

One-pot Synthesis of Polyethylene-based Block Copolymers via a Dual Polymerization Pathway

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ABSTRACT: Polyethylene–poly(methyl acrylate) multiblock copolymers were obtained using a catalyst system consisting of a pentamethylcyclopentadienyl cobalt complex ($\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)\text{P}(\text{OMe})_3\text{I}_2$) and *iso*-butyl modified methylaluminoxane (MMAO). As the chain-growth mechanism, the self-switching between organometallic-mediated radical polymerization (OMRP) and coordination–insertion polymerization (CIP) is suggested. As a possible polymerization mechanism, we propose (1) the methyl and *iso*-butyl group transfers from Al to Co, and the single methyl acrylate (MA) unit insertion into the Me–Co and H–Co allows for the *in situ* formation of Co–C(COOMe) bonds as an initiator for OMRP of MA, (2) the migratory insertion of ethylene into Co–C(COOMe) bonds leads to the formation of an alkyl–Co species as active species for CIP of ethylene, and (3) MA insertion to the alkyl–Co to regenerate a Co–C(COOMe) bond. The architectures of copolymers were confirmed by various NMR, TGA/DSC and SEC analysis.

Polyethylene (PE) is the most common plastic used worldwide,¹ but the inherent nonpolar nature limits its application.^{2, 3} Nowadays, block copolymers consist of nonpolar olefins and polar monomers have attracted broad interest because of the advanced properties, such as barrier performances, microphase behavior and miscibility.^{4, 5} The common synthetic methodology of polyolefin–polar block copolymers is post-polymerization,^{6–9} wherein multiple catalysts operate consecutively or synergistically (Figure 1a).^{10–13} Emerging attention has been paid to switching polymerization, which integrates different catalytic cycles to produce well-defined block copolymers.^{14–16} Nevertheless, the strategy has been mostly applied to a combination of polar monomers, like methyl acrylate (MA), but not to nonpolar olefins. Generally, the combination of olefin-polymerization catalysts to polar groups, mechanistic compatibility, and match of reaction conditions, which further diminishes the possibility of finding a suitable catalytic system.^{17–20} Monteil, Mecking, and their co-workers have shown that a salicylaldiminato Ni(II) catalyst performs both coordination–insertion polymerization (CIP) and free radical polymerization simultaneously, yet majority of the chain growth cycles are independent of each other, providing mixtures of homopolymers.^{21, 22} More recently, Harth group has reported the photo-switchable polymerization for the synthesis of polyolefin–polar block copolymers using a cationic diimine Pd(II) complex that mediates CIP and free radical polymerization sequentially (Figure 1b).^{23–25} Since the polymerization catalyst is altered only once *in situ* between two different polymerization cycles, its application is yet limited to AB diblock or ABA triblock copolymers. Yet, it remains a challenge to automate the switching

polymerization systems and prepare polyolefin–polar multiblock copolymers.²⁶

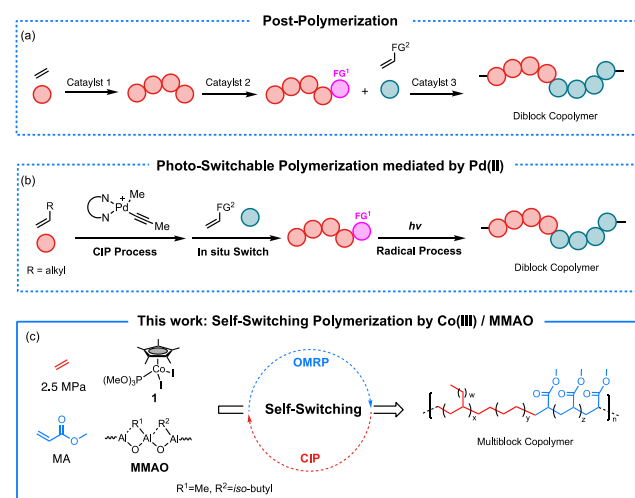


Figure 1. Strategies for the synthesis of polyolefin–polar block copolymer.

We focused on cobalt catalysts because organocobalt(III) complexes are known to catalyze the organometallic-mediated radical polymerization (OMRP)^{27, 28} and CIP process.^{29, 30} Herein, we report the synthesis of multiblock copolymers consisting of PE and PMA using pentamethylcyclopentadienyl cobalt complex ($\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)\text{P}(\text{OMe})_3\text{I}_2$, **1**) and *iso*-butyl modified methylaluminoxane (MMAO). A dual self-switching pathway is proposed to be responsible between OMRP of MA and CIP of ethylene (Figure 1c).

Table 1. Copolymerization of MA/ethylene mediated by **1**/MMAO for multiblock copolymers synthesis. [a]

Entry	MA (mL)	Time (h)	Activity (kg/mol·h)	$M_{n,NMR}$ (kg/mol) [c]	$M_{n,SEC}$ (kg/mol) [b]	\bar{D} [b]	Average Block Number [c]	PMA <i>meso</i> diad abundance (%) [d]	MA i. r. (%) [e]
1	1.0	6	1.70	9.2	9.0	7.3	4	51.8	2.3
2	1.0	12	1.16	17.5	17.6	2.7	4	50.6	2.8
3	1.0	18	1.31	22.0	21.8	3.1	6	51.1	3.1
4	1.0	22	1.51	23.5	23.8	2.9	10	52.6	3.9
5	0.2	22	3.23	-	1.2	1.7	-	-	0.5
6	0.4	22	2.51	5.1	4.5	4.5	6	50.4	1.6
7 ^[f]	2.0	10	0.61	7.3	7.1	4.7	4	52.2	15.7
8 ^[g]	1.5	10	0.54	10.8	11.0	2.1	4	52.0	17.5

[a] Reaction condition: **1** (9.8 μ mol, 2.0 mM), MA, MMAO (Al/Co = 340) and PhCl (3.0 mL) were added into an autoclave and then stirred at 30°C under 2.5 MPa ethylene. [b] Determined by SEC using polystyrene standards and corrected by universal calibration, using the Mark-Houwink parameters of LLDPE. [c] Average Block Number estimated by $^1\text{H}/^{13}\text{C}$ NMR spectra (Figure S6). [d] Determined by ^1H NMR spectra. [e] *i. r.* = Incorporation ratio in mol% determined by ^1H NMR spectra. [f] 1.5 MPa ethylene. [g] 1.0 MPa ethylene.

The cobalt-catalyzed copolymerization of MA/ethylene was investigated with the ratio of [MA]/[MMAO]/[**1**] as 1100/340/1 under 2.5 MPa ethylene. First, complex **1**, MA, MMAO and a solvent (PhCl) were placed in an autoclave and then the system was pressurized with ethylene. Thus, it is likely that the polymerization of MA started before introduction of ethylene. As shown in Table 1, entries 1-4, the longer reaction time gradually increased the molecular weight (M_n) with the higher MA incorporation ratio. The higher MA feed concentration resulted in higher MA incorporation ratio at the expense of activity and molecular weight (Table 1, entries 4-6). And decreasing the pressure of ethylene from 2.5 MPa to 1.0 MPa resulted in a significant drop in molecular weight and activity, but evidently higher incorporation ratios of MA (Table 1, entries 7-8).

Taking entry 2 of Table 1 as an example, the resultant copolymer was fully identified as follows. The SEC curve exhibits monomodal distribution with a slight tailing ($M_n=17.6$ kDa, $\bar{D}=2.74$). The ^1H NMR spectrum exhibited both an atactic PMA and a branched PE block with a 2.8 mol% incorporation of MA (Figure 2a). Notably, we could detect the carbon at the junction of PE and PMA, labelled as “i” in Figure 2b (see Section 4.1 in SI).³¹ The quantitative ^{13}C NMR spectrum also shows a similar incorporation ratio 2.5 mol%. Assuming both ethylene and MA units coexist in one polymer chain, average molar mass can be calculated based on ethylene content ($MW = 28$) \times ($x\%$) and MA ($MW = 86$) \times ($(100 - x)\%$). And the average number of units per chain can be calculated as 583 ethylene units and 15 MA units. We assume that the two chain-ends of majority of the copolymers are PMA and PE since, (i) the copolymerization starts from PMA segment due to the experimental procedure and (ii) chain-end analysis based on NMR spectra (Figures S3-5) showed most of the other chain-end is CH_3 and no signal was detected for olefinic groups which would exist if chain-transfer via β -hydride elimination takes place (see page S9 for further discussions). Accordingly, the relationship between the average number of MA per chain (N_{MA}) and the average number of PMA block per chain (N_{PMA}) described as equation (1):

$$\frac{N_{MA}}{2N_{PMA} - 1} = \frac{A_a}{A_i} \quad (1)$$

Where, A_a is the area of carbonyl of MA and A_i is the area of junction unit in quantitative ^{13}C NMR analysis.

Every polymer chain contains 2 PMA blocks in average, which suggested the formation of multiblock copolymers. Total number of blocks in average estimated as tetrablock, namely, the copolymer could be best presented as PE-*b*-PMA-*b*-PE-*b*-PMA (Figure S7). To unambiguously verify the block structure, the products were analyzed by diffusion-ordered spectroscopy (DOSY NMR),^{23, 32, 33} wherein both PMA and PE blocks shared a single diffusion coefficient with a sharp peak. Soxhlet extraction has been applied to further support that PMA units belong to copolymers rather than PMA/PE blend (see Section 4.2 in SI).^{22, 23} After extraction, only insoluble fraction was detected with a 2.5 % incorporation of MA. The SEC chart displayed a M_n of 16.9 kDa with a \bar{D} of 2.91 similar to that of the fresh polymers, suggesting that the two different compositions belong to the same copolymer. Notably, the differential scanning calorimeter (DSC) analysis exhibited semi-crystalline property with two glass transition temperature ($T_{g,PE} = -68$ °C, $T_{g,PMA} = 16.5$ °C), crystalline temperature ($T_{c,PE}=116$ °C), and melting point temperature ($T_{m,PE} = 130$ °C). Two different stages in the thermogravimetric analysis (TGA) curve can be reasonably attributed to PMA and PE, respectively.

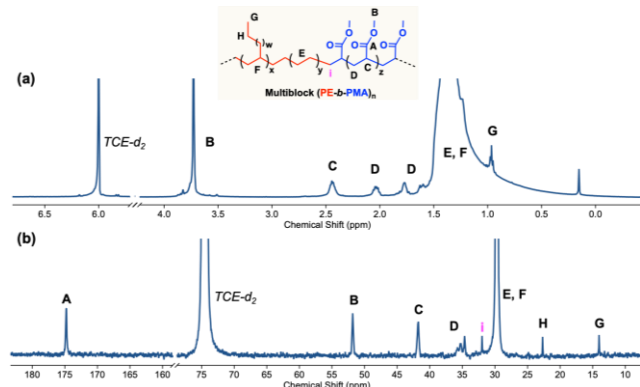


Figure 2. Characterizations of multiblock copolymers in Table 1, entry 2. (a) ^1H NMR spectrum of the copolymer. (b) ^{13}C NMR spectrum of the copolymer.

As a possible mechanism for the multiblock copolymers, we propose a dual polymerization pathway, wherein the OMRP of MA and CIP of ethylene were self-switched by **1**/MMAO system. First, the **1**/MMAO-mediated polymerization of MA was

performed with a ratio of $[MA]/[MMAO]/[1]=1100/340/1$. Followed by the linear first-order kinetic plot, a 30 min induction period was observed (Figure S33). The M_n of PMA increased properly with conversion with a slight deviation from the theoretical values, which may originate from the inefficient initiation of radicals.³⁴⁻³⁶ Spin-trapping experiment was conducted to determine the propensity towards homolytic cleavage of Co-C bonds in the presence of N-tert-butyl-a-phenylnitronone (PBN). The ESR spectroscopy of obtained nitroxide showed a signal with a_N of 1.437 mT and a_H of 0.290 mT, characteristic of the nitroxide product from the addition of PMA macromolecular radicals to PBN.³⁷ A significant deactivation was observed in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) possibly because of the interaction between TEMPO and Co center (Figure S35).^{38, 39} MALDI-TOF spectrum of resultant PMA in the presence of TEMPO showed three main series signals in accordance with $[TEMPO + (MA)_n + H]Na^+$, $[TEMPO + (MA)_n + H]K^+$ and $[TEMPO + (MA)_n + CH_3]K^+$, respectively (Figure 3a). This result suggested that both methyl and iso-butyl group transferred from Al to Co center during the initiation (Figure 3b). It is well known that an *iso*-butyl group undergoes β -hydride elimination to initiate polymerization as a hydride. Furthermore, the tacticity of PMA also supports the radical mechanism (see Section 4.3 in SI). Therefore, we can suggest that **1**/MMAO-mediated polymerization of MA runs as OMRP pathway. In parallel, we conducted the ethylene polymerization mediated by **1**/MMAO under the condition of $[1]/[MMAO]=1/340$ (Table S2 and section 4.5 in SI). Therefore, it is likely that the cyclopentadienyl cobalt (III) complexes mediated CIP of ethylene.

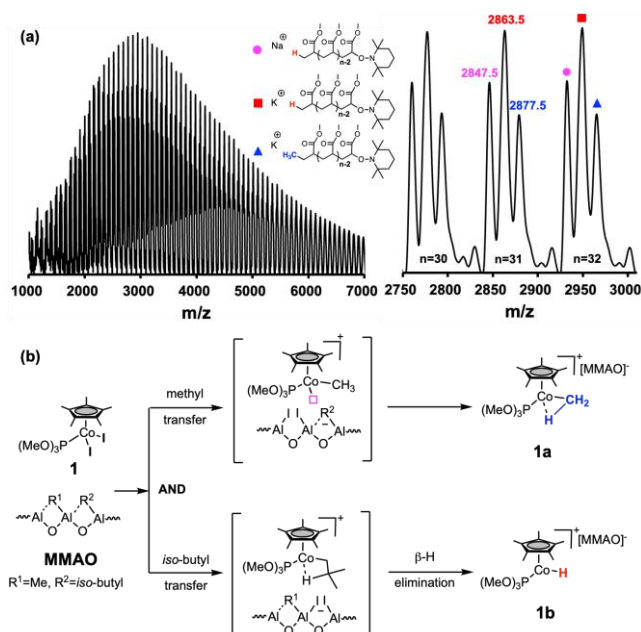
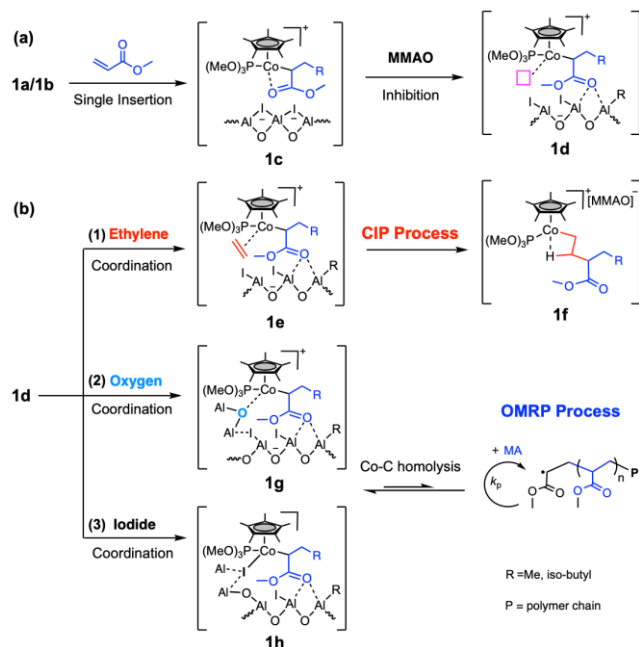


Figure 3. OMRP of MA mediated by **1**/MMAO. (a) MALDI-TOF spectrum of the PMA in the presence of TEMPO. (b) Proposed generation of active species.

Based on above, we propose a self-switching mechanism described in Scheme 1. Once the active species is generated as shown in Figure 3b, single MA unit insertion into both the Me-Co and H-Co allows the *in situ* formation of Co-C(COOME) bonds (**1c**).^{30, 40, 41} where the chelation of the carbonyl oxygen completes 18-electron configuration at Co(III).⁴² Generally, the intramolecular chelation stabilizes the structure, resulting a

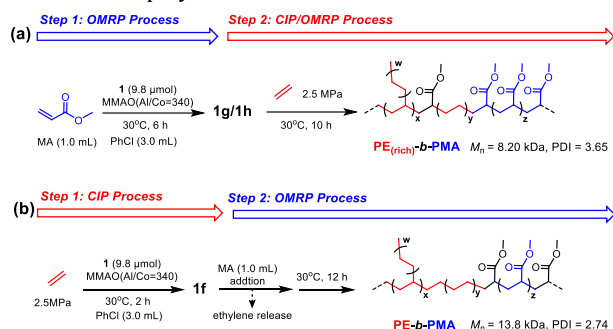
higher bond dissociation energy for Co-C bonds.⁴³ Interaction of the ester group in **1c** with the Lewis acidic $[-O-Al(Bu/Me)-]_n$ moiety of MMAO generates the 16-electron species **1d** having a vacant coordination site (Scheme 1a). Here we propose that there are three possible pathways (Scheme 1b): (1) When ethylene coordinates to the Co center, a cationic 18-electron ethylene-Co(III) intermediate **1e** undergoes the CIP process due to the low barrier;⁴⁴ (2) If the oxygen moiety of MMAO coordinates to the vacant site instead of ethylene, the cationic 18-electron Co(III) species **1g** is more favorable to OMRP process through the homolysis of Co-C bonds;⁴⁵⁻⁴⁷ (3) The iodide could transfer back to Co center resulting the neutral 18-electron Co(III) species **1h**, which also initiates OMRP process. It is expected that homolytic cleavage of C-Co bond in **1g/1h** would be favorable than **1f** because the resultant α -carbonyl radical species are more stable than alkyl radical thermodynamically.



Scheme 1. The proposed switching mechanism for CIP of ethylene and OMRP of MA.

To further explore the switching property between two catalytic circles, sequential monomer addition methods were performed to evaluate whether the intermediates **1g/1h** and **1f** can effectively initiate CIP of ethylene and OMRP of MA, respectively (Scheme 2 and Section 4.5 in SI). First, the OMRP of MA was performed for 6 h to reach 28% conversion of MA. Intermediates **1g/1h** are expected to exist. To the system, was pressurized with ethylene (Scheme 2a). After addition of ethylene, during the second step, MA conversion increased to 31%, indicative of that OMRP is still active during CIP process and resulting in an ethylene-rich block (PE_(rich) block). The SEC chart displayed an obvious shift and confirmed the chain extension (Figure S80). Under this condition, 0.15 mol% of the chain-end was assigned to a vinyl group, likely resulting from chain-transfer by β -hydride elimination from an alkyl-Co species (Figures S50, S53). The DOSY NMR spectrum gave a single diffusion coefficient for all the copolymer with a weak signal assigned to PE oligomers. Soxhlet extraction was conducted to separating the block copolymers from the side PE oligomers. After that, the DOSY NMR spectrum gave one single diffusion coefficients for

copolymers. The opposite order of the sequential addition was also examined: the CIP of ethylene catalyzed by **1**/MMAO was conducted under 2.5 MPa ethylene for 2 h to form **1f**. After ethylene release, MA was added to the solution to produce a block copolymer (Scheme 2b). A clear peak at 31.9 ppm detected by ^{13}C NMR spectrum is assignable to the junction unit. The DOSY NMR spectrum shared two different diffusion coefficients for both the PE precursor and the target copolymer. The thermal properties were analyzed by TGA/DSC to confirm the architecture of diblock copolymer PE-*b*-PMA (see Section 4.5 in SI). Therefore, we envision that the intermediate **1g/1h** and **1f** could initiate the following CIP of ethylene and OMRP of MA respectively. In this regard, we proposed that the OMRP of MA and CIP of ethylene can be switched reversibly, providing the multiblock copolymers.



Scheme 2. Sequential monomer addition methods. (a) Switch OMRP to CIP/OMRP. (b) Switch CIP to OMRP.

In summary, a dual polymerization pathway for synthesis of $(\text{PE-}b\text{-PMA})_n$ multiblock copolymers has been established using the $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)\text{P}(\text{OMe})_3\text{I}_2]/\text{MMAO}$ catalytic system. The mechanistic aspects have been proposed, wherein the methyl and *iso*-butyl group transferred from Al to Co, and then the single MA insertion occurred, generating Co–C(COOMe) bonds. The three different pathways lead to OMRP of MA and CIP of ethylene, completing the self-switching polymerization cycle. Considering the uncontrolled switching property, it still remains a challenge to prepare the multiblock copolymers with on-demand sequence. It seems that introducing stimulus-responsive functional groups to modify the metal coordination sphere has potential to control the switchable process in the future. We believe that the dual pathway polymerization will open up new avenues to prepare di- and/or multi- polyolefin-polar block copolymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization of resultant polymers, and additional spectroscopic data (PDF)

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Notes

The authors declare no competing interests.

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