



Comparison of various ATRP techniques for synthesis of polar block copolymers with polyolefins

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ABSTRACT

The polyolefin active ester exchange (PACE) technique allows efficient integration of coordination-insertion polymerization (CIP) with atom transfer radical polymerization (ATRP) to synthesize polyolefin-polar block copolymers. In this study, the PACE strategy was extended from previously reported SARA (supplemental activators reducing agents) ATRP to ICAR (initiators for continuous activator regeneration) ATRP, ARGET (activator regenerated by electron transfer) ATRP, and photoinitiated ATRP. All approaches showed good compatibility with the PACE-prepared macroinitiators, yielding well-defined block copolymers with low dispersities and a good agreement of theoretical and experimental molecular weights. Each technique had some advantages and limitations. SARA ATRP minimized side reactions but was limited by heterogeneous reaction conditions. ICAR ATRP was simple to set up and inexpensive, yet it generated new chains from free-radical initiators and contaminated block copolymers. ARGET ATRP required a specific selection of reducing agents and copper catalysts. PhotoATRP achieved the fastest polymerization but required proper solvents. By expanding the compatible techniques, the PACE strategy can be applied to various conditions and monomers for polyolefin-polar block copolymers.

1. Introduction

Block copolymers (BCPs), comprised of two or more covalently linked, chemically distinct polymer segments, have garnered attention due to their ability to self-assemble into well-defined nanostructures. [1–3] The integration of distinct polymer blocks enables access to novel physical properties, unattainable from the individual homopolymers.

The synthesis of BCPs frequently relies on distinct polymerization approaches for each segment. A prime example is polyolefin-polar vinyl block copolymers (PO-polar BCPs). The synthesis of PO-polar BCPs presents a synthetic challenge because each block is made by a fundamentally different polymerization mechanism. Polyolefins (POs) are typically synthesized via coordination-insertion polymerization using metal catalysts, as introduced by Phillips.[4] Later Ziegler and Natta brought coordination-insertion polymerization to the foreground of the

plastic industry.[5,6] Kaminsky et al. demonstrated utilization of metallocene and post-metallocene catalysts activated by methylaluminoxane (MAO) dramatically increased polyolefin production by a factor of 10,000.[7,8] These early-transition metal catalysts are extremely sensitive to oxygen and polar monomers, and the high oxophilicity makes them prone to catalyst poisoning. On the other hand, late-transition metal catalysts exhibit excellent tolerance to polar monomers.[9] In 1995, late-transition-metal-catalyzed olefin polymerization was pioneered by Brookhart et al., a robust process that enabled the incorporation of polar functionalities into the polyolefin backbone.[10,11] In contrast, the polar blocks are usually synthesized by reversible deactivation radical polymerization (RDRP) techniques.[12] ATRP (atom transfer radical polymerization) is one of the most widely employed approaches to obtain well-defined polar blocks.[12–15] Coordination-insertion and ATRP are highly efficient processes for their respective

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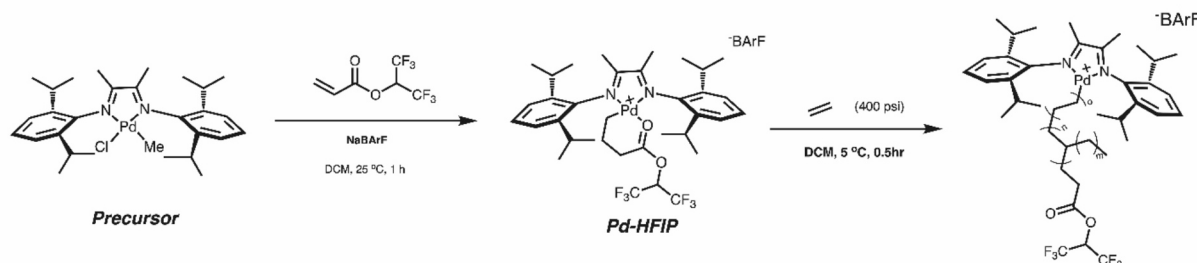
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monomers. However, they cannot be directly used for the synthesis of the other block.[16] Polymerizing polar vinyl monomers under coordination-insertion conditions using diimine Pd catalysts resulted in limited incorporation.[17] An excess of polar monomer will halt the polymerization process completely.[10,18,19] Conversely, olefinic monomers are not compatible with ATRP, due to very slow activation of the respective dormant species.[20] PO-polar BCPs remain highly appealing targets as they combine the advantageous characteristics of both components.[21,22] Polyolefins are the most commercially used polymers due to their low price and chemical and thermal stability. Polar blocks, on the other hand, offer a rich array of functional groups that control hydrophilicity, adhesion, and reactivity. Early attempts to achieve PO-polar BCPs via a single polymerization route faced roadblocks.[23] For example, Brookhart-type catalysts can incorporate a single polar vinyl unit at the chain end but cannot continue the extension to form a block.[24] Other examples of single-technique or one-pot approaches often required harsh conditions and low yield.[25,26].

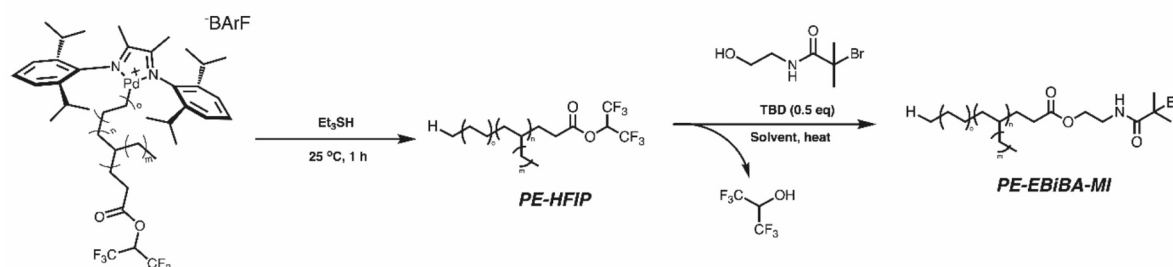
Recognizing the limitations of the “one-method for two-blocks” strategy,[13,27,28] the “two-for-two” paradigm was adopted.[16,29–33] The first block (polyolefin) was synthesized by coordination-insertion polymerization,[7,32,33] and then converted into a macroinitiator (MI) to grow the second, polar block via controlled radical polymerization. Ye and coworkers previously demonstrated such work, synthesizing diblock copolymers of PE and polystyrene/poly(*n*-butyl

acrylate) using a chelated diimine Pd^{II} complex containing a 2-bromoisobutyrate end-groups. However, the catalyst exhibits low activity (TOF = 154/h) and incomplete activation.[34] Matyjaszewski and Rieger synthesized polypropylene-*b*-polyacrylate using a tandem approach of a metallocene-mediated polymerization of propylene followed by ATRP, where the preparation of a vinyl-terminated polypropylene (PP) was achieved using a zirconocene/methyl aluminoxane catalyst. This vinyl-terminated PP was then functionalized and used as a macroinitiator for ATRP to prepare block copolymers containing polar segments.[35] Harth and coworkers introduced MILRad (metal-organic inversion light-initiated radical polymerization),[16,32,36,37] where a living coordination-insertion polymerization of ethylene (using a Brookhart-type Pd catalyst) produced a polyolefin terminated with a tertiary halide. The metal-polymer bond was cleaved via light irradiation, forming polyolefin-based macroradicals.[13,27,28] This macroradical could directly initiate a free-radical polymerization to form the second block (SI, section 3) Otherwise, it could be trapped by a functional nitroxide-based radical trap.[31,32,37] The PACE approach, presented in Scheme 1, introduced a functionalized α -chain end during the polyolefin synthesis through the formation of a chelated diimine Pd(II) catalysts, which carried a strongly electron-withdrawing ester end-groups (e.g., pentafluorophenyl or hexafluoroisopropyl ester).[33] Following the polyolefin block synthesis, the ester end-groups of the polyethylene (PE) underwent transesterification with a tertiary-bromide

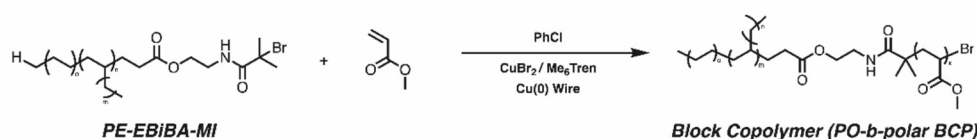
Step 1 Chelated diimine Pd catalyst produces chain-end-functionalized PE



Step 2 Post functionalization produces Macroinitiator



Step 3 Atom Transfer Radical Polymerization produces Block Copolymers



Scheme 1. A general synthetic scheme of preparing macroinitiators and block copolymers via the PACE process. Ethylene polymerization with hexafluoroisopropyl diimine Pd(II) macrochelate (Pd-HFIP) forming PE-HFIP. Next, transesterification with 2-hydroxyethyl α -bromoisobutyramide (HOBIBA) yielded amide-linked polyethylene macroinitiator (PE-EBiBA-MI). Step 3, synthesis of PE-*b*-polar block copolymer through ATRP. PE: Polyethylene. EBiBA: ethyl α -bromoisobutyramide. TBD: Triazabicyclodecene. NaBARF: Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. DCM: Dichloromethane.

containing alcohol (e.g., 2-hydroxyethyl α -bromoisobutyramide, HOBIBA or 2-hydroxyethyl α -bromoisobutyrate, HOBIB) to install an “active” initiating functionality in near quantitative yields.

Both the MILRad functionalization and PACE strategies have enabled the synthesis of PO-polar block copolymers by combining coordination-insertion polymerization and ATRP in chlorobenzene, a low-polarity solvent.[38–40] The initial studies demonstrated that second (polar) block growth was successful from PACE-prepared macroinitiators using SARA ATRP (supplemental activators and reducing agents ATRP).[32] SARA ATRP is a well-established technique that employs comproportionation of Cu(II) with Cu(0) metal.[41,42] The Cu(0) reduces Cu(II) to Cu(I), an activator complex for ATRP at a controlled rate. No external radical initiator is used to regenerate the activator, avoiding the introduction of free radicals that could cause side reactions. Thus, SARA ATRP is an efficient ATRP method,[43] yielding polymers with low dispersity and predictable molecular weights under appropriate conditions, but it introduced more soluble Cu complex into the system via comproportionation.

In this study, we explored other ATRP variants[44–46] to address the challenges of SARA ATRP (Scheme 2A). As shown in Scheme 2, we demonstrate that these variants are highly compatible with PACE-derived polyolefin macroinitiators. In particular, we examine ICAR ATRP (Initiators for Continuous Activator Regeneration ATRP),[47,48] ARGET ATRP (Activator Regenerated by Electron Transfer ATRP),[49–52] and photoATRP (Photoinduced ATRP).[46,53,54] Each of these ATRP techniques regenerates the low concentration of the active Cu(I) catalyst through a different mechanism without requiring a solid metal reductant. ICAR ATRP (Scheme 2B) utilizes a thermal radical initiator (e.g., AIBN, azobisisobutyronitrile) to continuously reduce a small portion of Cu(II) to Cu(I). ARGET ATRP (Scheme 2C) employs chemical reducing agents (such as tin(II) 2-ethylhexanoate) to maintain a low concentration of Cu(I) activator in solution.[51,52] Finally, photoATRP (Scheme 2D) relies on light and photocatalysts (e.g., Rhodamine 6G, methylene blue) to reduce Cu(II) into Cu(I), using light as the reducing stimulus.[53,55–57] These approaches also enable significantly lower copper catalyst concentrations to be used.

ICAR, ARGET, and photoATRP all showed good compatibility with PACE-prepared polyethylene macroinitiators for extending polar blocks.

The results demonstrate that the PACE strategy is not limited to SARA ATRP but can be used with all three ATRP variants, achieving well-controlled polymerizations, well-defined block copolymers, and high reproducibility. By choosing an appropriate ATRP technique, a wider range of polar monomers and polyolefin blocks can be combined in block copolymers. This expansion significantly widens the range of attainable functional polyolefin-polar BCP materials.

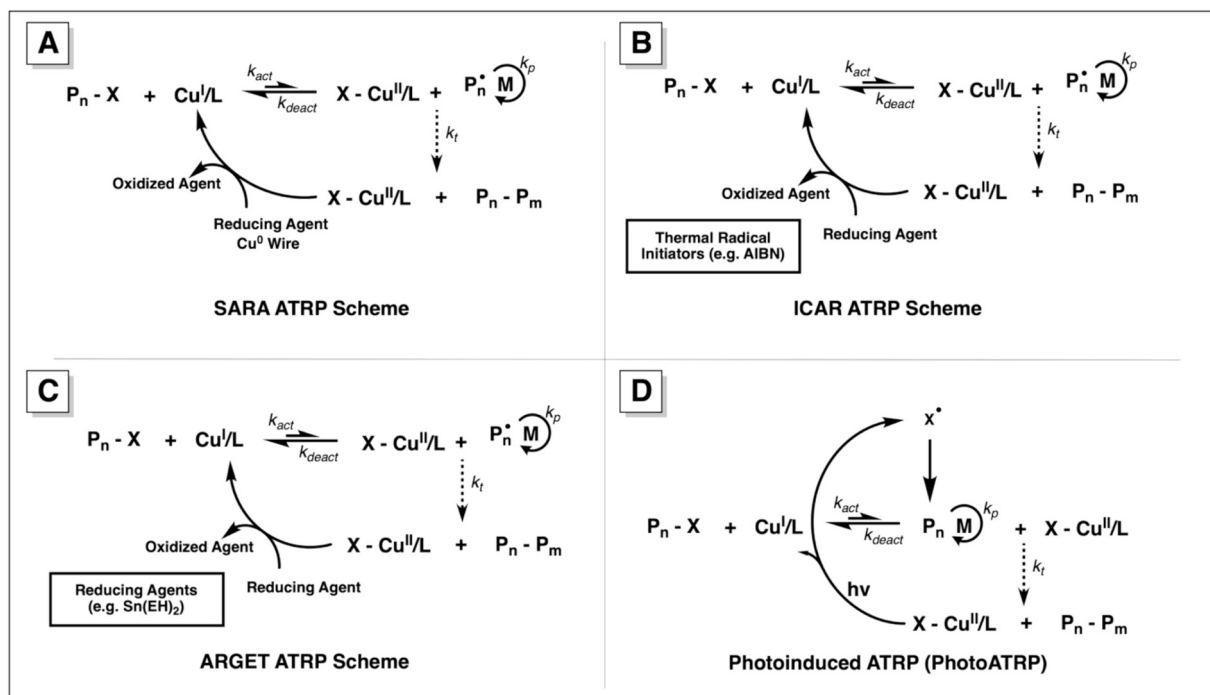
2. Results and Discussion

2.1. Synthesis of Hexafluoroisopropyl-amide terminated-polyethylene (PE-HFIP)

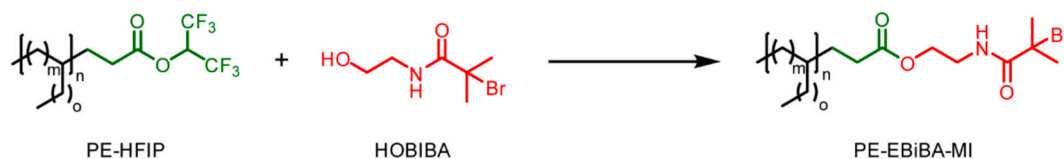
The chelated diimine Pd(II) complex (Pd-HFIP) was synthesized via the single coordination-insertion of 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA) following the approach as outlined in the Supporting Information section 2.1C. The coordination-insertion polymerization (CIP) of ethylene was performed in a mechanically stirred Parr® reactor utilizing a Pd-HFIP solution prepared in chlorobenzene (SI section 2.2A). Due to the chelated structure of the complex, semi-telechelic polyethylene bearing hexafluoroisopropyl ester moiety (PE-HFIP) was directly generated. The premature chain transfer was suppressed by exerting a high pressure of 400 psi, and the PE-HFIP polymer chain was released only from the metal center upon the addition of the quenching reagent (triethylsilane), ensuring that each polymer chain incorporated the desired end-functionality, confirmed by the characteristic peaks at 5.77, 2.51, and 1.84 ppm in the ^1H NMR of the purified homopolymer (Fig. 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.

2.2. Amide-linked PACE-prepared macroinitiator synthesis

Polyethylene-based PACE macroinitiators (PE-EBiBA-MI) were prepared by transesterification of PE-HFIP with 2-hydroxyethyl α -bromoisobutyramide (HOBIBA) in the presence of triazabicyclodec-5-ene (TBD) in toluene at 85 °C (Scheme 3, SI Section 2.2B). The installation of this bromoisobutyramide group at the end of this PE-based macroinitiator enables it to initiate further atom-transfer radical polymerization



Scheme 2. Various regenerative ATRP schemes that require minimal catalyst concentration. (A) SARA ATRP (B) ICAR ATRP (C) ARGET ATRP (D) PhotoATRP.



Scheme 3. Synthesis of PE-EBiBA-MI, polyethylene-based macroinitiator linked with 2-hydroxyethyl α -bromoisobutyramide.

(ATRP) of acrylate monomer to yield polyethylene-polyacrylate block copolymers.

The functionalization efficiency of the macroinitiator was determined by comparing the ratio of the protons associated with the terminal carbons at 1.96 ppm and the protons corresponded to the carbon adjacent to the oxygen at 2.34 ppm (Fig. S2), in which a near-quantitative functionalization was observed for the amide-linked macroinitiator.

Chlorobenzene was selected as the solvent for following ATRP to form the polar-polyethylene block copolymers as chlorobenzene offers good solubility for polyethylene macroinitiator, acrylate monomers, and polyethylene-polyacrylate block copolymers.[30,32,33] Following the synthesis of block copolymers in chlorobenzene, the GPC traces were converted to number-based GPC distribution and deconvoluted prior to analysis, using the methods outlined in SI section 3. Small-molecule analogues, HOBIB and HOBIBA, were first used to mimic the initiator behavior as both the analogues and the macroinitiator bear the same tertiary-bromide end group to carry out the model studies for the optimization of reaction parameters before using the macroinitiator for the subsequent block copolymerization.

2.3. SARA ATRP

Previous studies had established that PACE-derived polyolefin macroinitiators are highly compatible with SARA ATRP. SARA ATRP was chosen as the initial method to extend polar blocks from the PACE-derived PO macroinitiators. SARA ATRP is a well-established, low-catalyst ATRP approach. The comproportionation of Cu(0) and Cu(II) avoids the use of free-radical initiator.[15,47] Thus, undesired side reactions, such as homopolymer formation, can be minimized. Compared to ARGET or photoATRP, SARA ATRP also prevents over-reduction of the deactivator species. These characteristics rendered SARA ATRP as the first choice for assessing the compatibility of PACE macroinitiators with controlled radical polymerization.

PE-*b*-PMA block copolymers were successfully synthesized via the SARA approach, utilizing PACE-prepared macroinitiators.[33] The SARA ATRP studies confirmed that PACE-derived macroinitiators can efficiently initiate well-controlled block copolymerizations in chlorobenzene. Near-quantitative initiation efficiency and controlled chain extension were reported.[33] Linear semilogarithmic plots between conversion of methyl acrylate and reaction time were observed in the kinetic experiments, demonstrating the strong compatibility of ATRP-based methods with the PACE strategy for synthesizing well-defined PO-containing BCPs.

SARA ATRP was an initial strategy for extending the second block from the PACE-prepared MI in which polymerization kinetics and control depend on the copper surface area to reaction volume ratio.[58] The wire should be immersed to maintain a consistent Cu(I)/Cu(II) ratio. This limits the scalability of the reaction, where a partial exposure of the wire can alter the polymerization kinetics and reduce the reproducibility. These constraints led us to investigate alternative ATRP methods such as ICAR, ARGET, and photo ATRP.

2.4. ICAR ATRP

2.4.1. Model studies (Homopolymerization)

ICAR ATRP is a versatile ATRP variant, in which thermal radical

initiators (e.g., AIBN) continuously regenerate a controlled amount of Cu(I), in situ. Various azo-initiators can be used, enabling polymerization over a wide range of temperatures. Initially, methyl acrylate (MA) was polymerized using HOBIB – a small molecule analogue containing a tertiary alkyl bromide group with, AIBN as the thermal initiator.

Table 1. Summarizes the results of the homopolymerization of ma via icar atrp in chlorobenzene. for entry 1, the temperature was set to 60 °C, and the slow reaction reached a monomer conversion of 3.5% after 24 h. However, for entry 2, the reaction temperature was increased to 65 °C, resulting in a higher conversion of 30.6% after 16 h. A similar pattern was observed in entries 3 and 4. The initial reaction temperature was 75 °C, which was later decreased to 65 °C after 2 h and 3 h, respectively. The monomer conversion reached 63% and 75%, accordingly. The dispersities of obtained homopolymers increased slightly when the samples were exposed to higher temperatures due to lower stationary concentration of Cu(II)/L deactivators.

In entry 5, the reaction temperatures were further increased to 70 °C, at which conversion reached to 76% after 24 h. The initial temperature of the polymerization for entry 6 was set at 75 °C and then decreased to 70 °C after 2 h. Due to the longer reaction time compared to entry 3b, the dispersity of the PMA homopolymer decreased further from 1.16 to 1.07.C.

The entries 8 to 10 demonstrate the effect of AIBN concentration. Insufficient AIBN may result in incomplete reduction of Cu(II) to Cu(I), limiting the formation of the activator complex. On the other hand, excess radicals generated from AIBN may function as additional initiators for methyl acrylate monomers. In entry 8, reducing AIBN concentration to 170 ppm resulted in a lower conversion of 17.6%. However, the agreement between the theoretical and GPC-based molecular weight indicated slow yet well-controlled polymerization. On the contrary, as shown in entry 9, increasing the HOBIB:AIBN ratio to 1:0.25 (420 ppm of AIBN) resulted in 77.2% conversion, similar to the value observed in entry 5. However, the GPC-based molecular weight ($M_{n,GPC} = 18,800$) was significantly lower than the theoretical M_n ($M_{n,theo} = 33,200$), which indicated formation of new chains from AIBN. The HOBIB-initiated chains remained well-controlled with a modest increase in dispersity ($D = 1.15$) as the activator/deactivator equilibrium was well maintained, and extra radicals are consumed as initiators.

A similar trend was observed in entry 10, where the ratio of HOBIB to AIBN was further increased to 1:0.3, and a near quantitative conversion of acrylate was observed. However, the GPC molecular weight ($M_{n,GPC} = 24,600$) was significantly lower than the theoretical M_n ($M_{n,theo} = 39,200$). Therefore, it can be concluded that under the given reaction conditions, 350 ppm of AIBN was within the optimal radical initiator concentration to form a sufficient activator population for efficient polymerization without a large population of polymer chains formed by excess AIBN.

A kinetic investigation of ICAR ATRP of MA using HOBIB was performed (Fig. 1). As illustrated in Fig. 1A, a gradual unimodal peak shift from high to low elution volume was observed in the GPC traces, indicating controlled and successful polymerization of MA in chlorobenzene. This was further corroborated by the decrease in dispersity, which demonstrated that controlled PMA synthesis is achievable in chlorobenzene via ICAR ATRP.

2.4.2. Block copolymerization by ICAR ATRP

Polyethylene-poly(methyl acrylate) block copolymers (PE-*b*-PMA)

Table 1
Poly(methyl acrylate) prepared via ICAR ATRP in chlorobenzene ^{a)}.

#	Temp. (°C)	[CuBr ₂] ₀ (ppm)	DMF (vol%)	[AIBN] ₀ (ppm)	Time _{rxn} (h)	MA Conv. (%)	M _{n,th}	M _{n,GPC}	D
1	60	236	8	350	24	3.5%	1,000	–	–
2	65	227	9	350	16	30.6%	6,800	6,700	1.11
3 ^{b)}	75→65	236	5	350	16	63.0%	13,800	16,600	1.16
4 ^{c)}	75→65	236	5	350	16	74.0%	16,100	18,200	1.13
5	70	227	9	350	24	76.0%	16,600	18,700	1.09
6 ^{d)}	75→70	227	9	350	24	83.0%	18,100	24,100	1.07
7	75	236	5	350	18	81.1%	17,700	19,000	1.13
8 ^{e)}	70	227	9	170	24	17.6%	7,600	6,300	1.14
9 ^{e)}	70	227	10	420	24	77.2%	33,200	18,800	1.15
10 ^{e)}	70	227	9	490	24	91.1%	39,200	24,600	1.14

a) Methyl acrylate was the monomer used for ICAR ATRP in chlorobenzene. [HOBIB]:[MA]:[CuBr₂]:[Me₆Tren]:[AIBN] = 1:250:0.1:0.3:X. The ratio of AIBN is based on the stated AIBN concentration. Initial ratio of the monomer to initiator specified in the table. Reaction temperature specified in the table. Total reaction volume approximately 2.1 ± 0.1 mL. The initial concentration of monomers, [M]₀ = 5.2 ± 0.1 M. All reagents deoxygenated with N₂ prior to polymerization. b) Reaction temperature changed from 75 °C to 65 °C at t = 2 h. c) Reaction temperature changed from 75 °C to 65 °C at t = 3 h. d) Reaction temperature changed from 75 °C to 70 °C at t = 2 h. e) [HOBIB]:[MA]:[CuBr₂]:[Me₆Tren]:[AIBN] = 1:500:0.1:0.3:X. The value X (for AIBN) specified in the table.

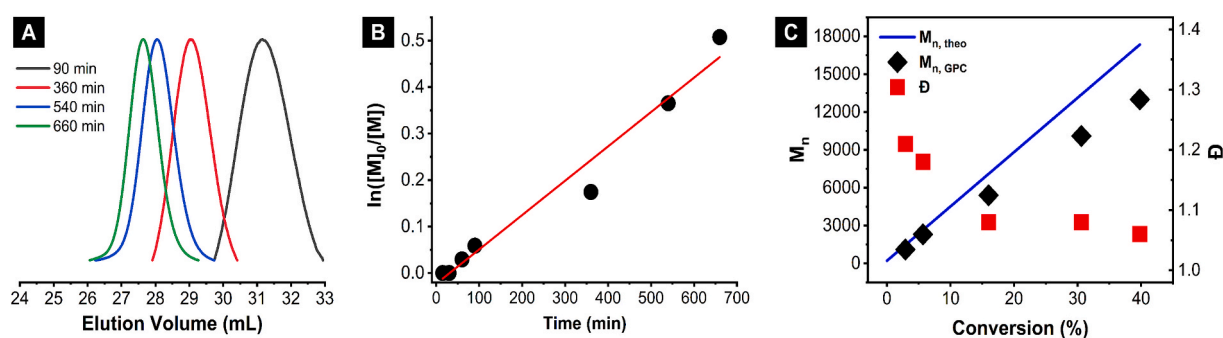


Fig. 1. Poly(methyl acrylate) synthesized using 2-hydroxyethyl α -bromoisobutyrate (HOBIB) initiator via ICAR ATRP. (A) The GPC traces of purified samples over the time span from 1.5 to 11 h. (B) Dependence of $\ln([M]_0/[M])$ on time and (C) dependence of molecular weight on conversion in relation with dispersity. Molar ratios: [HOBIB]:[MA]:[CuBr₂]:[Me₆Tren]:[AIBN] = 1:500:0.1:0.3:0.2. [MA]₀ = 5.1 M, chlorobenzene as solvent (45 v/v%) at 70 °C. All reagents were deoxygenated with N₂ prior to polymerization. Total reaction volume = 2.19 mL.

were synthesized using an amide-linked PACE-prepared macroinitiator (PE-EBiBA-MI). The red peak in Fig. 2A corresponds to the macroinitiator, while the black peak corresponds to the block copolymers obtained after ICAR ATRP, where a small amount of unreacted macroinitiator was observed at ~ 27 mL elution volume. The original GPC traces were further converted to a chain-number distribution and deconvoluted to estimate the molar ratio of the block copolymer and macroinitiator peaks (Fig. 2B). The detailed procedure for deconvolution and the calculation of initiation efficiency is outlined in SI section 3. The minor peak aligned with the original macroinitiator peak. The major peak, associated with block copolymers (black dots), was integrated to 94%, and the minor peak (red dots) was integrated to 6%. These results indicate that ICAR ATRP is compatible with PACE-prepared macroinitiators, as evidenced by the high initiation efficiency. Fig. 2C shows a gradual unimodal shift in peak elution volume from high to low with increasing reaction time, and Fig. 2D presents a linear semilogarithmic relationship between conversion and time, demonstrating controlled polymerization and high initiation efficiency.

Table 2 presents PE-*b*-PMA synthesized by utilizing ester- and amide-linked PACE-prepared macroinitiators. Entries 1–6 used an ester-linked macroinitiator. Identical conditions were used for entries 1–2, resulting in conversions of 4.2% and 3.4% at 3 h. Similarly, entries 3–4 were prepared under the same conditions, yielding 4.5% and 4.4% conversions at 6 h. The reaction time was increased to 20 h for entries 5 and 6, and PMA homopolymer with high MW was successfully synthesized. Identical conditions were employed for entries 5–6, where the difference in conversion was less than 3%, indicating reproducibility even at higher conversion. Furthermore, dispersity reached 1.02 for entry 6, with a close match between theoretical and experimental molecular weight.

Entries 7–8 employed amide-linked macroinitiators, achieving conversions of 64.1%, 66.3%, and 64.7% at 27 h under identical conditions, with a close match between theoretical and experimental molecular weights. In addition, the ¹H DOSY NMR analysis of purified PE-*b*-PMA (Fig. S6) showed signals that corresponded to the PE block (1.25–0.83) ppm and the PMA block (3.66, 2.28, 1.92, 1.67) arranged in a single diffusion coefficient. This observation confirmed that the formed blocks were covalently bonded with each other.

Fig. 2 and Table 2 confirmed that ICAR ATRP in chlorobenzene enables controlled synthesis of PE-polar BCs, close to the results obtained from the case of SARA ATRP. The homogeneous nature of ICAR ATRP, where catalyst, ligand, and the initiators are fully dissolved, ensures uniform reaction conditions throughout the entire experimental process. Furthermore, by selecting thermal initiators with different activation energies, the ICAR approach can be tuned to accommodate a wider range of monomers, as will be reported in the future.

2.5. ARGET ATRP

2.5.1. Model studies (Homopolymerization)

Activator Regenerated by Electron Transfer (ARGET) ATRP continuously reduces Cu(II) to form Cu(I) to maintain the ATRP equilibrium. However, unlike ICAR ATRP, ARGET ATRP employs chemical reducing agents instead of thermal radical initiators, thereby avoiding the generation of new chains. Common ARGET reducing agents include tin(II) 2-ethylhexanoate and ascorbic acid that allow fine control over the Cu(II)/Cu(I) ratio.

Results from ICAR ATRP, Section 3.1, demonstrated effective block copolymerization with PACE-prepared macroinitiators. However,

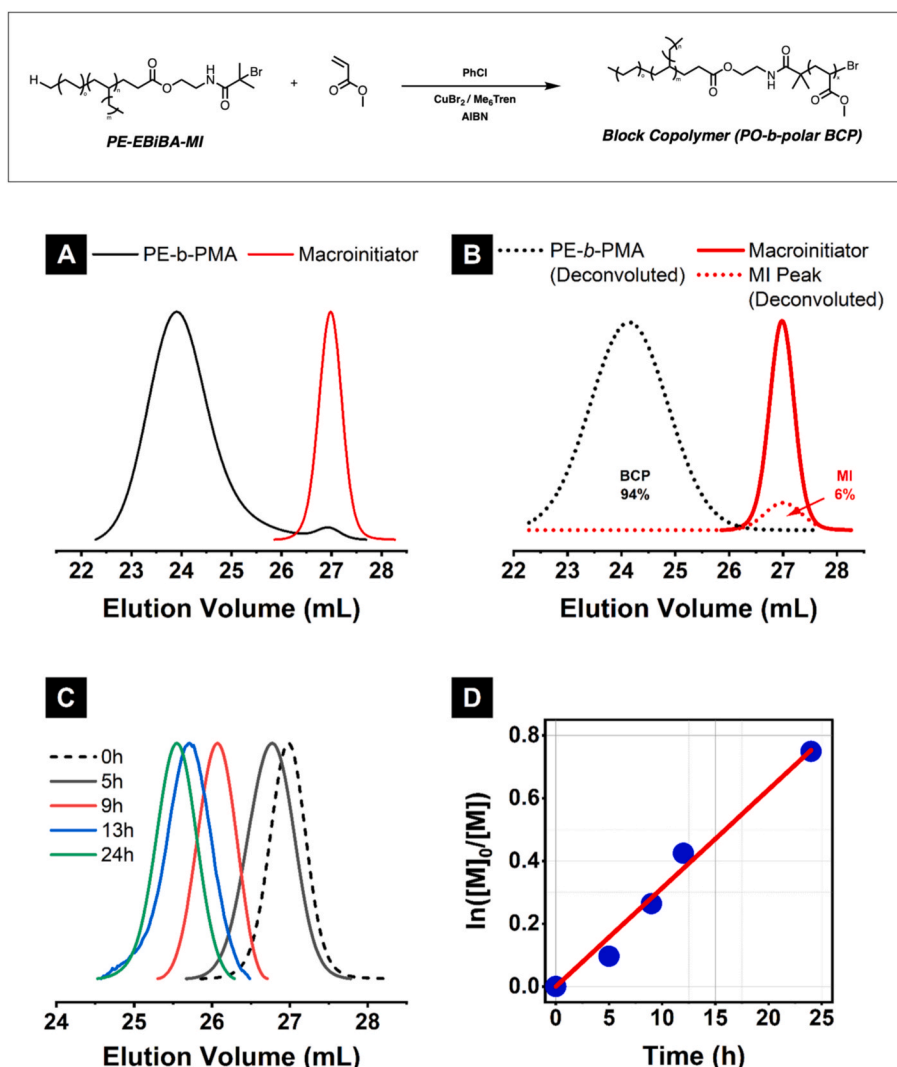


Fig. 2. Polyethylene-*b*-poly(methyl acrylate) synthesized with amide-linked macroinitiator. Amide-linked macroinitiator: $M_n = 16,400$, $D = 1.02$. (A) weight-based THF GPC traces of the macroinitiator and PE-*b*-PMA block copolymer sample, (B) Deconvoluted chain-number based THF GPC traces of the macroinitiator and PE-*b*-PMA block copolymer sample (R^2 value: 96%) (C) THF GPC traces, weight-based, (D) dependence of $\ln([M]_0/[M])$ on time, Molar ratios: [Macroinitiator]:[MA]:[CuBr₂]:[Me₆Tren]:[AIBN] = 1:500:0.1:0.3:0.2. Chlorobenzene as solvent (50 vol%) at 70 °C. [MA]₀ = 4.4 M. [CuBr₂] = 200 ppm.

Table 2

PE-*b*-PMA block copolymers prepared via the PACE-ICAR approach ^{a)}.

#	[M] ₀	MI Linkage	V _{rxn} (mL)	[CuBr ₂] ₀ (ppm)	DMF (%)	Time (h)	MA Conv. (%)	$M_{n,th}$	$M_{n,GPC}$	D_{BCP}
1	5.2	Ester	0.65	230	7.00	3	4.2%	11,900	11,300	1.02
2	5.2	Ester	0.65	230	7.00	3	3.4%	11,800	11,000	1.03
3	5.2	Ester	0.65	230	7.00	6	4.5%	12,000	11,400	1.04
4	5.2	Ester	0.65	230	7.00	6	4.4%	12,000	11,300	1.04
5	4.2	Ester	0.48	190	9.90	20	62.4%	41,300	47,800	1.05
6	4.2	Ester	0.48	190	9.90	20	59.6%	40,100	38,400	1.02
7	4.4	Amide	0.76	200	7.60	27	66.3%	44,900	40,900	1.20
8	4.4	Amide	0.76	200	7.60	27	64.7%	44,200	40,300	1.20

a) Molar ratios: [Macroinitiator]:[MA]:[CuBr₂]:[Me₆Tren]:[AIBN] = 1:500:0.1:0.3:0.2. All reagents were deoxygenated with N₂ prior to block copolymerization. Chlorobenzene (45 vol%) at 70 °C used as solvent. Total reaction volume and initial molar ratio specified in the table. MA, methyl acrylate, was the monomer for the second block using ICAR ATRP. Macroinitiators: Ester-linked macroinitiator: $M_n = 9,600$, $D = 1.03$. Amide-linked macroinitiator: $M_n = 16,400$, $D = 1.02$.

before attempting the desired block copolymerization via ARGET ATRP, we first conducted MA homopolymerization model studies. PMA was synthesized under ARGET conditions in chlorobenzene using HOBIB as the small molecule initiator. The homopolymers closely paralleled the block copolymers, apart from a slight difference in the rate of polymerization. Specifically, PMA growth was slightly slower when using the PE macroinitiator compared to the HOBIB initiator. The difference is

likely due to the macroinitiator's large and hydrophobic polyethylene backbone ($M_n \sim 10,000 - 15,000$). The presence of a significant amount of MI reduced the overall polarity of the medium relative to the small-molecule system.

To better replicate the environment with a non-polar polyethylene backbone present as the macroinitiator, isooctane was introduced to ARGET ATRP model reactions. Isooctane and LDPE have similar

dielectric constants of 1.9 and 2.2, respectively. Therefore, the introduction of isooctane could represent the effect of the dissolved polyethylene backbone. This adjustment allowed us to predict and optimize the subsequent block copolymerization reaction.

Table 3 summarizes MA homopolymerization via ARGET ATRP using HOBIB as the initiator. Entries 1–3 pertain to PMA synthesis in the absence of isooctane, where the MA conversion reached up to 65.2% and 65.9% at 20 h (entries 1 and 2). These nearly identical conversions under the same reaction conditions indicate the reproducibility of the ARGET system. Additionally, the M_n and dispersity measured from GPC analysis also showed good agreement with the theoretical molecular weight. Extending the reaction time to 24 h (entry 3) resulted in an increased conversion, up to 69.1%.

Entries 4–8 present the synthesis of PMA with 25 wt% isooctane added to the reaction medium. The addition of isooctane, to better mimic the dissolution of the non-polar macroinitiator in the target reaction, resulted in a lower conversion of 55.6% (entry 4). This decrease can be attributed to the decrease in polarity by the introduction of isooctane. However, the dispersity did not change, while a good match between theoretical and experimental molecular weights was observed. A similar reproducibility in monomer conversion was observed in entries 5 and 6, with a small decrease in CuCl_2 concentration from 95 ppm to 70 ppm.

In entries 1–6, the ratio of reducing agent (tin(II) 2-ethylhexanoate) to initiator was maintained at 0.09:1. However, in entries 7 and 8, the ratio of tin(II) 2-ethylhexanoate to initiator was increased, resulting in a faster conversion. For instance, the conversion reached to 60.2% and 92.3%, when the $\text{Sn}(\text{EH})_2$ to initiator ratio was increased to 0.18 and 0.36, respectively.

The results from the model studies presented in Table 3 indicate that ARGET ATRP can be successfully conducted in chlorobenzene. High reproducibility was observed even in the presence of isooctane, a low-polarity solvent that decreases K_{ATRP} and polymerization rate.[59] PMA homopolymers synthesized by ARGET ATRP were analyzed further kinetically (Fig. S5). A gradual unimodal peak shift from high to low elution volume and a linear semilogarithmic relationship between conversion and time were observed.

2.5.2. Block copolymerization by ARGET ATRP

Following the successful synthesis of PMA in chlorobenzene, the PE-based macroinitiator was used to prepare the PE-*b*-PMA block copolymer. A gradual increase in the unimodal peak from 90 min to 1260 min indicated successful polymerization under the optimized reaction condition (Fig. 3A). An induction period was observed in the earlier samples, as indicated by a slight deviation in the conversion at the 390 min point in Fig. 3B. However, a linear semilogarithmic kinetic plot and good temporal control were observed, while a close match between theoretical and experimental molecular weight and a low dispersity of below 1.20 were maintained throughout the 21 h kinetics experiment.

As shown in Table 4, despite the limited amount of macroinitiators, various conditions were tested for the synthesis of PE-*b*-PMA block

copolymer via ARGET ATRP. In entries 1 and 2, PE-*b*-PMA block copolymers were synthesized under the same conditions. The conversions reached 26.1% and 74.9% at 9 h and 24 h, respectively. The dispersity was maintained at 1.03, indicating controlled polymerization even at higher conversions above 70%. For entries 3 and 4, the monomer concentrations and the DMF vol.% were increased to investigate the possibility of reaching higher conversion, where the conversions reached up to 91.2% and 54.3% for entries 3 and 4, respectively. A relatively good match between the theoretical and experimental weight was maintained at conversions above 90% in a comparatively shorter time, while maintaining a low dispersity.

ARGET ATRP showed high compatibility with PACE-prepared macroinitiators. As shown in Table 4, all PE-*b*-PMA copolymers exhibited low dispersities below 1.1 and excellent agreement between theoretical and experimental molecular weights. These polymerization processes were well-controlled with minimal side reactions.

2.6. PhotoATRP

2.6.1. Model studies (Homopolymerization)

PhotoATRP is notable for its fast polymerization and the wide range of photocatalysts.[60–63] ICAR and ARGET ATRP both regenerate Cu(I) activator through in situ radical initiators or chemical reducing agents. However, photoATRP uses light as an external stimulus to regenerate Cu (I). This enables straightforward external regulation; a polymerization can be paused or restarted by turning the light off or on, respectively. The combination of temporal control and the diversity of available photocatalysts makes photoATRP an attractive strategy for PACE-macroinitiators in chain extension.

Rhodamine 6G (R6G) is a common photocatalyst used for the synthesis of PMA via photoATRP in the presence of HOBIB as the initiator analog (Table 5).[57] In entries 1 and 2, R6G was used as the photocatalyst however, entry 1 used DMSO as the solvent, while PhCl was used for entry 2. The MA conversion was much lower for PhCl (23.9%) than DMSO (86.6%) because of the use of low-polarity solvent chlorobenzene, which slowed down the polymerization rate.

In entries 3 to 5, increasing amounts of photocatalyst were employed. The conversion increased from 24% to 68% as the photocatalyst concentration was raised from 38 ppm to 475 ppm, while the copper catalyst concentration and reaction time were kept constant. In entries 6–7, the same conditions were used to confirm the reproducibility of the system, where the conversion reached 16.8% and 17.6% at 7 h. A high concentration of copper catalyst and a low concentration of photocatalysts were employed in these two entries, which led to relatively slower polymerization.

In entries 8 and 9, a lower concentration of CuBr_2 and a higher concentration of R6G were used. These conditions induced faster polymerization with monomer conversion of 45.5% and 49.5% at 2 h, respectively. The conversion was approximately 30% higher despite having a shorter reaction time. Similar to entries 6 and 7, relatively similar conversions were observed between the two samples.

Table 3
Poly(methyl acrylate) prepared via the ARGET ATRP in chlorobenzene ^{a)}.

#	[M] ₀	V _{rxn} (mL)	[CuCl ₂] ₀ (ppm)	[Sn(EH) ₂]:[I]	DMF (%)	Isooctane (wt%)	Time _{rxn} (h)	Conv. (%)	M _{n,th}	M _{n,GPC}	D
1	4.8	2.3	95	0.09	11	0	20	65.2%	11,400	10,900	1.14
2	4.8	2.3	95	0.09	11	0	20	65.9%	11,600	9,800	1.14
3	4.8	2.3	95	0.09	13	0	24	69.1%	12,100	11,700	1.11
4	4.8	2.3	95	0.09	13	25	24	55.6%	9,800	9,000	1.12
5	3.5	3.2	70	0.09	10	25	24	53.2%	9,400	8,400	1.12
6	3.5	3.2	70	0.09	10	25	24	50.4%	8,900	7,500	1.12
7	4.7	2.4	95	0.18	13	25	24	60.2%	10,600	11,500	1.08
8	4.7	2.4	95	0.36	13	25	24	92.3%	16,100	15,500	1.14

a) Methyl acrylate was as monomer for ARGET ATRP. HOBIB was used as the initiator. Initial ratios of the monomer to initiator and reducing agent to initiator are specified in the table. Catalyst concentration specified in the table. Chlorobenzene at 90 °C was used as the solvent. Pressure release vial (volume = 1 dram) was used as the reaction vessel. All reagents were deoxygenated with N₂ prior to polymerization. [HOBIB]:[MA]:[CuCl₂]:[Me₆Tren] = 200:1:0.03:0.09.

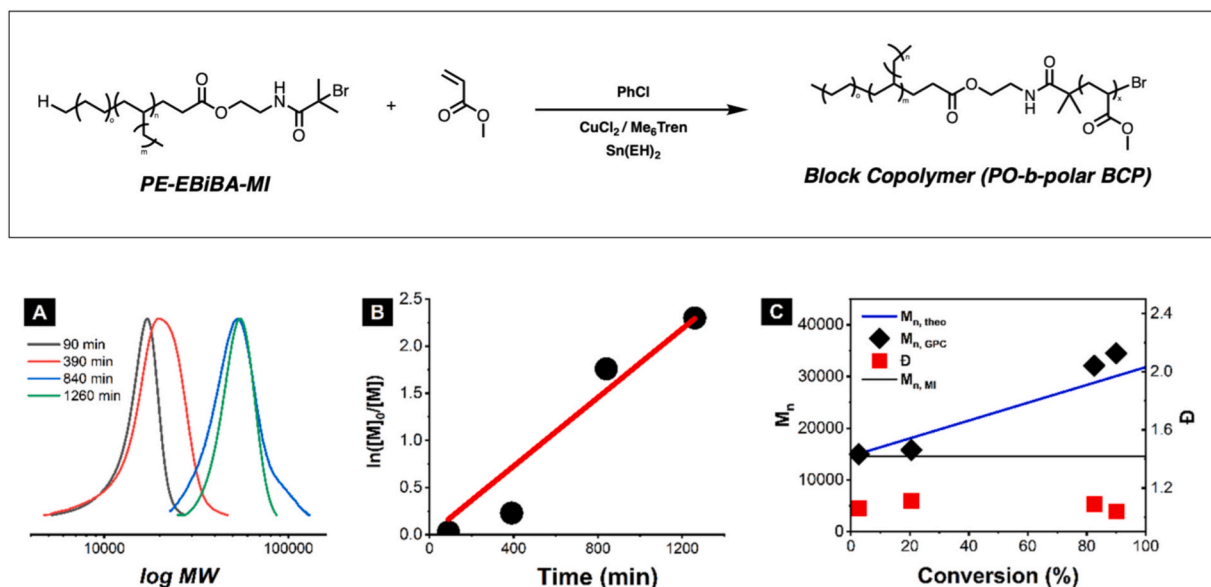


Fig. 3. Polyethylene-*b*-poly(methyl acrylate) synthesized with PE-E*B*iBA-MI. Amide-linked MI, $M_n = 14,600$, $D = 1.09$, used as macroinitiator. (A) THF GPC traces, weight-based, (B) dependence of $\ln([M]_0/[M])$ on time, (C) dependence of molecular weight on conversion. Molar ratios: [Macroinitiator]:[MA]:[CuCl₂]:[Me₆Tren]:[Sn(EH)₂] = 1:200:0.03:0.09:0.09. All reagents were deoxygenated with N₂ prior to block copolymerization.

Table 4

PE-*b*-PMA block copolymers prepared via the PACE-ARGET approach ^{a)}.

#	[M] ₀	V _{rxn} (mL)	[CuCl ₂] ₀ (ppm)	Time (h)	DMF (vol.%)	[Sn(EH) ₂]:[I]	MA Conv. (%)	M _{n,th}	M _{n,GPC}	D _{BCP}
1 ^{b)}	3.5	3.2	70	9	1.6	0.09	26.1	22,300	21,400	1.03
2 ^{b)}	3.5	3.2	70	24	1.6	0.09	74.9	30,700	28,200	1.03
3 ^{c)}	4.5	1.0	90	21	14.2	0.09	91.2	30,200	36,400	1.04
4 ^{c)}	4.4	0.5	90	15	14.2	0.12	54.3	23,900	23,500	1.07

a) Molar ratios: [Macroinitiator]:[MA]:[CuCl₂]:[Me₆Tren]:[Sn(EH)₂] = 1:200:0.03:0.09:0.09. All reagents were deoxygenated with N₂ prior to block copolymerization. Chlorobenzene (45 vol%) at 90 °C used as solvent. Total reaction volume and initial molar ratio specified in the table. MA, methyl acrylate, was the monomer for the second block using ARGET ATRP. b) Amide-linked MI, $M_n = 14,600$, $D = 1.09$. c) Macroinitiator: amide-linked MI, $M_n = 17,800$, $D = 1.02$.

Table 5

Poly(methyl acrylate) prepared via the photoATRP approach in chlorobenzene ^{a)}.

#	Solvent	[M] ₀	[CuBr ₂] ₀ (ppm)	[PC] ₀ (ppm)	Intensity (%)	DMF (%)	Time _{rxn} (h)	MA Conv. (%)	M _{n,th}	M _{n,GPC}	D
1	DMSO	4.9	200	40	75	11	3	86.6%	37,500	29,900	1.10
2	PhCl	5.0	200	38	75	11	3	24.0%	6,900	7,800	1.28
3	PhCl	4.7	200	55	100	16	3	35.1%	15,300	13,200	1.21
4	PhCl	4.7	200	220	100	16	3	59.9%	26,000	24,300	1.31
5	PhCl	5.0	200	475	100	11	3	68.0%	29,500	22,300	1.29
6	PhCl	4.8	650	20	75	13	7	16.8%	7,400	7,800	1.12
7	PhCl	4.8	650	20	75	13	7	17.6%	7,800	8,400	1.12
8	PhCl	4.3	50	120	100	11	2	45.5%	19,800	25,300	1.49
9	PhCl	4.3	50	120	100	11	2	49.5%	21,500	20,500	1.64
10	PhCl	4.1	200	50	100	14	6	52.5%	22,800	19,500	1.24
11 ^{b)}	PhCl	4.1	200	50	100	14	6	33.8%	14,800	12,600	1.16

a) Methyl acrylate was the monomer used for Photo ATRP in presence of HOBIB as initiator. Initial monomer concentration, photocatalyst concentration, and copper-catalyst concentration are specified in the table. Chlorobenzene, with approximately 15% DMF, at room temperature used as the solvent. (DMF % specified in the table). Temperature controlled using fan-equipped photoredox box. (Wavelength = 525 nm) Pressure release vial (volume = 1 dram) used as the reaction vessel. Reaction conditions: [CuBr₂]:[Me₆Tren] = 1:3. [HOBIB]:[MA] = 1:500. All reagents deoxygenated with N₂ prior to polymerization. b) Isooctane used as a mimic of non-polar macroinitiators. Isooctane wt% set as 9%. PC: Photocatalyst.

In entries 10 and 11, the effect of isooctane was investigated. All conditions were kept constant except for the presence of isooctane. The conversion reached 52.5% without isooctane in entry 10. However, when 9 wt% of isooctane was added to the reaction medium, the conversion decreased to 33.8%. The presence of a nonpolar component, such as isooctane or highly branched polyethylene, slows the polymerization for photoATRP in chlorobenzene.

PMA synthesized by photoATRP using HOBIB was also investigated

through a kinetic experiment (Fig. 4). Fig. 4A displays THF GPC traces, where a gradual peak shift from high to low elution volume indicates controlled polymerization of methyl acrylate in chlorobenzene. Fig. 4B shows a good correlation between semilogarithmic conversion and time. Finally, Fig. 4C demonstrates good agreement between theoretical and experimental molecular weights. The dispersity decreased continuously from 60 min to 180 min, with a slight uptick observed in the 270 min sample.

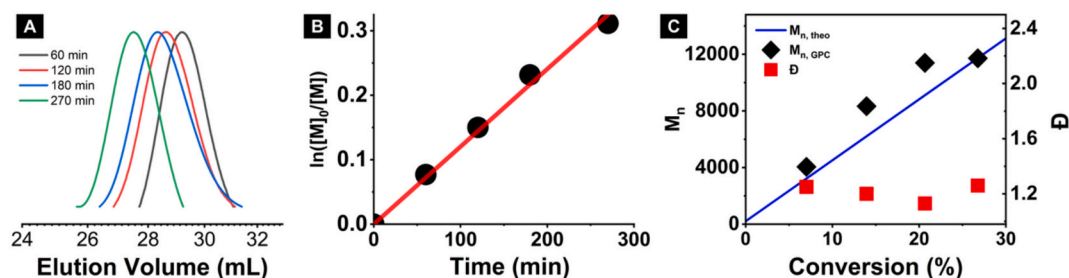


Fig. 4. Poly(methyl acrylate) synthesized with HOBIB via Photo ATRP. (A) THF GPC traces at time = 1 h to 4.5 h. (B) Dependence of $\ln([M]_0/[M])$ on time, (C) dependence of molecular weight on conversion. Molar ratios: [HOBIB]:[MA]:[CuBr₂]:[Me₆Tren]:[Rhodamine 6G] = 1:500:0.1:0.3:0.0125. [MA]₀ = 4.7 M, chlorobenzene as solvent (42%). Green light (525 nm) used as light.

Source. A photoredox box with a fan used to maintain consistent temperature and light intensity. All reagents were deoxygenated with N₂ prior to polymerization. Total reaction volume = 2.38 mL

2.6.2. Block copolymerization by PhotoATRP

The model studies demonstrated that fast and controlled polymerizations of methyl acrylate in chlorobenzene were achieved via photoATRP. A PE-based macroinitiator was then employed in place of HOBIB to prepare PE-*b*-PMA block copolymer in the target studies.

Table 6 shows various conditions evaluated for the synthesis of PE-*b*-PMA via photoATRP. Entries 1 through 4 employed identical polymerization conditions. For entries 1 and 2, conversions reached 16.2% and 14.9% after 1 h. For entries 3 and 4, the reaction time was increased to 2 h. The conversions reached 22.4% and 21.5%, respectively. The experimental molecular weights closely match the $M_{n,theo}$. In entry 5, extending the reaction time to 3 h resulted in approximately 5% increase in conversion, with a slight decrease in dispersity. The R6G concentration was increased by two-fold in entry 6, resulting in a higher conversion of 33.33% with an increase in dispersity from 1.20 to 1.56. This indicates that an excess amount of photocatalyst decreased the concentration of the deactivator complex and compromised control over polymerization. In entry 7, increasing copper catalyst concentration to 330 ppm led to 24.4% conversion without a significant decrease in dispersity. Finally, analysis of the results summarized in Table 6 indicates that copper(II) bromide at 180 ppm and R6G at 50 ppm are within the optimal range for the controlled polymerization of methyl acrylate via photoATRP in chlorobenzene.

Fig. 5A displays unimodal peak growth from 60 min to 300 min in THF GPC traces and Fig. 5B shows a semilogarithmic relationship without signs of incubation. A slight deviation between the experimental and theoretical molecular weight was observed in Fig. 5C. Furthermore, the dispersity remained low, between 1.1 and 1.2, indicating that PACE-prepared macroinitiators are compatible with photoATRP using R6G in chlorobenzene.

Rhodamine 6G can be applied using relatively long-wavelength (525 nm) green light. Another advantage of photoATRP over other approaches is its faster polymerization rate. Compared to SARA ATRP (Section 2.4), ICAR ATRP (Section 2.5) and ARGET ATRP (Section 2.6), photoATRP was carried out to reach high conversion in a shorter time.

Table 6

PE-*b*-PMA block copolymers prepared via the PACE-photo approach^a.

#	[M] ₀	V _{rxn} (mL)	Target DP	[CuBr ₂] ₀ (ppm)	[PC] ₀ (ppm)	Time _{rxn} (h)	MA Conv. (%)	$M_{n,theo}$	$M_{n,GPC}$	D
1	4.1	2.71	500	180	50	1	16.20%	25,000	22,000	1.02
2	4.1	2.71	500	180	50	1	14.90%	24,500	28,600	1.18
3	4.1	2.71	500	180	50	2	22.40%	27,700	31,800	1.23
4	4.1	2.71	500	180	50	2	21.50%	27,300	31,400	1.21
5	4.1	2.71	500	180	50	3	27.80%	30,000	34,900	1.20
6	7.0	2.38	800	180	100	3	33.33%	41,000	38,100	1.56
7	7.0	2.38	800	330	50	3	24.43%	34,900	33,000	1.20

a) Molar ratios: [Macroinitiator]:[MA]:[CuBr₂]:[Me₆Tren]:[R6G] = 1:500:0.1:0.3:0.0125. All reagents were deoxygenated with N₂ prior to block copolymerization. Chlorobenzene as solvent (50 vol%) in a temperature-controlled photo-redox box, using 525 nm Kessil lamp. Total reaction volume and initial molar ratio specified in the table. MA, methyl acrylate, was the monomer for the second block using ARGET ATRP. [DMF]₀ = 15 ± 1%. Amide-linked MI, M_n = 18,060, D = 1.02.

Furthermore, poly(methyl acrylate) was successfully prepared in a controlled manner using Rhodamine 6G and 525 nm green light.^[64] Relatively long-wavelength green light did not induce polyolefin degradation. Typically, shorter wavelengths (300 nm for polyethylene and 370 nm for polypropylene) are needed for the C–C bond cleavage.^[65]

Despite its straightforward setup and fast rate, photoATRP presents several challenges. Ensuring uniform light intensity across all spatial points within the photoreactor box can be challenging, as variations in vial position, stirring rate, sample number, or lamp age may alter the photoredox environment. Cu(I) (re)generation is directly controlled by the light intensity. Thus, the fluctuations can compromise the control of polymerization, leading to broader dispersity and lower reproducibility.

2.7. Comparison of four approaches for PACE macroinitiators to prepare block copolymers

Previous studies illustrated that both PACE and MILRad strategies can successfully integrate two distinct polymerization methods into a single process. This study broadened the scope of PACE-based block copolymer synthesis beyond SARA ATRP. The methods investigated include ICAR, ARGET, and photoATRP to achieve methodological flexibility (Fig. 6).

PACE allowed a pathway to prepare polyolefin-polar block copolymers. SARA, ICAR, ARGET, and PhotoATRP presented unique strengths and weaknesses when used in conjunction with the PACE approach, which are summarized in Fig. 6. Specific monomers or experimental constraints may require a different ATRP type/reaction condition for optimal results. For all of the ATRP approaches investigated, the PACE-derived macroinitiators were successfully integrated to form well-defined block copolymers. This was evidenced by low dispersity of the block copolymers, gradual increase of molecular weight distributions, and close agreement between theoretical and measured molecular weights. These indicate efficient initiation and controlled chain growth across all systems.

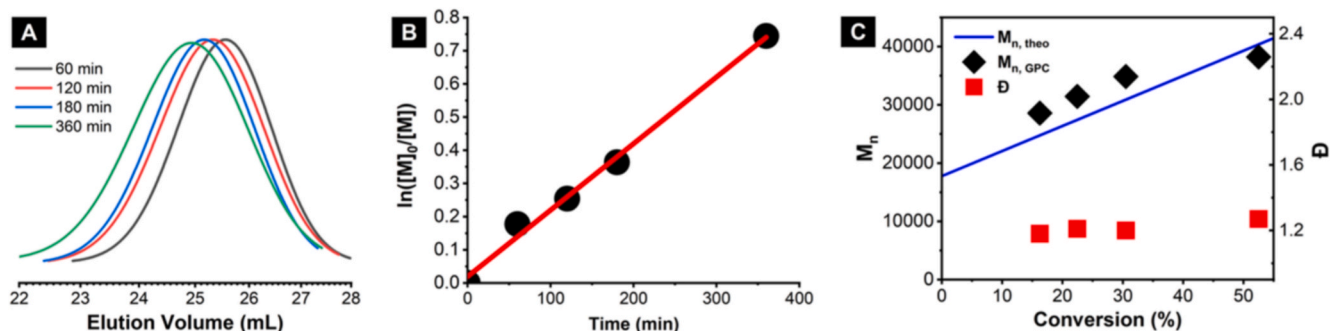
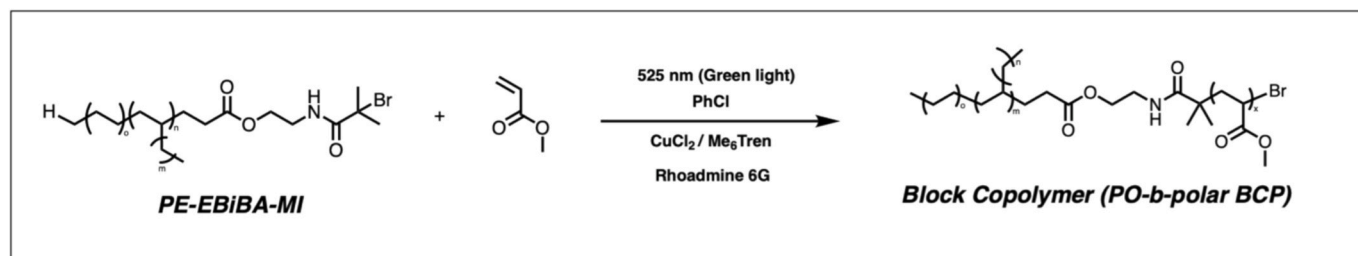


Fig. 5. Polyethylene-*b*-poly(methyl acrylate) synthesized with PE-EBiBA-MI. (A) THF GPC traces, weight-based, (B) dependence of $\ln([M]_0/[M])$ on time, (C) dependence of molecular weight on conversion. Molar ratios: [Macroinitiator]:[MA]:[CuBr₂]:[Me₆Tren]:[Rhodamine 6G] = 1:500:0.1:0.3:0.0125. Chlorobenzene as solvent (50 vol%) in a temperature-controlled photo-redox box, using 525 nm Kessil lamp. [MA]₀ = 4.1 M. [CuBr₂] = 185 ppm. [Rhodamine 6G] = 50 ppm.

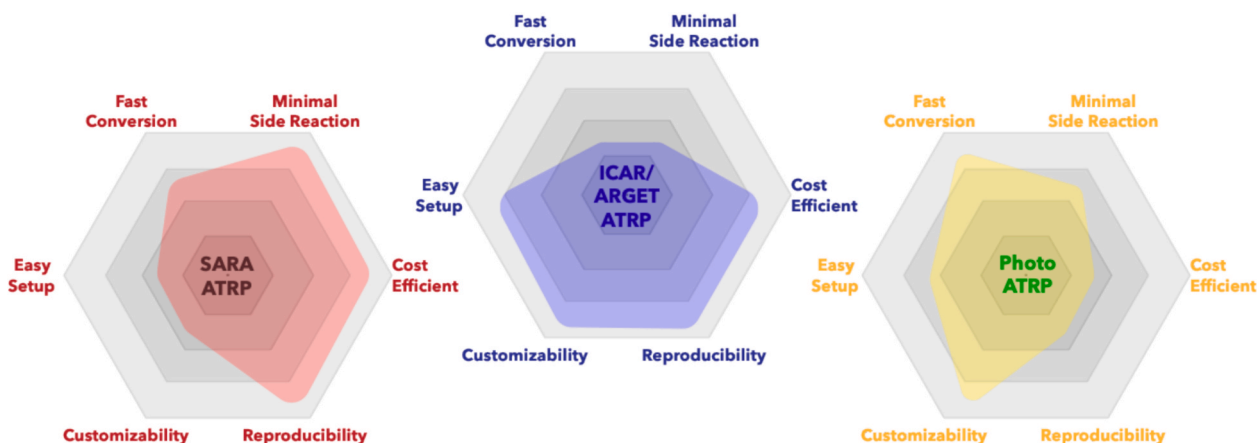


Fig. 6. Comparison of SARA, ICAR/ARGET, and PhotoATRP for block copolymerization of PACE-prepared macroinitiators.

Among the evaluated techniques, SARA ATRP yielded polymerizations with minimal side reactions, good molecular weight control, and high reproducibility. However, full submersion of the copper wire should be maintained throughout the experiment for consistent kinetics and the predetermined surface area-to-volume ratio (Fig. 6, left).

In contrast, ICAR and ARGET ATRP operate in homogeneous solutions. They are simpler to set up and eliminate the need for solid metal or specialized external photoreactors. However, in ICAR ATRP, thermal radical initiators can compete with macroinitiators, potentially leading to homopolymer formation. In ARGET ATRP, excessive reduction of the deactivator complex can generate excessive Cu(I). This may disturb the ATRP equilibrium and slow down deactivation, increase dispersity, and diminish control over the polymerization (Fig. 6, middle).

PhotoATRP exhibited the fastest polymerization rates and yielded well-controlled polymers. However, the control and reproducibility of polymerization rely on the uniformity of light intensity and minimal light scattering. This external factor increases the risk of fluctuations in the activator concentrations. Reproducibility requires careful

optimization, such as standardized vial positioning, consistent stirring rate, and light-intensity testing (Fig. 6, right). The findings from examining different ATRP strategies establish the versatility of the PACE approach. PACE-prepared macroinitiators consistently showed well-controlled polymerization throughout different techniques.

3. Conclusion

In summary, the PACE method enables the synthesis of polyolefin-polar block copolymers by seamlessly transitioning from coordination-insertion polymerization to RDRP. In this study, we successfully expanded the PACE approach in terms of its application beyond the previously utilized SARA ATRP to include ICAR, ARGET, and photoATRP.

4. Author Contributions

The manuscript was written through the contributions of all authors.

All authors have given approval to the final version of the manuscript.

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CRediT authorship contribution statement

Khidong Kim: Writing – original draft, Investigation, Data curation. **Stephen Don Sarkar:** Writing – original draft, Formal analysis, Data curation. **Jacobo Strong:** Investigation, Formal analysis. **Kaito Takahashi:** Investigation. **Halil Ibrahim Coskun:** Methodology. **Rongguan Yin:** Methodology. **Eva Harth:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Data curation, Conceptualization. **Krzysztof Matyjaszewski:** Writing – review & editing, Writing – original draft, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2026.114723>.

Data availability

Data will be made available on request.

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