

Materials, experimental procedures, flow reactor setups, and characterization of products; crystallographic data of C1-HEA complex (PDF)

Accession Codes

Deposition Number 2478370 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

The manuscript was written through the contributions of all authors. CRediT: **Stephen Don Sarkar** conceptualization, data curation, formal analysis, methodology, validation, visualization, writing - original draft, writing - review & editing; **Eva Harth** conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, validation, writing - review & editing.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wiles, C.; Watts, P. Continuous Flow Reactors, a Tool for the Modern Synthetic Chemist. *Eur. J. Org. Chem.* **2008**, *2008* (10), 1655−1671.

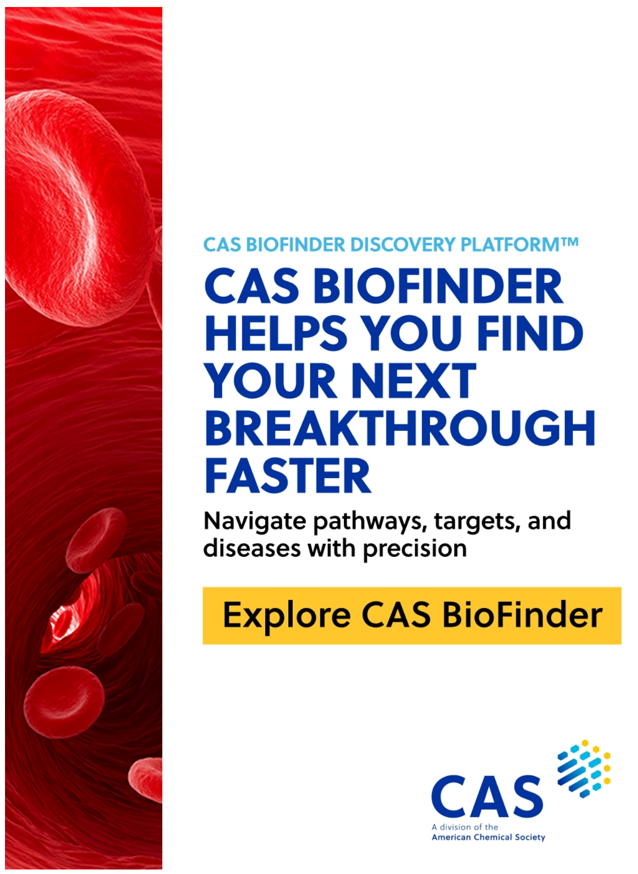
(2) Wilms, D.; Klos, J.; Frey, H. Microstructured Reactors for Polymer Synthesis: A Renaissance of Continuous Flow Processes for Tailor-Made Macromolecules? *Macromol. Chem. Phys.* **2008**, *209* (4), 343−356.

(3) Rossetti, I.; Compagnoni, M. Chemical reaction engineering, process design and scale-up issues at the frontier of synthesis: Flow chemistry. *Chem. Eng. J.* **2016**, *296*, 56−70.

(4) Guidi, M.; Seeberger, P. H.; Gilmore, K. How to approach flow chemistry. *Chem. Soc. Rev.* **2020**, *49* (24), 8910−8932.

(5) Hone, C. A.; Kappe, C. O. Towards the Standardization of Flow Chemistry Protocols for Organic Reactions. *Chem.:Methods* **2021**, *1* (11), 454−467.
(6) Reis, M. H.; Leibfarth, F. A.; Pitet, L. M. Polymerizations in Continuous Flow: Recent Advances in the Synthesis of Diverse Polymeric Materials. *ACS Macro Lett.* **2020**, *9* (1), 123−133.
(7) Zaquen, N.; Rubens, M.; Corrigan, N.; Xu, J.; Zetterlund, P. B.; Boyer, C.; Junkers, T. Polymer Synthesis in Continuous Flow Reactors. *Prog. Polym. Sci.* **2020**, *107*, No. 101256.
(8) Feng, H.; Lu, X.; Wang, W.; Kang, N.-G.; Mays, J. W. Block Copolymers: Synthesis, Self-Assembly, and Applications. *Polymers* **2017**, *9* (10), No. 494.
(9) Klaikherd, A.; Nagamani, C.; Thayumanavan, S. Multi-Stimuli Sensitive Amphiphilic Block Copolymer Assemblies. *J. Am. Chem. Soc.* **2009**, *131* (13), 4830−4838.
(10) Schattling, P.; Jochum, F. D.; Theato, P. Multi-stimuli responsive polymers − the all-in-one talents. *Polym. Chem.* **2014**, *5* (1), 25−36.
(11) Politakos, N.; Avgeropoulos, A. Advances and Applications of Block Copolymers. *Polymers* **2023**, *15* (13), No. 2930.
(12) Huang, C.; Zhu, Y.; Man, X. Block copolymer thin films. *Phys. Rep.* **2021**, *932*, 1−36.
(13) Nagaki, A.; Miyazaki, A.; Tomida, Y.; Yoshida, J.-i. Anionic polymerization of alkyl methacrylates using flow microreactor systems. *Chem. Eng. J.* **2011**, *167* (2), 548−555.
(14) Nagaki, A.; Miyazaki, A.; Yoshida, J.-i. Synthesis of Polystyrenes−Poly(alkyl methacrylates) Block Copolymers via Anionic Polymerization Using an Integrated Flow Microreactor System. *Macromolecules* **2010**, *43* (20), 8424−8429.
(15) Ramsey, B. L.; Pearson, R. M.; Beck, L. R.; Miyake, G. M. Photoinduced Organocatalyzed Atom Transfer Radical Polymerization Using Continuous Flow. *Macromolecules* **2017**, *50* (7), 2668−2674.
(16) Rubens, M.; Latsrisaeng, P.; Junkers, T. Visible light-induced iniferter polymerization of methacrylates enhanced by continuous flow. *Polym. Chem.* **2017**, *8* (42), 6496−6505.
(17) Baeten, E.; Haven, J. J.; Junkers, T. RAFT multiblock reactor telescoping: from monomers to tetrablock copolymers in a continuous multistage reactor cascade. *Polym. Chem.* **2017**, *8* (25), 3815−3824.
(18) Zhu, N.; Huang, W.; Hu, X.; Liu, Y.; Fang, Z.; Guo, K. Chemoselective polymerization platform for flow synthesis of functional polymers and nanoparticles. *Chem. Eng. J.* **2018**, *333*, 43−48.
(19) Zhu, N.; Huang, W.; Hu, X.; Liu, Y.; Fang, Z.; Guo, K. Enzymatic Continuous Flow Synthesis of Thiol-Terminated Poly(δ-Valerolactone) and Block Copolymers. *Macromol. Rapid Commun.* **2018**, *39* (8), No. 1700807.
(20) Zhu, N.; Feng, W.; Hu, X.; Zhang, Z.; Fang, Z.; Zhang, K.; Li, Z.; Guo, K. Organocatalyzed continuous flow ring-opening polymerizations to homo- and block-polylactones. *Polymer* **2016**, *84*, 391−397.
(21) Den Haese, M.; Gemoets, H. P. L.; Van Aken, K.; Pitet, L. M. Fully biobased triblock copolymers generated using an unconventional oscillatory plug flow reactor. *Polym. Chem.* **2022**, *13* (30), 4406−4415.
(22) Sarkar, S. D.; Dau, H.; Harth, E. Synthesis of polyethylene-polyacrylate block copolymers in continuous flow. *Chem.* **2024**, *10* (9), 2872−2886.
(23) Rutkowski, S.; Zych, A.; Przybysz, M.; Bouyahyi, M.; Sowinski, P.; Koevoets, R.; Haponiuk, J.; Graf, R.; Hansen, M. R.; Jasinska-Walc, L.; Duchateau, R. Toward Polyethylene−Polyester Block and Graft Copolymers with Tunable Polarity. *Macromolecules* **2017**, *50* (1), 107−122.
(24) Nakamura, A.; Ito, S.; Nozaki, K. Coordination−Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109* (11), 5215−5244.
(25) Bae, C.; Hartwig, J. F.; Boaen Harris, N. K.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. Catalytic Hydroxylation of Polypropylenes. *J. Am. Chem. Soc.* **2005**, *127* (2), 767−776.
(26) Boaen, N. K.; Hillmyer, M. A. Post-polymerization functionalization of polyolefins. *Chem. Soc. Rev.* **2005**, *34* (3), 267−275.
(27) Patel, K.; Chikkali, S. H.; Sivaram, S. Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications. *Prog. Polym. Sci.* **2020**, *109*, No. 101290.
(28) Stürzel, M.; Mihan, S.; Mülhaupt, R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116* (3), 1398−1433.
(29) Boffa, L. S.; Novak, B. M. Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes. *Chem. Rev.* **2000**, *100* (4), 1479−1494.
(30) Lu, Y.; Hu, Y.; Wang, Z. M.; Manias, E.; Chung, T. C. Synthesis of new amphiphilic diblock copolymers containing poly(ethylene oxide) and poly(α-olefin). *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (20), 3416−3425.
(31) Chung, T. C.; Lu, H. L.; Janvikul, W. A novel synthesis of PP-b-PMMA copolymers via metallocene catalysis and borane chemistry. *Polymer* **1997**, *38* (6), 1495−1502.
(32) Lu, B.; Chung, T. C. New Maleic Anhydride Modified PP Copolymers with Block Structure: Synthesis and Application in PP/Polyamide Reactive Blends. *Macromolecules* **1999**, *32* (8), 2525−2533.
(33) Wiedemann, T.; Voit, G.; Tchernook, A.; Roesle, P.; Göttker-Schnetmann, I.; Mecking, S. Monofunctional Hyperbranched Ethylene Oligomers. *J. Am. Chem. Soc.* **2014**, *136* (5), 2078−2085.
(34) Kaneyoshi, H.; Matyjaszewski, K. Synthesis of a linear polyethylene macromonomer and preparation of polystyrene-graft-polyethylene copolymers via grafting-through atom transfer radical polymerization. *J. Appl. Polym. Sci.* **2007**, *105* (1), 3−13.
(35) Koo, K.; Marks, T. J. Silanolytic Chain Transfer in Ziegler−Natta Catalysis. Organotitanium-Mediated Formation of New Silapolyolefins and Polyolefin Architectures. *J. Am. Chem. Soc.* **1998**, *120* (16), 4019−4020.
(36) Xu, G.; Chung, T. C. Borane Chain Transfer Agent in Metallocene-Mediated Olefin Polymerization. Synthesis of Borane-Terminated Polyethylene and Diblock Copolymers Containing Polyethylene and Polar Polymer. *J. Am. Chem. Soc.* **1999**, *121* (28), 6763−6764.
(37) Lin, W.; Niu, H.; Chung, T. C. M.; Dong, J.-Y. Borane chain transfer reaction in olefin polymerization using trialkylboranes as chain transfer agents. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (16), 3534−3541.
(38) Imuta, J.-i.; Kashiwa, N.; Toda, Y. Catalytic Regioselective Introduction of Allyl Alcohol into the Nonpolar Polyolefins: Development of One-Pot Synthesis of Hydroxyl-Capped Polyolefins Mediated by a New Metallocene IF Catalyst. *J. Am. Chem. Soc.* **2002**, *124* (7), 1176−1177.
(39) Kurosawa, H.; Shiono, T.; Soga, K. Synthesis of α,ω-dialkenyl isotactic poly(propylene) using bis(4-methyl-3-pentenyl)zinc as a chain transfer reagent. *Macromol. Chem. Phys.* **1994**, *195* (10), 3303−3309.
(40) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. Iron and Cobalt Ethylene Polymerization Catalysts Bearing 2,6-Bis(Imino)Pyridyl Ligands: Synthesis, Structures, and Polymerization Studies. *J. Am. Chem. Soc.* **1999**, *121* (38), 8728−8740.
(41) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization. *Science* **2006**, *312* (5774), 714−719.
(42) Wei, J.; Zhang, W.; Sita, L. R. Aufbaureaktion Redux: Scalable Production of Precision Hydrocarbons from AlR3 (R = Et or iBu) by Dialkyl Zinc Mediated Ternary Living Coordinative Chain-Transfer Polymerization. *Angew. Chem., Int. Ed.* **2010**, *49* (10), 1768−1772.

(43) Pitet, L. M.; Amendt, M. A.; Hillmyer, M. A. Nanoporous Linear Polyethylene from a Block Polymer Precursor. *J. Am. Chem. Soc.* **2010**, *132* (24), 8230−8231.
(44) Gao, H.; Tan, Y.; Guan, Q.; Cai, T.; Liang, G.; Wu, Q. Synthesis, characterization and micellization of amphiphilic polyethylene-b-polyphosphoester block copolymers. *RSC Adv.* **2015**, *5* (61), 49376−49384.
(45) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. Utility of a Ruthenium Metathesis Catalyst for the Preparation of End-Functionalized Polybutadiene. *Macromolecules* **1997**, *30* (4), 718−721.
(46) Diallo, A. K.; Michel, X.; Fouquay, S.; Michaud, G.; Simon, F.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. α-Trialkoxysilyl Functionalized Polycyclooctenes Synthesized by Chain-Transfer Ring-Opening Metathesis Polymerization. *Macromolecules* **2015**, *48* (20), 7453−7465.
(47) Kaneyoshi, H.; Inoue, Y.; Matyjaszewski, K. Synthesis of Block and Graft Copolymers with Linear Polyethylene Segments by Combination of Degenerative Transfer Coordination Polymerization and Atom Transfer Radical Polymerization. *Macromolecules* **2005**, *38* (13), 5425−5435.
(48) Lu, Y.; Hu, Y.; Chung, T. C. M. Syntheses of diblock copolymers polyolefin-b-poly(ε-caprolactone) and their applications as the polymeric compatilizer. *Polymer* **2005**, *46* (23), 10585−10591.
(49) 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* (16), 2755−2766.
(50) 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* (24), 8923−8925.
(51) Yan, T.; Walsh, D. J.; Qiu, C.; Guironnet, D. One-Pot Synthesis of Block Copolymers Containing a Polyolefin Block. *Macromolecules* **2018**, *51* (24), 10167−10173.
(52) Yan, T.; Guironnet, D. Polyethylene Containing Triblock Copolymers Synthesized by Post-polymerization Functionalization. *Macromolecules* **2020**, *53* (11), 4338−4344.
(53) Dau, H.; Tsogtgerel, E.; Matyjaszewski, K.; Harth, E. One-For-All Polyolefin Functionalization: Active Ester as Gateway to Combine Insertion Polymerization with ROP, NMP, and RAFT. *Angew. Chem., Int. Ed.* **2022**, *61* (33), No. e202205931.
(54) Kim, K.; Strong, J.; Sarkar, S. D.; Nguyen, D.; Dau, H.; Al-Aman, D. A. A.; Dadashi-Silab, S.; Harth, E.; Matyjaszewski, K. Polyethylene-poly(methyl acrylate) Block Copolymers from PACE-SARA ATRP: Utilizing Polyolefin Active Ester Exchange-Based Macroinitiators in Atom Transfer Radical Polymerization. *Macromolecules* **2025**, *58* (3), 1337−1348.
(55) Otten, M.; Klein Gebbink, I.; Schara, P. J.; Tomović, Ž.; Lutz, M.; Bruijnincx, P. C. A.; Thevenon, A. Post-Polymerization Modification of Polyethylene through Photochemical Oximation and Consecutive Ketonization. *J. Am. Chem. Soc.* **2025**, *147* (26), 22827−22838.
(56) Johnson, L. K.; Mecking, S.; Brookhart, M. Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts. *J. Am. Chem. Soc.* **1996**, *118* (1), 267−268.
(57) Hong, S. C.; Jia, S.; Teodorescu, M.; Kowalewski, T.; Matyjaszewski, K.; Gottfried, A. C.; Brookhart, M. Polyolefin graft copolymers via living polymerization techniques: Preparation of poly(n-butyl acrylate)-graft-polyethylene through the combination of Pd-mediated living olefin polymerization and atom transfer radical polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (16), 2736−2749.
(58) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. Chain Walking: A New Strategy to Control Polymer Topology. *Science* **1999**, *283* (5410), 2059−2062.
(59) Makiguchi, K.; Satoh, T.; Kakuchi, T. Diphenyl Phosphate as an Efficient Cationic Organocatalyst for Controlled/Living Ring-Opening Polymerization of δ-Valerolactone and ε-Caprolactone. *Macromolecules* **2011**, *44* (7), 1999−2005.
(60) Corrigan, N.; Almasri, A.; Taillades, W.; Xu, J.; Boyer, C. Controlling Molecular Weight Distributions through Photoinduced Flow Polymerization. *Macromolecules* **2017**, *50* (21), 8438−8448.
(61) Corrigan, N.; Manahan, R.; Lew, Z. T.; Yeow, J.; Xu, J.; Boyer, C. Copolymers with Controlled Molecular Weight Distributions and Compositional Gradients through Flow Polymerization. *Macromolecules* **2018**, *51* (12), 4553−4563.
(62) Corrigan, N.; Zhernakov, L.; Hashim, M. H.; Xu, J.; Boyer, C. Flow mediated metal-free PET-RAFT polymerisation for upscaled and consistent polymer production. *React. Chem. Eng.* **2019**, *4* (7), 1216−1228.



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